A

THESIS

ON

"Effective Utilization of LD slag"

Submitted in the partial fulfillment of the requirements of the degree

Of

MASTER OF TECHNOLOGY

In

INDUSTRIAL METALLURGY

By

Arnab Dastidar

(Enrolment No- 16544003)

Under the supervision of

Dr. Nikhil Dhawan

Assistant Professor

DEPARTMENT OF METALLURGICAL AND MATERIALS ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY ROORKEE

ROORKEE-247667(INDIA)

MAY 2018

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the dissertation, entitled "Effective Utilization Of LD slag" in partial fulfillment of the requirements for the degree of Master of Technology in the Department of Metallurgical and Materials Engineering with specialization in "Industrial Metallurgy", Indian Institute of Technology Roorkee, is an authentic record of my own work carried out during the period from May, 2017 to May 2018, under the supervision of Dr. Nikhil Dhawan, Assistant Professor, Department of Metallurgical and Materials Engineering, Indian Institute of Technology, Roorkee.

The matter embodied in the dissertation has not been submitted to any of the University/Institute for the award of any other degree.

Date: ....

Place: Roorkee

(ARNAB DASTIDAR)

CERTIFICATE

This is to certify that the abov statemen made by the candidate is correct to the best of My knowledge.

(Dr. NIKHIL DHAWAN)

Assistant Professor

Dept. of MMED

IIT Roorkee

ACKNOWLEDGEMENT

I would like to express my deep indebtedness, sincere gratitude, respect and heartiest thanks to my supervisor Dr. NIKHIL DHAWAN (Assistant Professor) Department of Metallurgical and Material Engineering, Indian Institute of Technology, Roorkee for his valuable supervision and encouragement throughout the project. I also want to thanks my family for their moral support. I would also like to show my gratitude to Institute Instrumentation Center (IIC) for providing me the instrument facilities for smooth completion of my research work. I would like to thank all research scholars, especially Ashwini Kumar, Veeranjan Raypudi and Amit Barnwal for their help. I would also like to thank all my friends for their continuous support during my work. Last but not least, I would not like give my sincere thanks to everyone who had supported me for their support.

CONTENTS

Abstract

India is the fourth-largest manufacturer of steel following China, Japan and the US. Presently in India, due to limited modes of practices of utilization, huge amount of iron and steel slag dumped in yards of each production unit leading to grave pollution to whole environment. An efficient approach to overcome these problems is the slag utilization. Presently in India the LD slag is only being utilized for cement, concrete, road & sinter making which is not enough. Therefore in this project an attempt has been made to utilize LD slag for making ceramic tiles & also for CO_2 capture which will serve the dual purpose of reducing air pollution & producing $CaCO_3$.

INTRODUCTION

S lag is a by-product generated by action of various fluxes upon gangue materials present in the iron ore during the process of pig iron making in blast furnace and steel manufacturing in steel melting shop. Generally, the slag consists of various combinations of calcium, magnesium manganese and aluminium silicates. The cooling process of slag is responsible mainly for generating different types of slags required for various end-use consumers. The cooling process does not alter the chemical composition of slag greatly but physical properties vary widely with the changing process of cooling.

The slag produced at blast furnace during pig iron manufacturing is called blast furnace slag. The slag produced at steel melting shop with the help of LD convertor is known as LD slag. Slag output obtained during pig iron and steel production is variable and depends mainly on composition of raw materials and type of furnace. Typically, for ore feed containing 60 to 65% iron, blast furnace (BF) slag production ranges from about 300 to 540 kg per tonne of pig or crude iron produced [1]. Lower grade ores yield much higher slag fractions, sometimes as high as one tonne of slag per tonne of pig iron produced. Steel slag output is approximately 20% by mass of the crude steel output.

Generation of LD slag

As mentioned earlier LD slag is generated In SMS during crude steel making with the help of LD convertors. The primary raw materials used hot metal from blast furnace and the scrap. The scrap proportion in conventional LD convertor is restricted to 20-30% of the total charge

The LD- vessels are eccentric in shape. After the vessel is pre-treated to a white heat, it is ready to take the charge. The LD section is provided with overhead hot metal charging cranes for charging the hot metal in the to the converters, semi-portal scrap charging cranes, a gas cleaning plant to clean the LD gases from dust and to let the clean gas to the atmosphere. Each converter is having a tilting mechanism, for oxygen lances and the lance lowering and rising mechanism arrangement, bins to store the raw materials, a scale car to collect the raw materials from the bins, to weigh and charge them into converters through the chutes provided in the hood above the converters. The charging starts with the addition of a few hundred kilogram of calcinated lime or dolomite through the overhead chutes which protect the lining of the converter. Oxygen of 99.5% purity and at a pressure of 10-12 kg/ cm2 is blown into the bath at the rate of 7,000-10,000 Nm3/ hr. Immediately ignition takes place and preferential oxidation starts. A chemical reaction occurs, where the oxygen reacts with carbon and silicon generating the heat necessary to melt the scrap and oxidize impurities.

Some typical reactions taking place in the converter are as follows:

$Fe+[O]=FeO$

$2(FeO)+1/2O_2(g)=Fe_2O_3$

$[C]+[O]=CO(g)$

$C+(FeO)=CO(g)+Fe$

$[Si]+2[O]=SiO_2$

$CaO+SiO_2=CaSiO_3$

$[Si]+2(FeO)=SiO_2+2Fe$

$[Mn]+[O]=MnO$

$[Mn]+(FeO)=MnO+Fe$

$(MnO)+(SiO2)+1/2O2=MnO_2.SiO_2$

.

PROPERTIES OF LD SLAG

The chemical & physical properties of LD slag is summarized in the following tables

Table1: Chemical Composition and Major Phases of Typical LD Slag

Sl	Chemical composition	Major phases& wt%
1	SiO_2-12.16%	Tricalcium silicates-0-20%
2	Al_2O_3-1.22%	Dicalcium silicates 30-60%
3	FeO-26.30%	Other silicates-0-10%
4	CaO-47.88%	Magnesiocalciowustite 15-30%
5	MnO-0.28%	Dicalcium aluminoferrite 10-25%
6	MgO-0.82%	Lime-0-15%
7	P_2O_5-3.33%	Periclase 0-5%
8	Na_2O-0.036%	Flourite 0-1%
9	K_2O-0.071%	

Table 2: *Composition of several phases in LD slag*

	Composition (wt%)								
Mineral phase	CaO	SiO_2	FeO	Mn	MgO	P_2O_5	Al_2O	TiO_2	Cr_2O_3
Di-calcium silicate	58.00	33.84	0.54	—	0.01	3.62	0.67	0.50	0.04
Tricalcium silicate	68.20	25.70	2.15	1.55	0.08	1.10	0.30	0.37	—
Dicalcium ferrite	49.64	1.48	48.11	0.36	4.24	0.02	—	—	—
Dicalcium ferrite Titanate	52.70	2.55	33.31	0.88	0.43	0.32	3.25	8.53	0.39
Magnesio Wustite	2.12	2.08	61.80	17.50	5.68	—	—	—	—

Table 3:- Physical Properties of Indian Steel Slag

S. No.	Properties	Test Method	Steel Slag
1	Aggregate Impact Value	IS:2386 (IV)	8 – 11%
2	Los Angeles Abrasion Value	IS:2386 (IV)	8 – 10%
3	Flakiness Index	IS:2386 (I)	12%
4	Elongation Index	IS:2386 (I)	8%
5	Water Absorption	IS:2386 (III)	1-1.6%
6	Specific Gravity(Kg/cm^3)	IS:2386 (III)	3220
7	Bulk Density (Kg/cm^3)	IS:2386 (III)	2100

Table 4: Characteristics and applications of steel slag[11]

Characteristics	Application
Hard, wear-resistance, adhesive and rough	As aggregates for roads and hydraulic construction
Porous and alkaline	Waste water treatment
FeOx and its components	Iron reclamation
CaO, MgO, FeO, MgO, MnO componets	Fluxing agent
Cementitious components (C_3S, C_2S and C_4AF)	Cement and concrete production
CaO, MgO components	CO_2 capture and flue gas desulfurization
FeO, CaO, SiO_2 components	Raw material for cement clinker
Fertilizer components (CaO, SiO_2, MgO, FeO)	Fertilizer and soil improvement

UTILIZATION TREND OF LD SLAG IN INDIA

1.Cement Making

. 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 P,05 results in corrosion of reinforced materials in concrete structure. If only 10% LD-slag is used in cement, the P,O, content will be around 0.3% which is not so harmful in portland slag cement (PSC), because low P,05 in PSC react; with alkali in slag contributing little strength of cement'". Therefore, more than 10% LD-slag use in PSC is not possible.

At Tata Steel, a project has been initiated in collaboration with Lafarge India to make a use of LD-slag in cement making The bench scale trial is being conducted at the Jojobera Cement Plant of Lafarge

Road / Concrete making

In India, huge amount of natural resources like soil and aggregates are being utilized for development of road projects like National Highway Development Program (NHDP), PMGSY (Pradhan Mantri Gram Sadak Yojana) and CMGSY (Chief Minister Gram Sadak Yojana) programs. This leads to resource exploitation of naturally available materials. In the 20th century, steel slag was found to be excellent aggregate as road paving material[2]. Air cooled blast furnace slag, as a substitute of store aggregate /chips, has been acceded by the Indian Road Congress (IRC) and Bureau of Indian Standards (BIS) for road construction[7]. On the other hand, Steel slag could become unstable because of its free lime (CaO) and free magnesia (MgO) with the consequent risk of expansion Thus their use is limited in road construction and is virtually excluded from use as fill under structures. Steel slag, as construction aggregate, is recommended only in those situations where the expansion is unlikely, as in the case of dense bitumen macadam, or in the places where expansion does not cause a serious problem. Their main use, therefore, is in the upper bituminous layers of the road structure or in the surface course [5]. Abrasion value, Impact value, crushing value and CBR values of the steel slag aggregates was found to be 30 percent, 13.90 percent, 5.20 percent, 8.27 percent and 15.57 percent respectively, well within permissible limit as per IS standards [13].

It was reported that the steel industry waste product is suitable and economical material for use in the road construction and the optimal mix is 15% steel slag mix in sub grade and in sub base for road construction[9]. It was also concluded in an investigation that slag may be utilized in the building of sub-grade and embankments. About 40 to 50% of slag material could be used to replace conventional aggregate for constructing layer of granular sub-base (GSB) and for bituminous layers it is not suitable [8]. Granulated blast furnace slag (GBFS) should be able to use as a partial replacement of unmodified aggregate up to 20-30% in the construction of granular sub base layers, also maximum un-soaked California Bearing Ratio (CBR) value was increased by 40.78% when 20% replacement with GBFS, whereas the 4-day soaked CBR value was increased by 46.60% [8].

The public works department (PWD) has permitted the utilization of iron and steel slag in construction of paved roads. In Bellary district, India, the first use of steel slag was exercised where a mega steel plants is situated[8]. Because of its expansive character due to hydration of free lime (CaO) or free magnesia (MgO), steel slag must be allowed for the weathering process before using as an aggregate in construction[18]. Slag can be used for rigid pavement construction in the equal ratio with combination of manufactured sand or river sand. But it is not recommended as a 100 percent replacement of natural sand for rigid pavement works

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 (2CaOSiO,) 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. Microstructural observation of laboratory sinter and plant sinter were taken up and found that characteristic microstructural 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.

soil stabilization and soil conditioner

Steel LD slag has been used as a liming agent for pasture in Northern Spain. Use of LD slag has been shown to increase the soil pH. Experiments have found that application of LD increased the soil pH linearly. The soil pH increased from 5.3 to 6.4 with the use of 7500Kg of slag/hectare, the second year response being higher i.e. 41% increase in soil pH with 3000Kg slag/hectare . In soil conditioning slags are efficient in soil neutralisation. In addition the siliceous liming materials improve soil structure and reduce fungal infections. Blast furnace slag can be used also in agriculture because of its high sorption capacity of phosphorus, which remains into the available form for the plants. Negative effects, resulting from steel slags use, could derive from their heavy metal concentrations, but such metals tend to bound to the slag matrix and thus they are not available for plants. All these factors contribute to underline positive effects of using slag as liming materials that lead to better yield of the crops, soil protection and reduction of natural resources consumption. NILANCHAL Refractories, a Tata group company manufacturing a soil conditioner-Growell. Growell is essentially enriched slag used as a soil conditioner or liming agent to acidic soils. Growell has been made by using the TISCO basic slag and it contains calcium, phosphates and other elements[21]. The product has been certified by the Union Ministry of Agriculture and the Fertilizer Association of India. It has been noted that application of Growell in acidic soil increases the yield by 25% and above, According to the results LD slag appears to be a useful liming material for correcting the acidic condition of soil. This is in natural range and show a positive effect on mustard and wheat seedling growth. Thus this can be used as a rural biotechnology for better plant growth.

Government of India, Ministry of Finance has notified that LD slag can be used as soil conditioner after its crushing, washing and adding with rock phosphates etc. LD slag contains 29% calcium in form of CaO. Slag is principally a lime based material that absorbs the oxides and trace elements arising from refining of iron. LD slag also contains phosphorous in the form of P_2O_5. So, LD slag has a limiting to ground lime stone and is used regularly to regulate the need of liming on acidic soil. Many field trials and experiments have shown significant improvement in crop yield and pasture quality.

Steel slag also has been used as amendment for metal contaminated soils.[3] The use and environmental assessment of LD slag is more recent P-spiked LD slag was used as a soil additive to improve physico-chemical soil properties and in situ stabilization of Cu and other trace metals in a sandy Cu-contaminated soil. The result found that soil pH increases with increase in incorporation rate of LD slag..

fertilizer in agriculture

Steel LD slag can also be used in fertilizers for agricultural applications The efforts have been made in Tata steel that LD slag after grinding to 300 mesh, can be used as a soil conditioner in paddy field, tea gardens etc. Nippon KokanKk Corporation (NKK) in Japan has developed a process to produce eco-friendly slow release potassium silicate fertilizer from the slag which is generated during the desiliconisation process of hot metal at steel mill. Using of slag's ingredient is the basic idea of NKK. In this process potassium carbonate pellets are added to molten slag, containing silicon dioxide as main ingredient in hot metal ladle and melted uniformly at 1673K. The molten mixture is collected from ladle, cooled and pulverized in to granular fertilizer. The produced fertilizer which is brackish gray in colour and comprises of vitric potassium silicate as its main ingradient and exhibits slower release effects than conventional quick acting chemical fertilizer such as potassium chloride, potassium sulphate and urea (NKK 2000). Many studies have been done for production of fertilizes from LD slag, semi-calcined dolomite and ammonium sulfate and their agricultural applications for agro-forestry, pasture farming. The influence of these materials on chemical composition of soil and grass to potential economic benefits of applying this new fertilizer to the soil were evaluated. According to soil type and agricultural use by adding a concentration of LD slag between 1.5 and 5.0t/ha, it is possible to achieve increase in soil pH and improve the soil quality and also productivity. The experimental works were carried out using pulverized LD slag for growing different vegetables and crops like tomato, potato, onion, spinach and wheat in acidic soil. Steel slag contains fertilizer components CaO, SiO_2, and MgO. In addition to these three components, it also contains components such as FeO, MnO, and P_2O_5, so it has been used for a broad range of agricultural purposes. Its alkaline property remedies soil acidity. In developed countries such as Germany, USA, France and Japan, converter slag is used to produce siliceous fertilizer, phosphorus fertilizer and micronutrient fertilizer

.

Experiments have found that application of LD increased the soil pH linearly. The soil pH increased from 5.3 to 6 with the use of 7500Kg of slag/hectare, the second year response being higher i.e. 41% increase in soil pH with 3000Kg slag/hectare [19]. In soil conditioning slags are efficient in soil neutralisation. In addition, the siliceous liming materials improve soil structure and reduce fungal infections.[20]

As it was pointed out earlier, even with all these types of utilization of LD slag, still the problem of slag dumping persists which results in serious environmental degradation. So there is an urgent need to utilize these slags in other applications also.

Literature Review

Statement of the problem

Management of solid waste is a challenge for efficient and cost-effective operation at any Steel Plant because the actual of waste generation is more than any other plants in India. Presently, India is the fourth-largest manufacturer of steel following China, Japan and the US. Presently in India, the generation of industrial solid waste by integrated iron and steel plants is nearly 270 million tonnes while, utilisation is only of 30%[4]

Slag generated during steelmaking in basic oxygen converter (LD-Converter) is one of the important waste materials in an integrated steel plant. Production rate of LD-slag is 150-180kg per ton of crude steel.[5] Total generation per annum is 0.98 million tonne in Tata Steel, about 1.28 million tonne in SAIL and worldwide generation is about 47 million tonne per annum

Considering an average of last three years, Steel plants in India has generated about 2.77 million tones of solid waste for an average production level of 4.0 million tones of crude steel. Out of the total waste generation of 2.77 million tones, 0.68 million tones(24.8%) was sold, 0.41 million tones was recycled (14%) and rest 1.67 million tones (60%) was dumped in dump yards. The data shows that the total generation of solid waste is abnormally high, the percentage of recycling/ reuse is very low and percentage of dumping is very high. Collection, transportation and dumping of waste are very expensive and a large area of land is needed. Steel Plants in India are facing space constraints due to filling up of old dump yards and limited site area available for opening of new dumping space. Moreover, high cost of dumping due t longer lead distance for future sites adds to this predicament.

Moreover dumping of slag has also creates a lot of environmental concerns. Porosity and permeability of soil can be reduced by iron and steel slag Leachate generation can be of great environmental concern from huge dumping of steel slag[5]. The major issue of concern for steel slag is its unscientific dumping sites neighbouring very close to the populated area due to leachate generation. These industrial solid wastes are environmentally hazardous in nature, mainly due to release of leachate, to the human beings and also pollute soil and water [6]. Steel slag utilization for agricultural purposes arises the possible leaching of heavy metals and consequently the change of soil properties affects the plants [7]. Enormous quantities of steel slag are deposited in Indian slag yards, may cause environmental pollution[8]. The unscientific dumping of iron and steel slag by the generators can also have harmful effects upon the aquatic environment in the vicinity of the increase in pH of water sources, leaching of heavy metals, and rapid rates of calcite precipitation which suffocate benthic habitats

OTHER MODES OF UTILIZATION OF LD SLAG

LD slag can also be utilized for:

1. Tile making
2. Calcium Carbonate formation & CO_2 capture

The table given below lists the papers where slag was used for above 2 applications.

Table5: Utilization of LD slag for tile making & CO_2 capture

Sl	NAME OF PAPER	MATERIALS USED	EXPERIMENTAL PROCEDURE	KEY FINDINGS
1	[4]	**EAF slag** **Ball clay(**SiO_2-48%, Al_2O_3-36%) **Silica & feldspar** Slag Composition SiO_2-20 Al_2O3-8.3 CaO-29 Fe0-32	Wet Mixing of raw materials in various proportion in a mixture for 60 min Drying in oven at 105°C for 24 hrs 5-6 wt% of water added & compacted in hydraulic press under 40MPA pressure Drying in an oven at 105°C for 24 Hrs before sintering at 1150°C for 1 hr	Max Wt % of slag that can be used is 40 wt% Silica & feldspar reduces porosity & increases flexural strength due to higher amount of anorthite phase formed

2	[6]	BFS waste product Clay, Kaolin & Sand Slag composition **SiO_2-41.2** **Al_2O_3-14.3** **CaO-32.7** MgO-7.3 FeO-0.8	milling using a ball mill dried at 110^o C,7 wt% of water is added. The humidified mixture were pressed at 130 bar pressure using press and formed into tiles. The wall tiles were dried at 110 ^{o}C and fired in an kiln (1130 ^{0}C for42min).	BFS usage increases anorthite formation, increases strength and lowers TEC of 33% of BFS in ceramic wall tiles results in an almost 25% increment in fired strength
3	[12]	electric arc furnace slag quartz powder (T-clay , B-clay and feldspar EAF slag composition: SiO2-20.3 Al_20_3-7.3 CaO-22.8 Fe2O3-42.4 Mg0-8	One kilogram batch of each composition was prepared by wet milling in a pot mill for 6 h at a speed of 35 rpm. The slurries were dried and disintegrated. Dry powders were thoroughly mixed with 5–6 wt.% water and rectangular bars (100 × 15 × 6 mm) and tiles (100 × 100 × 6 mm) were prepared using uniaxial compaction at a specific pressure of 25 MPa The compacted bars were dried at 110°C till the moisture content was reduced to < 0·5 wt.% and then fired in the temperature	1.Increase in firing temperature increases the shrinkage and density and reduces the apparent porosity and water absorption values for all the compositions 2.zero percent water absorption (vitrification) temperature reduces with increase in feldspar 3.strength increases with increase in the firing temperature but the increase is much significant above 1125°C firing. 4.For batches with higher feldspar content, strength decreases above 1125^{o}C due to over firing, grain growth and re-crystallization.

			range of 1100–1150°C for a soaking period of 1 h in an electric furnace	
4.	**[11]**	BF slag composition SiO_2-33-35 MgO-7-17 Al_2O_3-11-15 Fe_2O_3-0.7-2	The five slags were mixed with clay, whiting, feldspar and quartz powder in various proportions after which the mixtures were dry-milled to a fineness such that practically all the material passed a 200-mesh Tyler screen. 10% water was mixed and pressed under $20N/mm^2$ After drying at 100^0C for approximately 16 hours the tiles were fired in a globar electric furnace to temperatures ranging between 1200° and 1250^0C depending on the slag as well as on the composition for 4-5 hrs	Slag tiles are denser and have lower water absorption and higher resistance to abrasion than conventional split & quarry tile.
5.	[18]	BOF slag from 2 different steel plant of 3 different particle size range dehydrated at 105^oC for 24 hrs	0.5, 2, and 5 g of slag was mixed in 300 ml of water at atmospheric pressure & temperature of $25,50,90^0C$ for 240 hrs The slurry collected at specific time interval was filtered & filtrate was diluted in HNO_3 &	Ca leaches the most & Al least Rate of dissolution decreases with time Al conc of filtrate reaches a minimum level by the end of 240 h due to the precipitation of secondary

			analyzed with ICP-AES	compounds such as $H_4Al_2O_5$ minimum 120 h of carbonation is required under standard operating conditions to stabilize the steel slag before its usage in landfills & industrial purposes

Experimental Procedure

Materials used

LD slag from Tata Steel is the main material used. It was crushed using ball mill & sieved below 100 micron size. SRK clay, Silica & feldspar is also used for making pellets of tiles.

3.2 Instruments used in the study

In this study instruments were used which are described below.

3.2.1 Ball mill

Sample was received as bulk, so grinding was performed using ball mill followed by sieving and get different sizes of sample. After grinding, the powder was sieved in different size fractions but the work has been done on sample size 150 mesh sizes (100 microns) for experiments

Fig 1: Ball mill

3.2.2 Muffle Furnace

A proportional integral derivative controlled muffle furnace was used in this study as shown in Fig 3.2. Uniform heating mechanism has been carried out in this furnace. And the furnace have the outer dimensions of 24’’ x 16” x 14” (Fig.3.2).

The furnace consisted of heating zone of dimensions of 9” x 6” x 6”and the heating temperature range was from room temperature to 1200 deg C.

The furnace was well insulated in and there was no loss of heat during heating. Heating rate of the furnace was 20ºC/minute.

Fig 2: Muffle furnace

3.2.3 Glass wares

The beakers of 250 ml, measuring cylinders of various volumes (10 ml, 25ml, and 100ml), conical flask of 250ml, funnel of 40 mm diameter, and culture tubes of 15 ml used in this study were made up of borosilicate glass.

These beakers could sustain the temperature up to 250ºC and were used mainly for leaching of the samples. Conical flasks were used for the filtration after leaching. Glass funnel was used for filtration and culture tubes were used for keeping the prepared solution after dilution for flame photometer analysis

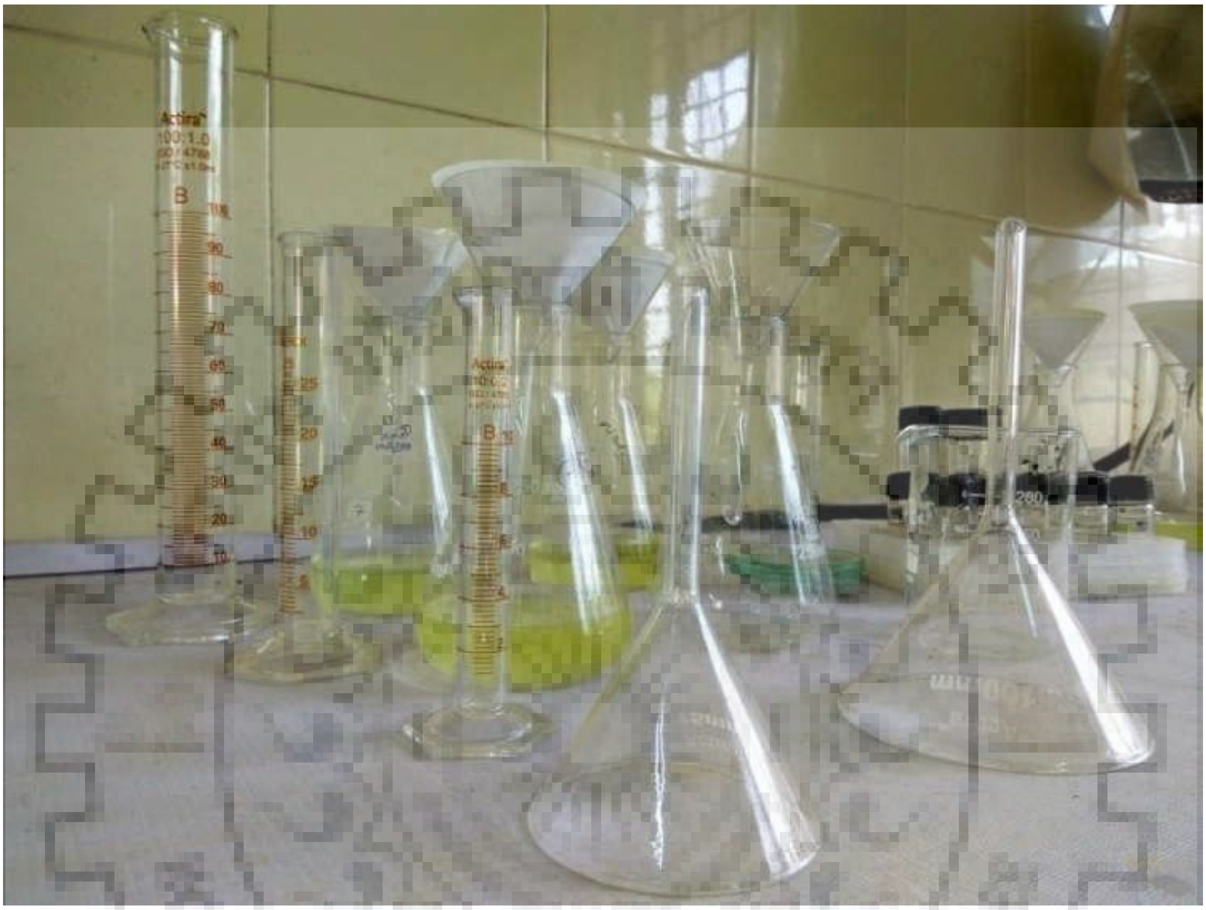


Fig 3: Glasswares

3.2.4 Magnetic stirrer, filter paper and Parafilm

Magnetic stirrers with ceramic hotplate (Cole Parmer) were used throughout study. These stirrers have the stirring speed of maximum 1500 rpm and temperature up to 250 deg C. Magnetic stirrer, filter paper and Parafilm are shown in Fig.4.

Parafilm was always used for covering the beaker during leaching to avoid any material loss during leaching. Whatman filter paper grade 1 having 110 mm diameter was used to filter the solution after leaching. All the leaching experiments were carried out in a 250 ml glass beaker placed on a magnetic stirrer with controlled temperature environment. All leaching experiments were carried out at atmospheric pressure with appropriate leaching media under continuous stirring at 900 rpm.

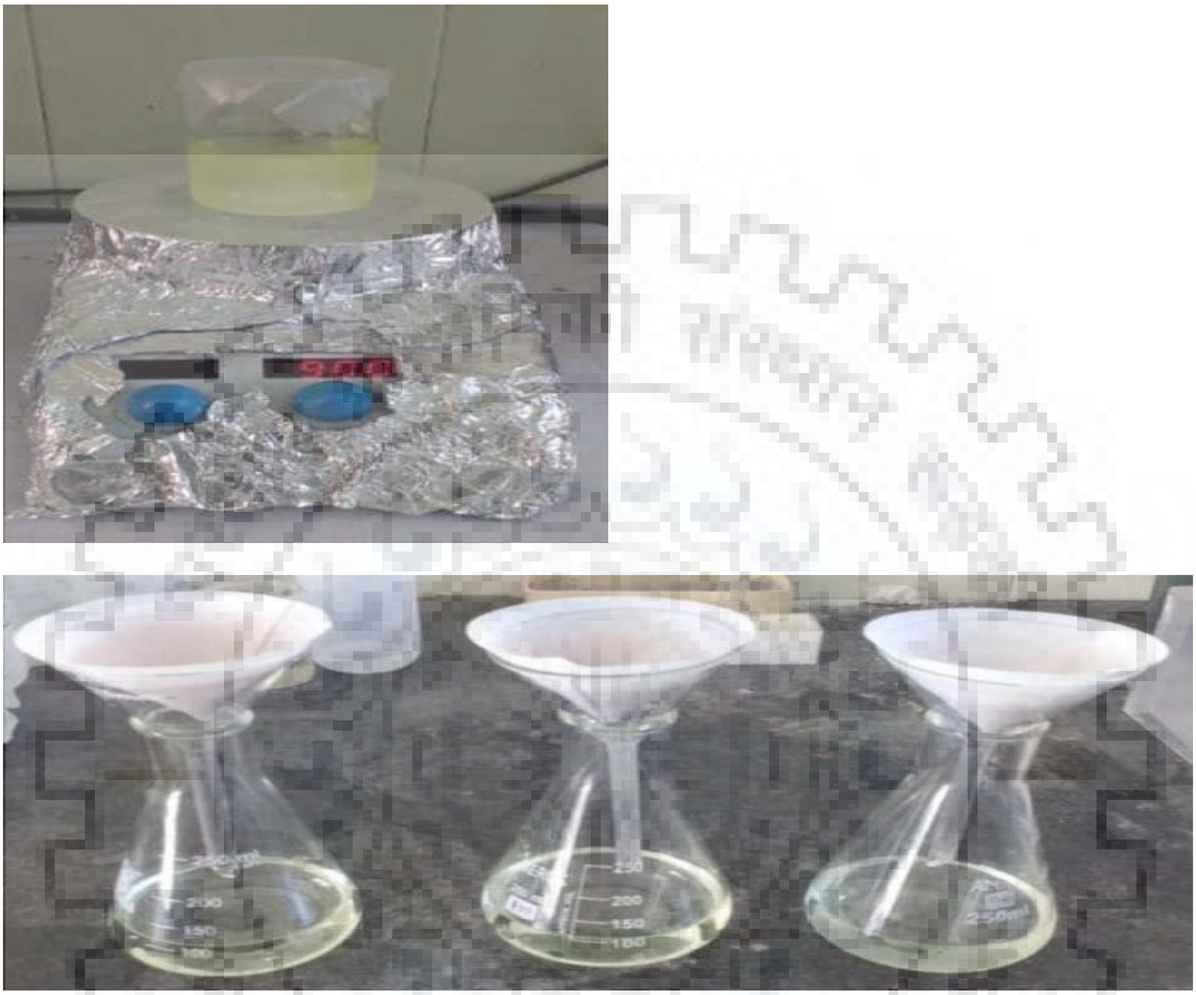


Fig 4: Magnetic stirrer, filter paper and Parafilm

3.2.5 Flame Photometer

Flame photometer is used to analyze the elements dissolved in the dissolution. Flame photometer of the solution has been carried out in systronics flame photometer. Elements which are sensitive to flame color. These elements are Ca, Li, Na, K and their presence in the sample changes flame color.

The systronic flame photometer (Fig.3.5) with compressor was used in this study. The instruments have two modes of analysis i.e. high concentration mode and low concentration mode. In high concentration mode, the standard solution of concentration should be in between 10- 100ppm whereas in case of low concentration mode standard solution should be in between 1-10 ppm for calibration. The high concentration mode was mostly used in this study to analyze the potassium content in the sample.

Fig 5: **Flame Photometer**

3.2.6 Scanning electron microscope

SEM having very high resolution (10nm), so it can be used to find the morphology, chemical composition, structural alteration of feed (FE-SEM Quanta 200 FEG) is shown in Fig.3.7.

Fig 6: SEM

3.2.8 X-Ray diffractometer

The X-ray diffraction study of the powdered sample was carried out using a RIGAKU Smart Lab X-ray diffractometer (Fig.7) using Co Kα (wavelength 0.154 nm) radiation.

Fig 7: XRD

3.2.8 Carbonation setup

Since mineral carbonation is the reaction of carbon dioxide (CO2) with basic minerals to form harmless solid carbonates. So, in this setup 2L capacity glass reactor consists of one inlet (CO2 gas supply) one outlet and another outlet which goes to manometer (pressure reading) shown in fig. 8

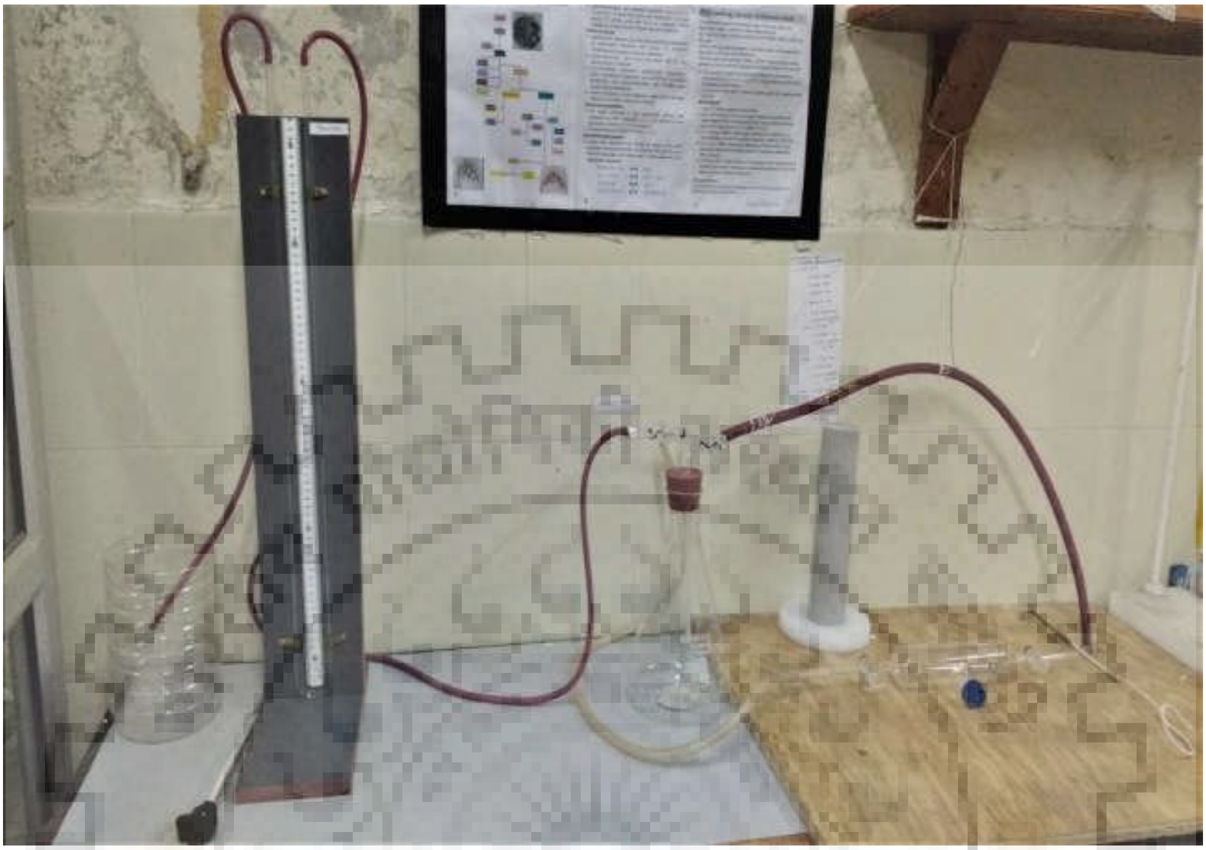


Fig 8: Carbonation Set up

X-ray Fluorescence

Major and minor constituents of various slag samples were analysed by XRF spectrometry on Phillips (PW-1400) X-ray spectrometer with Scandium and Rhodium targets using pentaerythritol (Al, Si), Thallium Acid Pathalate (Na, Mg), Germanium (P) and Lithium Fluoride (for heavier elements) as analyzing crystals in vacuum medium. International and in-house standard of appropriate compositions were used for calibration. Both major and minor elements were determined by pressed powered pellet technique.

Methodology

Calcium Carbonate Formation& $C0_2$ capture:

1. LD slag was crushed in a ball mill below 75 microns size

2. Leaching of LD slag was done in water, acetic acid, citric acid & Hcl
3. Filtration of the solution was done.
4. Ca content of the filtrate was found out by flame spectrometer.
5. Carbonation of the filtrate for 30 min at room temperature & normal pressure
6. Filtration of the carbonated solution. The solid amorphous powder filtered out is sent for XRD analysis

Tile making:

The major raw materials used were:

1. LD slag,
2. SRK clay,
3. Silica
4. Feldspar

1. First, LD slag from Tata Steel was crushed into powder, with particle sizes of 200 mesh size & below, in a ball mill for 15 min. The chemical composition of the raw materials are determined by XRF & Wet chemical analysis(for LD slag)
2. Initially, LD slag was well-mixed with SRK clay, K-feldspar (potash feldspar) and silica . In this process, the weight percentage of each raw material was varied as shown in table 6.

BATCH	**WT PERCENTAGE(%)**			
	LD SLAG	SRK CLAY	QUARTZ	FELDSPAR

A	60	40		
B	50	50		
C	40	40	10	10
D	40	30	20	10

3. After mixing, the mixture was dried in an oven at 110 _C for 24 h. The dried mixture was then re-crushed using mortar.
4. powder mixture was granulated and moistened by water. The amount of moisture introduced was approximately 5–6 wt.% per sample.
5. Granulated mixture of each composition was compacted by hydraulic press with pressure of 2.5,5,7.5 T/inch^2, yielding a circular pellet of tile of diameter 20mm.
6. The compacted body was dried in an electric oven at 110 _C for 24 h before sintering at 1100 ^oC for 1 h.
7. Finally, the naturally cooled samples were characterized in terms of bulk density, water absorption, phase present and the chemical composition.

Measurnment of Water Absorbtion Rate :

The measurnments are done according to IS-13630 code for ceramic tiles. Following procedure was followed

1. The pellets of tiles are placed in the oven at 110±5^{0}C, until it attains constant mass,
2. The pellets of tiles are cooled the tiles to room temperature.
3. Each tile specimen is weighed and the weight of individual test specimen (i.e. **m1**) is recorded in the observation sheet.
4. The pellets of tiles are placed vertically, with no contact between them, in water in the water bath so that there is a depth of 50 mm water above and below the tiles.
5. The water is heated until boiling and continue to boil for 2 h. After 2 h, the source of heat is switched off and allow the tiles to cool, still completely immersed in this water, over night.
6. The weight of the tile still suspended in water was also recorded(m3)

7. The pellets tiles from the water bath and remove the surface water from the tiles pieces by chamois leather.
8. Immediately weigh each tile and record the weight (i.e. **m2**) in the observation sheet.
9. Now place the specimens in the wire basket that is immersed in water and determine the weight of each specimen to the nearest 0.01g.

Calculation

1. Water Absorption

For each tile, calculate the water absorption in percentage (to the first decimal place) of the dry mass using the following formula.

Water absorption (%) = [(m2 – m1) / m1] * 100

Where,

m1 = mass of the dry tile, in g

m2 = mass of the wet tile, in g

Calculate the average water absorption of the sample as the average of the individual result.

4. RESULTS & DISCUSSIONS

4.1CHARACTERIZATION OF LD SLAG

4.1.1CHEMICAL COMPOSITION:

The chemical composition of LD slag was found out by both XRF & Wet Chemical Analysis. Its chemical composition is shown in the table given below:

Table 7: Chemical composition of LD slag

	LD SLAG	
	XRF	WCA
SiO_2	12.50	11.25
Al_2O_3	1.83	0.97
Fe_2O_3	18.99	9.91
CaO	58.24	42.19
MgO	2.985	5.16
Na_2O	0.087	0.26
K_2O	0.075	0.06
P_20_5	2.06	2.12

From the above table it is clear that

1. LD slag is generally a mixture of various oxides.
2. Almost 50% of the oxides present in LD slag is Calcium oxide.
3. LD slag also contains appreciable amount of silicon & iron oxides.
4. Trace amount of aluminium, phosphorus &magnesium oxides are also present

4.1.2XRD ANALYSIS:

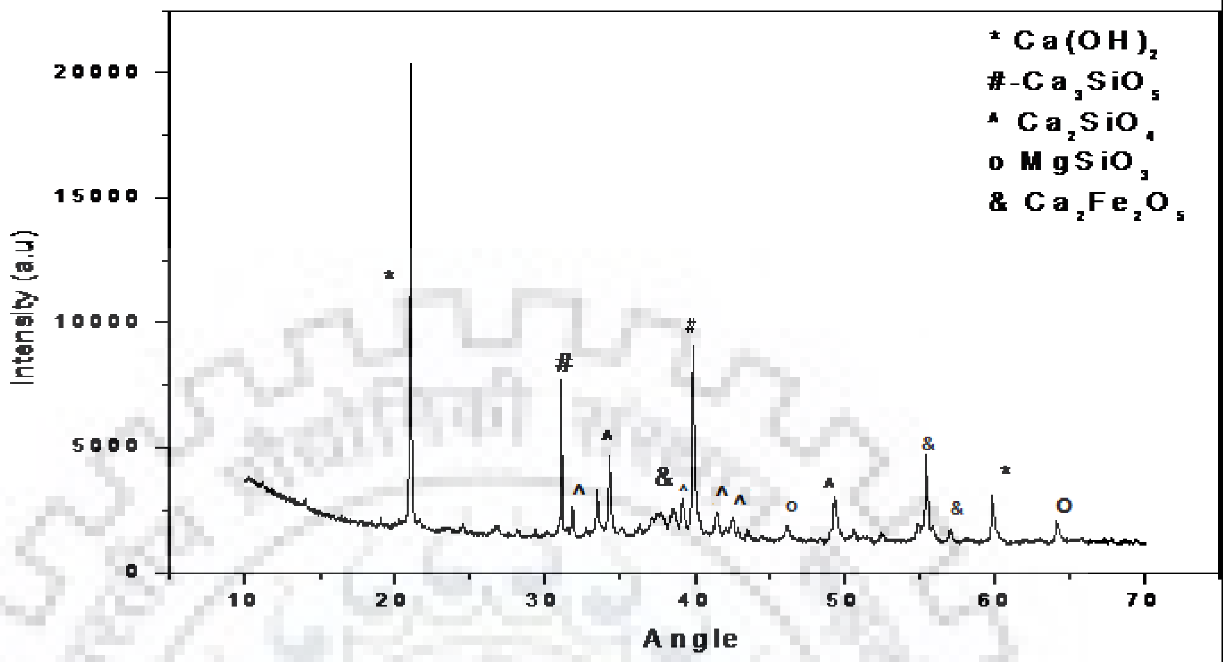
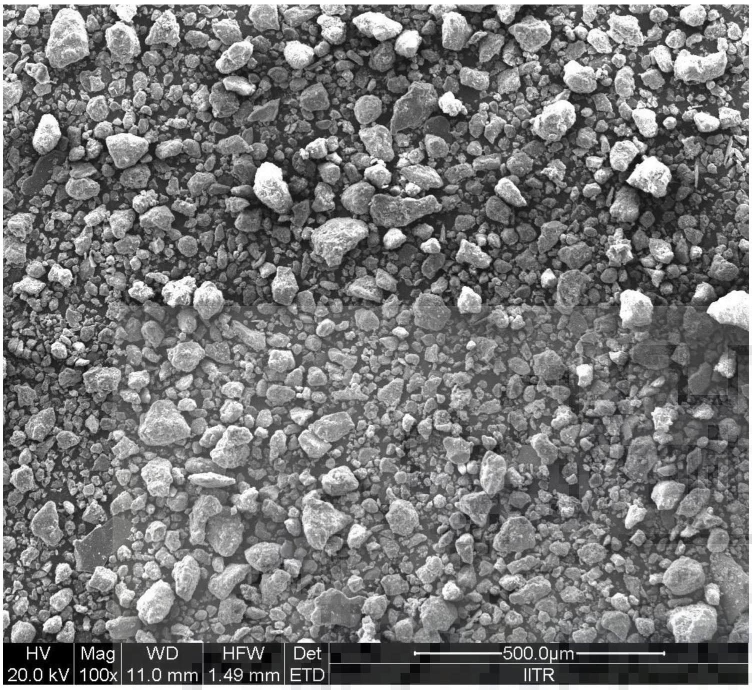


Fig 3: XRD analysis of LD Slag

From the above XRD analysis we can see that the major phases present in the LD slag are:

1. Calcium hydroxide
2. Tri-calcium silicate
3. Di-calcium silicate
4. Magnesium silicate
5. Calcium iron oxide.

4.1.3SEM EDAX ANALYSIS



ELEMENTS	**WT%**
O	45.71
Mg	1.65
Al	0.58
Si	4.2
Ca	40.21
Fe	6.86

Fig 4: SEM- EDAX analysis of LD Slag

.

The EDAX analysis shows that oxygen is the main element present in LD slag. It is expected since LD slag is basically a mixture of oxides. It also has got appreciable amount of Si & Ca

4.2LEACHING OF SLAG

Leaching of the slag is done to extract calcium from the LD slag , first by water & then by acids. The 3 acids used are hydrochloric acid, acetic acid & citric acid.

The reactions of Calcium silicates present in LD slag with water & acids taking place during the leaching are:

$Ca_2SiO_4 + H_2O = Ca(OH)_2 + SiO_2$

$Ca_2SiO_4 + CH_3COOH = Ca(CH_3COO)_2 + H_2O + SiO_2$

$Ca_2SiO_4 + HCl = CaCl_2 + H_2O + SiO_2$

$Ca_2SiO_4 + C_6H_8O_7 = Ca_3(C_6H_5O_7)_2 + H_2O + SiO_2$

Similarly the magnesium silicates & iron oxides present in LD slag also reacts with water & acids during leaching:

$MgSiO_3 + H_2O = Mg(OH)_2 + SiO_2$

$MgSiO_3 + CH_3COOH = Mg(CH_3COO)_2 + H_2O + SiO_2$

$MgSiO_3 + HCl = MgCl_2 + H_2O + SiO_2$

$MgSiO_3 + C_6H_8O_7 = Mg_3(C_6H_5O_7)_2 + H_2O + SiO_2$

$Fe_2O_3 + H_2O = Fe_2(OH)_2 + SiO_2$

$Fe_2O_3 + CH_3COOH = Fe(CH_3COO)_2 + H_2O + SiO_2$

$Fe_2O_3 + HCl = FeCl_3 + H_2O + SiO_2$

$Fe_2O_3 + C_6H_8O_7 = Fe(C_6H_5O_7) + H_2O + SiO_2$

These 3 acids are selected because of the higher solubility of calcium salts in water compared to the magnesium & iron salts so that the leaching of calcium can take place from LD slag. Iron salts are hardly soluble & a negligeable amount of magnesium is present. So after filtration, calcium will get extracted into the filtrate.

After that filtration was done & Ca content of the filtrate is determined with the help of the flame spectrometer. Then the Calcium extraction efficiency is determined with the help of the following formula:

$$\text{Ca extraction efficiency} = \frac{(\text{amount of Ca in the filtrate})}{(\text{amount of Ca in the slag})}$$

Amount of Ca present in the slag can be found out from the XRF analysis of LD slag.

The table given below gives the result of the leaching in water & acids.

Table 8: Leaching in water

S/L ratio (g/ml)	Stirring speed (rpm)	Temp (deg C)	Time (hr)	Ca extraction efficiency (wt%)

1:50	700	RT	6	2.128
1:50		RT	6	2.125
1:125		RT	30	2.246
1:50		RT	30	2.571
1:50	700	95	1	3.63

We see from the above table that leaching by water is not suitable as amount of Ca leached is very low

Table 9: Leaching of Slag by Acids

SOLVENT	CONC (M)	S/L RATIO (g/ml)	TEMP (^oC)	STIRRING SPEED (rpm)	TIME (Hr)	LR/ FEED SAMPLE	PH	Ca EXTRACTION (%)
ACETIC ACID	1	1:50	50	700	1	0.3225	3	36.771
CITRIC ACID	1	1:50	75	700	1	0.424	1	17.32
HCl	1	1:50	RT	700	1	0.142	1	60.741

So we see that leaching by Acetic Acid & HCl has got a very high calcium extraction efficiency. But the colour of Hcl filtrate is not found to be white. So that means that iron has also got leached out into the filtrate. So the filtrate of acetic acid is used for PCC formation.

XRD OF LR

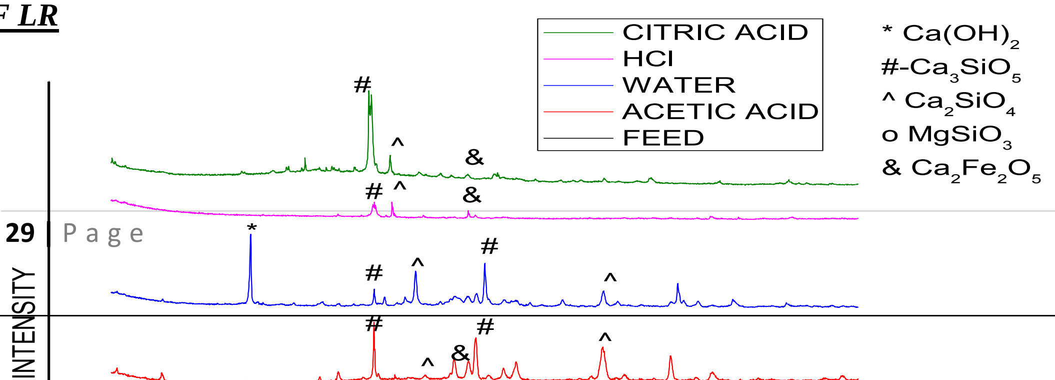


Fig 9: XRD of LR

XRD of the LR was done to find out which Ca bearing phase is getting leached out by acids & water. We find that $Ca(OH)_2$ phase is the most easily leachable phase but it still cant be leached out by water.

<u>CARBONATION OF ACETIC ACID FILTRATE</u>

The reaction taking place during Carbonation reaction are:

$Ca(CH_3COO)_2 + H_2O + CO_2 = CaCO_3 + CH_3COOH$

So from the above reaction we see that we not only form Calcium Carbonate, but we can also recycle the acetic acid back.

So after carbonation, filtration was done & XRD of the residue left was done

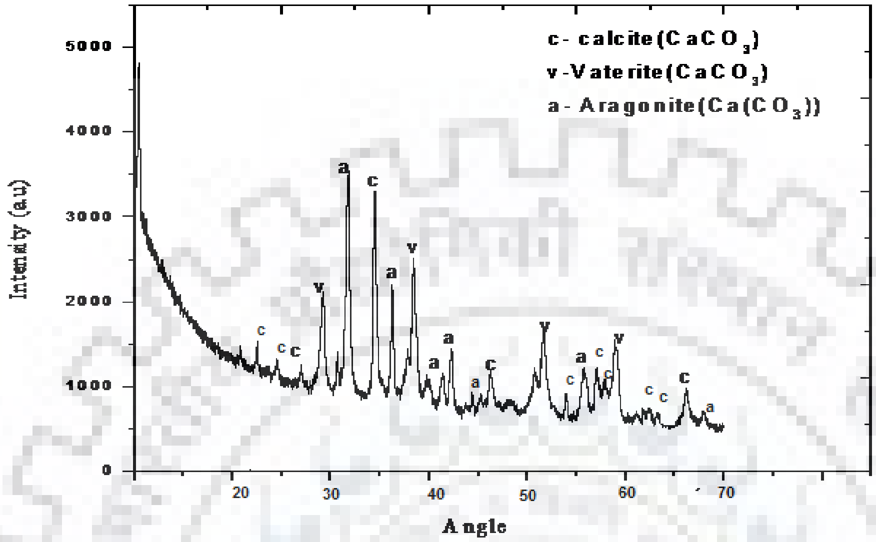


Fig10 : XRD of the Residue

From the above XRD analysis it is clear that we can get $CaCO_3$ with this process. The chemical formula of the 3 phases formed are same but their structure is different. Vaterite belongs to the hexagonal crystal system, whereas calcite is trigonal and aragonite is orthorhombic.

CHEMICAL ANALYSIS OF RAW MATERIALS FOR TILE MAKING

The table given below shows the chemical composition of raw materials for tile making

Table9: Chemical Analysis of raw materials

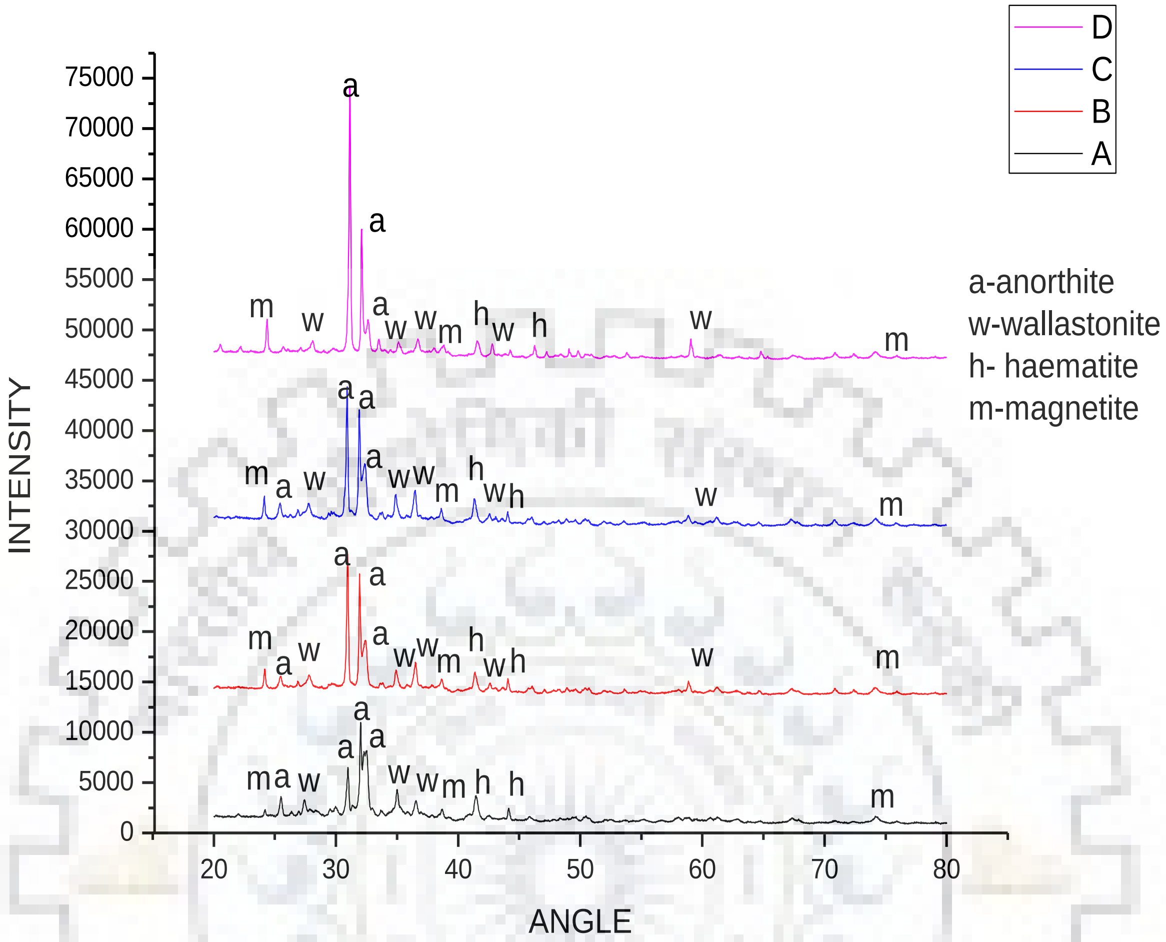
	LD SLAG		SRK CLAY	QUARTZ	FELDSPAR
	XRF	WCA			
SiO_2	12.50	11.25	49.7	98.11	65.99
Al_2O_3	1.83	0.97	34.94	0.41	17.45
Fe_2O_3	18.99	9.91	0.57	0.07	0.33
CaO	58.24	42.19	0.735	0.03	1.98
MgO	2.985	5.16	0.360	___	0.2
Na_2O	0.087	0.26	0.97	___	2.96
K_2O	0.075	0.06	6.07	___	8.46
P_20_5	2.06	2.12	___	___	___

SRK clay & feldspar used is high in silica & alumina content.

Quartz used is about 98 % SiO_2

XRD ANALYSIS OF PELLETS OF TILES

.



The 4 main phases present in the pellets of tiles are:

1. Anorthite (Al_2O_3. CaO .$2SiO_2$)
2. Wallastonite(CaO.SiO_2)
3. Haematite (
4. Magnetite

formation of anorthite and wollastonite inceramic could be associated with the reactions below:

CaO + Al2O3.2SiO2 (metakaolinite from clay)=Al2O3. CaO .2SiO2(anorthite)

CaO + SiO2(from clay and silica) =CaO.SiO_2 (wollastonite)

XRF OF PELLETS OF TILES

Table 10: XRF OF PELLETS OF TILES

	A	B	C	D
SiO_2	31.02	34.12	42.98	49.7
Al_2O_3	17.95	21.2	17.12	15.6
Fe_2O_3	9.65	7.6	7.53	5.4
CaO	29.05	23.2	20.2	17.4
MgO	2.54	2.94	1.88	1.34
Na_2O	0.95	1.1	1.05	0.77
K_2O	0.54	0.43	0.33	0,12

From the above table we can see that the tiles have got a high percentage of silica, alumina & calcium oxide

Water Absorbtion Rate Of Pellets of Tiles

	Mass	W2	WA%	AVG WA%
A	2.52	2.94	17.1	17.6
	2.54	3.02	19.2	
	2.6	3.02	16.5	
B	2.48	2.81	13.5	14.33
	2.54	2.89	14.1	
	2.56	2.95	15.4	
C	2.5	2.68	7.2	8.63
	2.58	2.84	10.2	
	2.55	2.76	8.5	
D	**2.6**	**2.74**	**5.4**	**5.26**
	2.52	**2.63**	**4.5**	
	2.57	**2.72**	**5.9**	

W1- Wt of Pellets

W2- Wt of Pellets saturated with water

WA%(Water Absorbtion Rate)= (W2-W1)/100

From the above table it is clear that Batch D has got the lowest water absorbtion rate. So its porosity is very low.

SUMMARY

1. In the present case scenario, utilization of steel slag has become matter of prime importance to avoid environmental concerns.
2. An effort has been made in this project to utilize LD slag for tile making & CO_2 capture.
3. LD slag consists of SiO_2, CaO, & iron oxides . The phases present in it are calcium hydroxide, calcium & magnesium silicates & calcium iron oxides.
4. Leaching of LD slag with water results in very low calcium extraction
5. Leaching of LD slag with acetic acid & HCl results in very high calcium extraction
6. The filtrate of Acetic acid leaching can be used for CO2 capture & calcium carbonate formation
7. Tiles made LD slag consists of phases like anorthite, wallastonite, silica & iron oxides.
8. Tiles made with 40% LD slag, 30% clay, 20% quartz & 10% feldspar has got the lowest porosity.

References:-

1. Awoyera et al. (2015) Influence of Electric Arc Furnace (EAF) Slag Aggregate Sizes on the Workability and Durability of Concrete, International Journal of Engineering and Technology (IJET), Vol 7 No 3 Jun-Jul 2015
2. Ahmed Ebrahim Abu El-Maaty Behiry (2013) Evaluation of Steel slag and crushed limestone mixtures as sub base material in flexible pavement, Ain shams Engineering Journal (2013) 4, 43-53.
3. Biradar, K. B., kumar, A. U. And Satyanarayana, P.V.V. (2014) Influence of Steel Slag and Fly Ash on Strength Properties of Clayey Soil: A Comparative Study, International Journal of Engineering Trends and Technology (IJETT) – Volume 14 Number 2 – Aug 2014
4. Brindha, D., Baskaran,T, and Nagan,S. (2010) Assessment of Corrosion and Durability Characteristics of Copper Slag Admixed Concrete, International Journal Of Civil And Structural Engineering, Vol. 1, no. 2, pp.192-211.
5. Bhagwan, J. and Guru Vittal, U. K.(2014) Use of Marginal Materials for Rural Road Construction - Some Recent Initiatives, Proceedings of Indian Geotechnical Conference IGC-2014 December 18-20, 2014
6. Buddhdev, B. G. and Varia, H. R. (2014) Feasibility Study on Application of Blast Furnace Slag in Pavement Concrete, International Journal of Innovative Research in Science, Engineering and Technology, Vol. 3, Issue 3, March 2014
7. Bharath, V. S. and Rao, P. R. M. (2015) Study on the Fibre Reinforced Concrete Using Steel Slag as the Coarse Aggregate Replacement, International Journal For Technological Research In Engineering Volume 2, Issue 7, March-2015
8. Humaria, M. S. Y. (2014) Impact of Iron and Steel Slag on Crop Cultivation: A Review. Curr World Environ 2014;9(1). Available from: http://www.cwejournal.org/?p=5746, http://dx.doi.org/10.12944/CWE.9.1.31
9. CPCB, http://www.cpcb.nic.in/newitems/24.pdf, 31, March 2016
10. Chaubey, S. and Ali Jawaid, S. M. (2016) Soil stabilization using steel slag, Global Journal for Research Analysis, Volume-5, Issue-1, January -2016.
11. Chaudhary, P. N. and Pal, J. (2002) An Overview of Treatment of Steel- Making Slag for Recovery of Lime and Phosphorus Values, http://eprints.nmlindia.org/4220/1/186- 190- PN_chaudhury.PDF - accessed on 22 June 2016

12. Chand, S., Paul, B., Kumar, M. (2015) An Overview of Use of Linz-Donawitz (LD) Steel Slag in Agriculture. Curr World Environ 2015;10(3). doi : http://dx.doi.org/10.12944/CWE.10.3.29
13. Chand, S., Paul, B. and Kumar, M. (2016) Sustainable Approaches for LD Slag Waste Management in Steel Industries: A Review, Metallurgist, Vol. 60, Nos. 1–2, May, 2016, DOI 10.1007/s11015-016-0261-3
14. Das et al. (2007) An overview of utilization of slag and sludge from steel industries, Resources, Conservation and Recycling 50 (2007) 40–57, doi:10.1016/j.resconrec.2006.05.008
15. Devi, V.S. and Gnanavel, B. K. (2014) Properties of concrete manufactured using steel slag, 12th Global Congress on Manufacturing and Management, GCMM 2014, Procedia Engineering 97 (2014) 95 – 104, doi: 10.1016/j.proeng.2014.12.229
16. Dhoble, Yogesh Nathuji and Ahmed, Sirajuddin, Use of Steel Slag as Engineering Material and Its Limitations (June 18, 2012). CAN2012 Tenth AES-ATEMA International Conference AES-ATEMA’ 2012 Tenth International Conference on Advances and Trends in Engineering Materials and their Applications (Montreal, Canada: June 18 – 22, 2012). Available at SSRN: http://ssrn.com/abstract=2157198
17. Deccan Herald (2016) http://www.deccanherald.com/content/418164/now-pwd-use-slag- building.html – accessed on 17 May 2016
18. Dippenaar, R. (2004) Industrial uses of slag—The use and re-use of iron and steelmaking slags, VII International Conference on Molten Slags Fluxes and Salts, The South African Institute of Mining and Metallurgy, 2004. http://www.pyrometallurgy.co.za/MoltenSlags2004/057-Dippenaar.pdf - accessed on 4 June 2016
19. epa.gov, https://www3.epa.gov/wastes/conserve/imr/irc-meet/06-slag.pdf - accessed on 15 May 2016
20. Firoz, A.S. (2014) Long Term Perspectives for Indian Steel Industry, http://steel.gov.in/Long%20Term%20Perspectives.pdf – accessed on 12 June 2016
21. GOI, 2013-2014, Government of India, Outcome Budget of Ministry of Steel, http://steel.gov.in/Outcome%20Budget%20 (2013- 14)/outcome%20budget.pdf
22. Huang, Y.H., Liu, C.J. (2008) Analysis on comprehensive utilization of electric furnace slag. Ind Heat (in Chinese) 2008; 37(5):4-6.
23. Humam, T. and Siddique, R. (2013) Properties of Mortar Incorporating Iron Slag, Leonardo Journal of Sciences, Issue 23, July-December 2013 p. 53-60

24. Huang Yi et al. (2012) An overview of utilization of steel slag, Procedia Environmental Sciences 16 (2012) 791 – 801
25. Humaria, M. S. Y. (2014) Impact of Iron and Steel Slag on Crop Cultivation: A Review. Curr World Environ 2014;9(1). doi : http://dx.doi.org/10.12944/CWE.9.1.31
26. http://blog.ficci.com/steel-slag/5291, accessed on 20 April 2016
27. http://pmgsy.nic.in/workshop.pdf - accessed on 14 June 2016
28. http://www.cpcb.nic.in/newitems/24.pdf - accessed on 15 June 2016
29.http://ibm.gov.in/writereaddata/files/11042015112113IMYB2014Slag(Advance)
31.http://planningcommission.gov.in/aboutus/committee/wrkgrp12/wgrep_cement.pdf
32. http://www.meconlimited.co.in/writereaddata/MIST_2016/sesn/tech_4/3.pdf -