VALORIZATION OF PAPER INDUSTRY LIME SLUDGE, BOILER ASH AND ETP SLUDGE

Ph.D. THESIS

by

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INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
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July, 2019

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A THESIS

Submitted in partial fulfilment of the requirements for the award of the degree

of

DOCTOR OF PHILOSOPHY

in

Environmental Science and Technology

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STUDENT'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "**VALORIZATION OF PAPER INDUSTRY LIME SLUDGE, BOILER ASH AND ETP SLUDGE**" in partial fulfilment of the requirements for the award of the Degree of Doctor of Philosophy and submitted in the Department of Paper Technology of the Indian Institute of Technology Roorkee, Saharanpur Campus, Saharanpur is an authentic record of my own work carried out during a period from January, 2014 to July, 2019 under the supervision of Prof. Dharm Dutt, Professor, Department of Paper Technology, Indian Institute of Technology Roorkee, Saharanpur Campus, Saharanpur and Prof. Vivek Kumar, Professor, Centre of Rural Development and Technology, Indian Institute of Technology Delhi, New Delhi.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other Institution.

Dated: **(PRABHAT VASHISTHA)**

SUPERVISOR'S DECLARATION

This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

(Dharm Dutt)
Supervisor

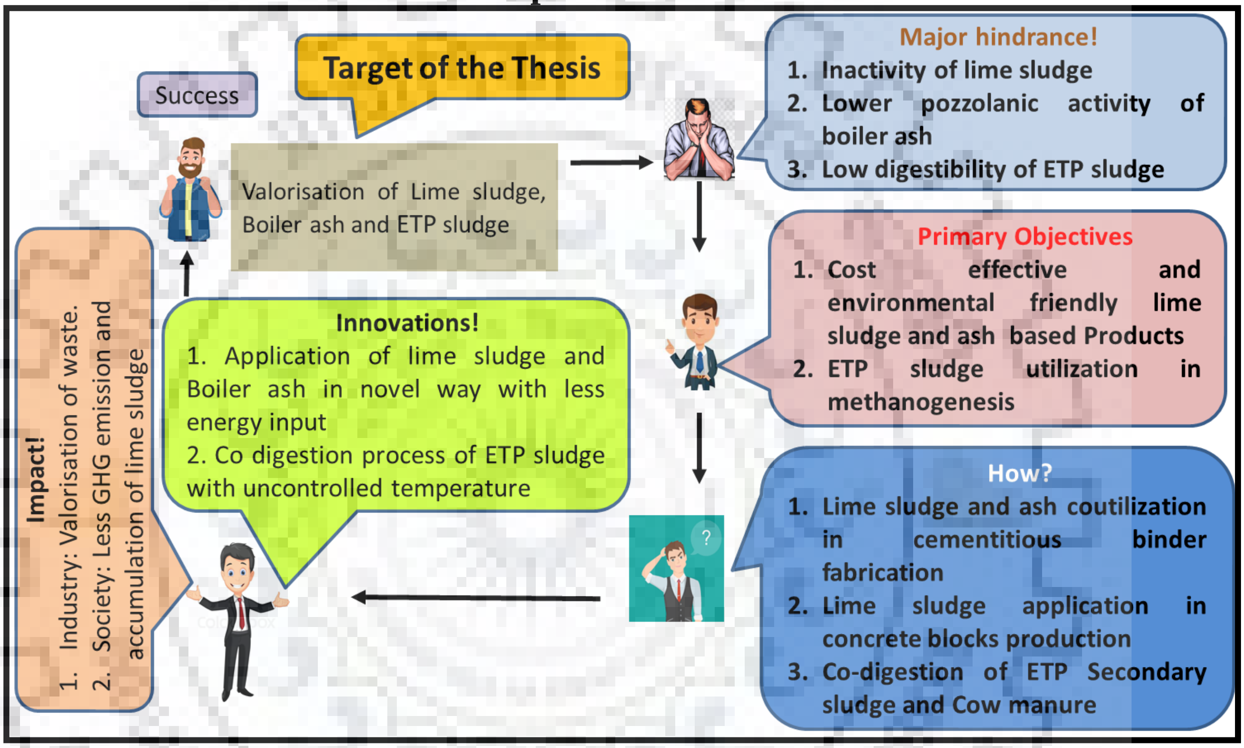
(Vivek Kumar)
Supervisor

Dated:

ABSTRACT

The industrial solid waste generation and its stockpile disposal have major environmental consequences. These consequences could be minimized through the solid waste application as a raw material in other industries. The current thesis focusses on application of paper industry solid waste in different applications like nanosilica synthesis, cementitious binder fabrication, application in concrete and methanogenesis.

Graphical Abstract



Boiler ash is utilized for the synthesis of nanosilica. The particle size of synthesized particles were found in the range of 10-25 nm. . FTIR, TEM and XRD studies confirmed the synthesis of nanosilica. Present study shows about 250 kg of nanosilica can be synthesized per ton of boiler ash with the nanosilica synthesis efficiency of almost 25%. Lime sludge application with nanosilica reduces the temperature of belite synthesis to 1000°C without addition of any chemical stabilizer and pre-calcination whereas conventionally, belite is synthesized above 1200°C. This method of belite based clinker synthesis is energy efficient and ecofriendly. The prepared clinker was mixed with Ground granulated blast furnace slag (GGBS) for the increment in early age strength as belite generally takes part in the development of late strength of concrete. The heat of hydration of developed binder, compressive strength and density of the prepared mortars complies the requirements of indoor and outdoor mortar applications. Lime sludge is also being utilized directly in the concrete with synthesized nanosilica and without nanosilica. The purpose was to increase the proportion of lime sludge application in concrete without affecting the compressive strength significantly. It provides a novel and relevant approach for bulk utilization of lime sludge with application of nanosilica synthesized from fly ash. This research will also be relevant for onsite utilization of paper industry boiler ash and lime sludge. It will cut down the transportation expenses of lime sludge and boiler ash disposal or utilization. Application of lime sludge with nanosilica in M25 grade of concrete found suitable. The concrete blocks with 30% application of lime sludge and 1% nanosilica produced sustainable concrete with increased compressive strength. 1% nanosilica addition with lime sludge resulted in 25% increased compressive strength in comparison to the blocks without nanosilica. It provides an edge of the 3 times more application of lime sludge and 30% less consumption of cement in concrete blocks without affecting the compressive strength significantly. The FE-SEM micrographs of concrete with 30% lime sludge and different proportion of nanosilica show a trend of increasing uniformity and microstructure compaction with increasing amount of nanosilica. Study provides a suitable route of value addition and valorization for lime sludge and fly ash. As another route of bulk utilization of lime sludge, it is also utilized with calcination at lower temperature than normal calcination temperature. The lime sludge is calcined at lower temperature of 650° C to convert metakaolinite in kaolinite. The MK (metakaolinite-$Al_2O_3.2SiO_2$) can make the lime sludge more reactive which makes it perfect raw material to use as cement additive.

$$\underset{\text{(Kaolinite)}}{Al_2Si_2O_5\,(OH)_4} \overset{(450\text{-}700\ ^0C)}{=} \underset{\text{(Metakaolinite)}}{Al_2Si_2O_7} + 2H_2O \quad (1)$$

Lime sludge calcined at low temperature of 650 °C can be applied productively as a pozzolana with cement. Compressive strength of produced concrete remains intact until 30% application of calcined lime sludge in binder. The pozzolanic behavior of lime sludge is due to the metakaolinite and calcium oxide produced after calcination of lime sludge at 650 0C. These are the sole reasons for increased lime sludge reactivity and accumulation of increased amount of calcium silicate hydrate (CSH) and hydrates of tetra calcium aluminates (TAH). The. Morphological study of concrete and heat of hydration of prepared binder also confirms the increased reactivity of lime sludge. The prepared binder is sustainable with 18% less production cost and emission of greenhouse gases. ETP sludge with cow manure is utilized for biogas production from anaerobic co-digestion (AD). It can stabilize the sludge with energy production at the same time. The AD process was performed at uncontrolled temperature in mesophilic range, which can be effective for small and medium scale of industries. The aim was to utilize the Paper ETP sludge (PSS) for the AD process and to Co-utilization of PSS with cow manure to check the effect of digestion. The reactor containing PPS only was started to generate biogas on 5th day of the reaction with 7.8% of methane. The cumulative methane yield attained to 13.5 ml/g volatile solid (VS) until day 30. The second reactor containing PPS and cow manure produced methane 134 ml/g VS until day 30. This study presents a more optimized process of anaerobic digestion of paper sludge and co-digestion of paper sludge with cow manure. The utilization of lime sludge and boiler ash of paper industry is recommended as material for construction applications while anaerobic digestion can be used for energy recovery from ETP sludge. These applications will also beneficial for reducing environmental wallop.

As I complete my voyage through this vast ocean of knowledge, I would like to thank all those who stood beside me and supported me for its successful and timely completion. Without their help, it wouldn't have been possible.

First of all, I would like to show my gratitude towards my supervisors, Prof. Vivek Kumar, Professor, Centre of Rural Development and Technology, Indian Institute of Technology Delhi, New Delhi and Prof. Dharm Dutt, Professor, Department of Paper Technology, Indian Institute of Technology Roorkee, Saharanpur Campus, Saharanpur. Working with them was a great experience. Their precious suggestions and discussions helped me to comprehend concepts on diverse topics. Their constant encouragement and support in various ways provided me the motivation for the research. I am fortunate to have Pathfinders like them and will always be thankful for their care and support.

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I thank the Almighty God, for we are all his creations and everything happens by his will.

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PRABHAT VASHISTHA

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LIST OF ABBREVIATIONS

OPC	Ordinary Portland Cement
DSC	Differential Scanning Calorimetry
XRD	X-Ray Diffraction
CSH	Calcium Silicate Hydrate
CASH	Calcium Aluminum Silicate hydrate
CH	Calcium Hydroxide
GGBS	Ground Granulated Blast Furnace Slag
SCM	Supplementary Cementitious Materials
C_2S	Dicalcium Silicate
LS	Lime Sludge
BA	Boiler Ash
FA	Fly Ash
XRF	X-Ray Fluorescence
LOI	Loss of Ignition
TEM	Transmission Electron Microscopy
FTIR	Fourier Transform Infrared Spectrophotometer
BET	Brunauer–Emmett–Teller
DTA/TGA	Differential Thermal Analysis / Thermogravimetric Analysis
NS	Nanosilica
IS	Indian Standard
C	Cement
FA	Fine Aggregates

CA	Coarse Aggregates
W	Water
CS	Compressive Strength
SEM	Scanning Electron Microscope
MK	Metakaolinite
ASTM	American Society for Testing and Materials
TAH	Tetra Calcium Aluminates
RLS	Raw Lime Sludge
CLS	Calcined Lime Sludge
LCA	Life Cycle Assessment
CFC	Chlorofluorocarbon
AD	Anaerobic Digestion
ETP	Effluent Treatment Plant
BMP	Bio Methane Potential
VS	Volatile Solid
PSS	Paper Secondary Sludge
TS	Total Solid
VFA	Volatile Fatty Acid
CLB	Calcined Lime Sludge Binder
RLB	Raw Lime Sludge Binder
INR	Indian National Rupees

LIST OF PUBLICATIONS

JOURNAL ARTICLES

1. **P. Vashistha**, S.K. Singh, D. Dutt, V. Kumar, "Sustainable Utilization of Paper Mill Solid Wastes via Synthesis of Nano Silica and Belite Based Clinker", Journal of Cleaner production 224 (2019) 557-565. https://doi.org/10.1016/j.jclepro.2019.03.20 (I.F.- 6.3).
2. **P. Vashistha**, S.K. Singh, D. Dutt, V. Kumar, "Valorization of paper mill lime sludge via application in building construction materials: A Review", Construction and Building Materials 211 (2019) 371-382. DOI: 10.1016/j.conbuildmat.2019.03.085 (I.F.- 4.1).
3. **P. Vashistha**, S.K. Singh, D. Dutt, V. Kumar, "Application of fly ash synthesized nanosilica and lime sludge in concrete: an environmental-friendly and sustainable solution". Clean Technologies and Environmental Policies. pp 1-13 https://doi.org/10.1007/s10098-019-01753-6 (I.F.- 2.3)
4. S. Kulkarni, **P. Vashistha**, S.K. Singh, V. Kumar, Sustainable utilization of deinking paper mill sludge for the manufacture of building bricks, Journal of Cleaner production 204 (2018) 321-333. https://doi.org/10.1016/j.jclepro.2018.09.028 (I.F.- 6.3).

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1. P. Vashistha, S.K. Singh, D. Dutt, V. Kumar, "Low temperature calcination of lime sludge to develop sustainable cementitious binder". Resources, conservation and recycling. (Under Review, Communicated on 26th July 2019)
2. P. Vashistha, M. Baghban, "Utilization of Industrial Solid Waste in Binder Fabrication: a review", Journal of Cleaner Production. (Communicated)
3. S.K. Singh, Aastha singh, B. Singh, P. Vashistha, "Application of Thermo-Chemically activated lime sludge in Production of Low Clinker Cementitious Binders". Journal of Cleaner Production. (Communicated on 10th September 2019)

CONFERENCE PROCEEDINGS

1. **P. Vashistha,** V. Kumar, "Paper mill lime sludge valorisation as partial substitution of cement in mortar", 8th IconSWM Conference on sustainable waste management, November 22-24, 2018 Vijayawada (A.P.)
2. **P. Vashistha**, V. Kumar, S.K. Singh, "Valorization of paper mill solid wastes: partial replacement of cement by application of lime sludge and boiler ash synthesized nano

silica in concrete" 5th World convention on recycling and waste management, September 11- 12, 2017 Singapore.

3. S K. Singh. P. Rekha, A. Singh, P. Vashistha, "Newer Cementitious Binder from Thermo-Chemically Activated Lime Sludge and Its Use in Mortar" (July 1, 2019). Available at SSRN: https://ssrn.com/abstract=3408912

4. V. Kumar, **P. Vashistha**, "Lime sludge: an emerging alternate construction building material for the partial replacement of fine aggregate", 2015 AIChE Annual meeting Nov 8-13, 2015 Salt Lake City, U.S.A.

CHAPTER - 1

INTRODUCTION

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CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

India produces about 13 million tons of paper, paperboard, and newsprint per annum, accounting to 3.18 % of the total world production (408 million tons per annum) [1]. Pulp and paper industries generate a diverse class of solid waste (e.g., lime sludge, boiler ash, fly ash, primary sludge, secondary sludge) from different operational processes [1, 2]. Total worldwide production of paper industries waste is over one million metric ton per year [3, 4]. Production of one-ton paper generates about 656 kg ash (boiler and fly ash) and 593 kg lime sludge [1, 5]. Therefore, a paper industry, during manufacturing generates more sludge than the merchandise, which is an environmental concern and cause of apprehension of modern times. **Fig. 1.1** indicates all the conceivable solid waste generated in the paper industry.

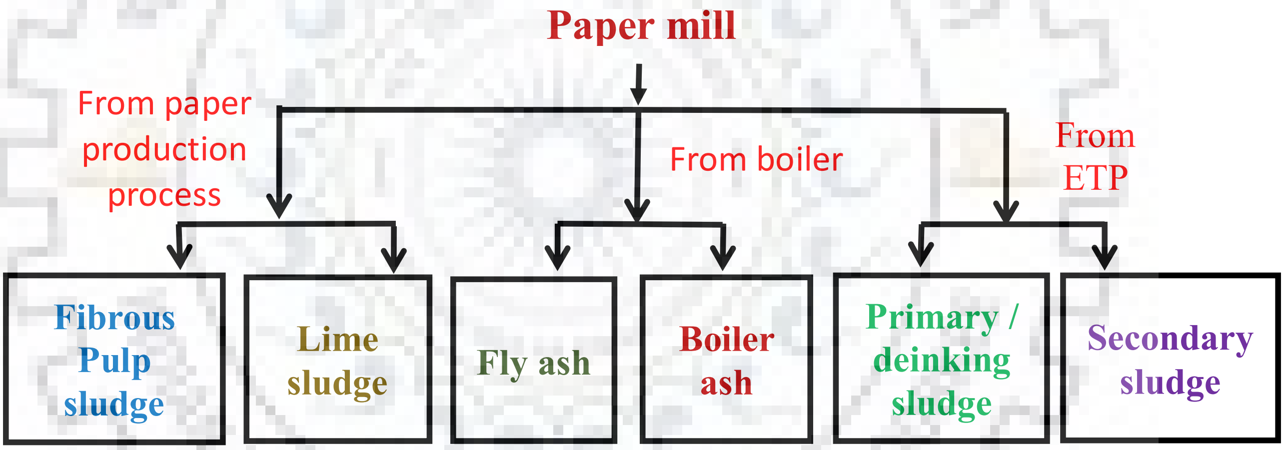

Fig. 1.1: Types of paper mill sludge

Therefore, development of novel products is needed to upsurge the utilization of these waste materials.

The lime sludge generation in such large quantities puts the pulp and paper industries among most polluting industries [2]. Lime sludge is generated in the chemical recovery section of the paper industries. **Fig. 1.2** demonstrates the lime sludge generation process.

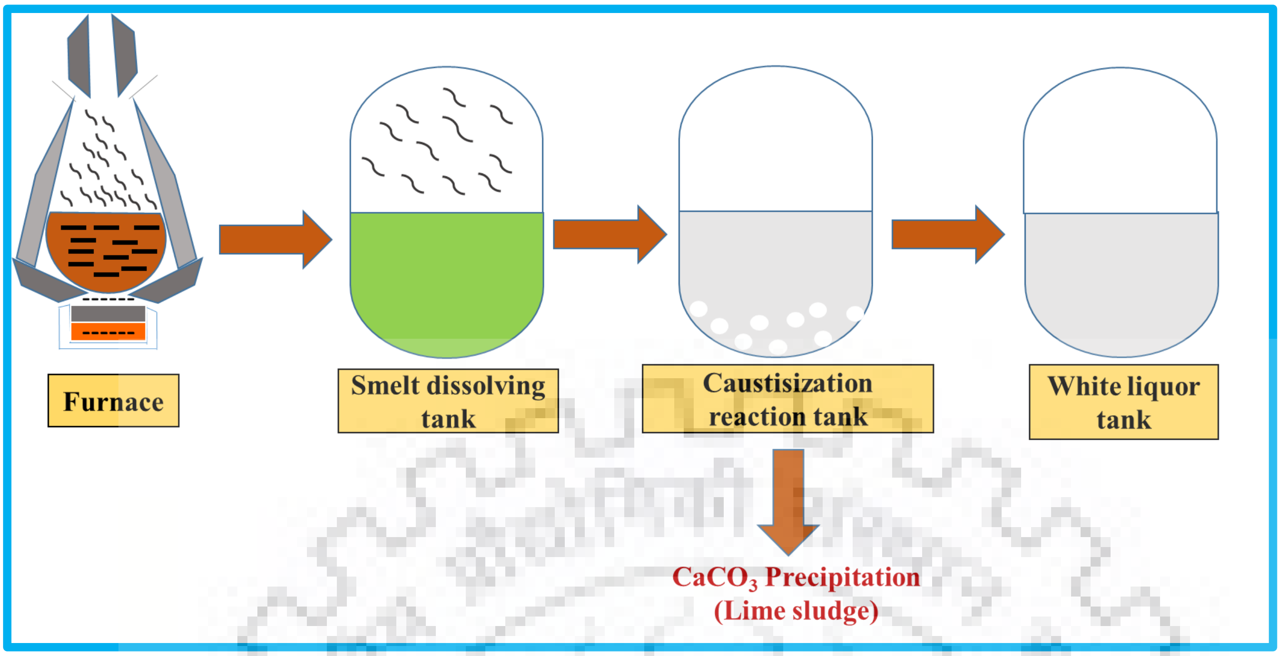

Fig. 1.2: Flow diagram for lime sludge generation in paper mill

All the integrated large-scale paper industries in India are equipped with chemical recovery system [3]. During the chemical recovery process, smelt i.e. chemicals in their molten stage are dissolved in water, to form green liquor. This green liquor is converted into white liquor by causticization process. In the causticization process, the smelt, which is mainly soda ash (Na_2CO_3) reacts with calcined lime (CaO) and produces caustic soda (NaOH) along with calcium carbonate (lime sludge) as a waste material [3, 4, 5]. Lime sludge can be recycled through the lime kiln, to reuse as lime (CaO) in the causticization process. However, lime recovery is an energy-intensive process (1530-1830 kcal/kg of lime). Agro residue based paper mills, release high silica (5-10%) in lime sludge and poses more significant problems such as scaling in lime kiln [3]. This is the reason why agro residue based paper industries generally choose to dispose off the lime sludge in landfill instead of recycling it.

Land applications and landfilling are the preliminary measures taken to dispose off paper mill lime sludge [6]. But the cost of landfilling is increasing because of taxes, stringent regulations, and decreasing potential with landfill space becoming scarce and expensive. Therefore, the utilization of lime sludge in value added products such as building construction materials is of high importance because of its quality [7]. Lime sludge utilization possibilities are illustrated in **Fig. 1.3**.

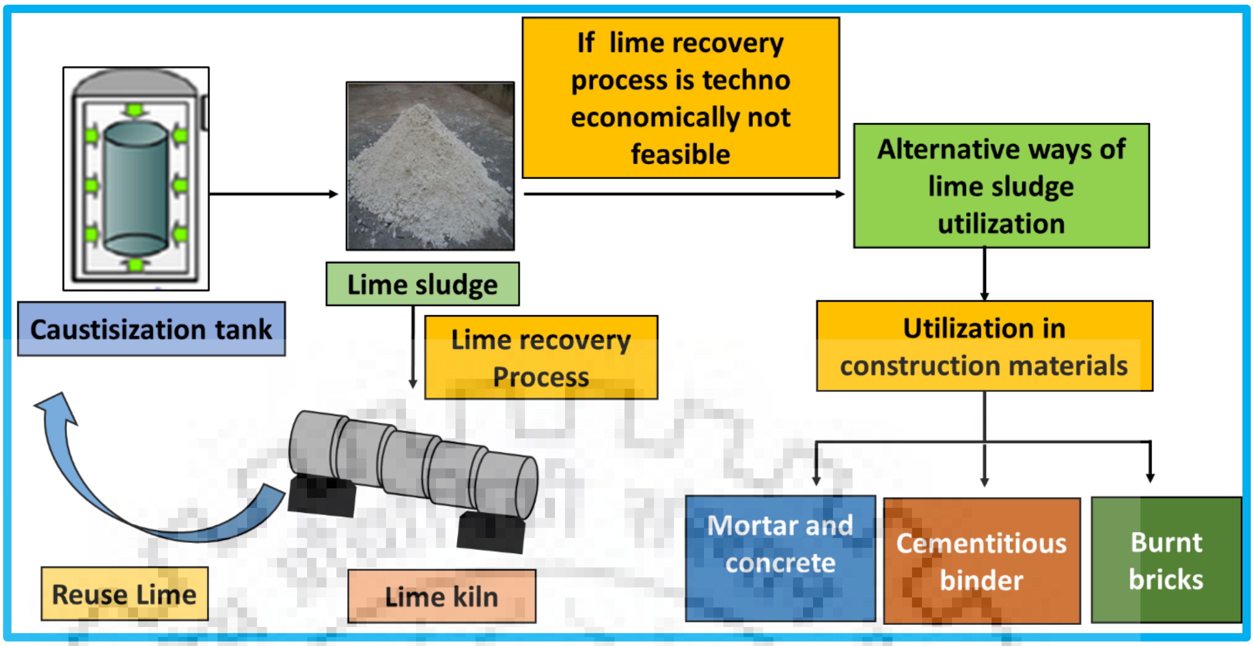

Fig. 1.3: Utilization Potential of Lime sludge

With the ever-growing world population, the demands of building materials are also increasing. The mismatch of demand and supply of building materials has thus become a concern for the construction sector [8]. Hence, to fill this gap and for the continuous supply of building materials, researchers are developing appropriate alternative solutions for construction materials [9]. Utilization of waste materials from different industries could be the solution to fulfill the gap of demand and supply in the construction industry. Several researchers review the requirement of waste utilization in construction industry [11-17]. Among various waste materials, lime sludge has high potential to be used as construction materials. At the same time, it is also an effective solid waste reduction approach. In recent years, lime sludge has been used with other wastes for manufacturing of various building construction materials.

1.2 APPLICATION OF LIME SLUDGE IN CEMENT FABRICATION

Cement remains the central facet to satisfy the ever-growing needs of global infrastructure and exponentially increasing building material demand. **Fig. 1.4** illustrates the year wise increment in the production of cement.

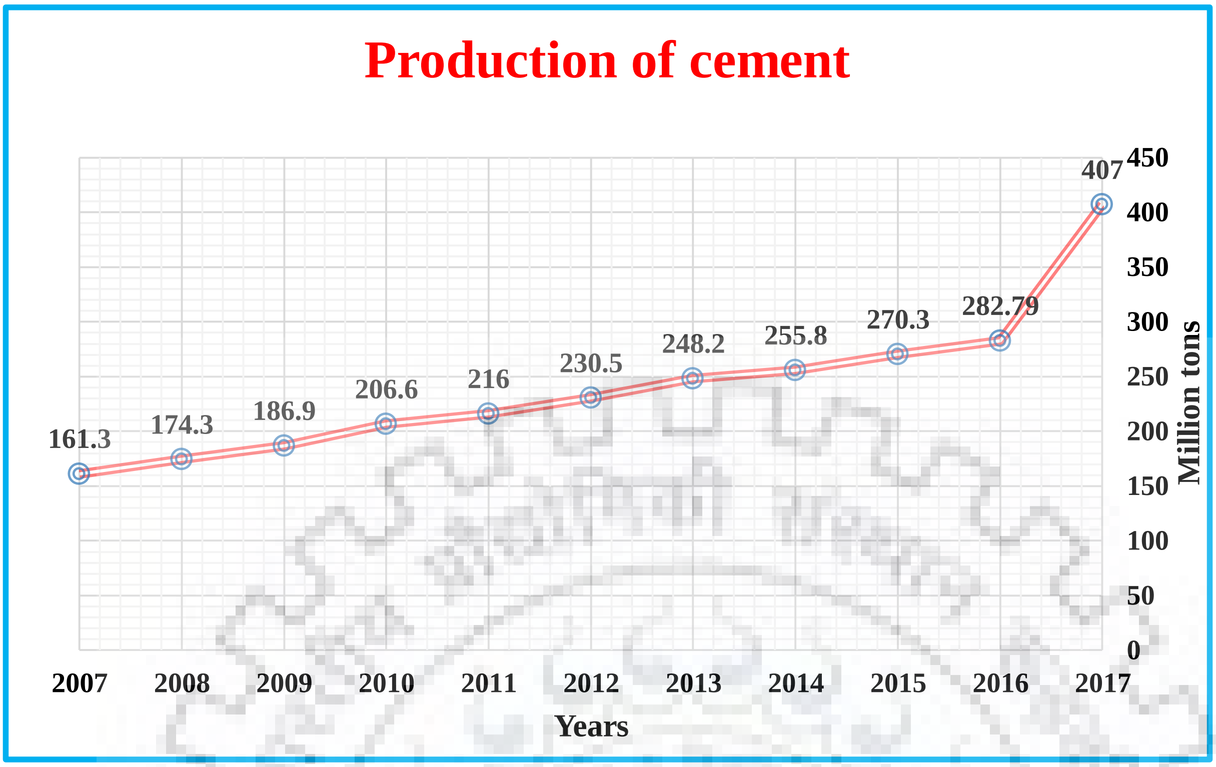

Fig. 1.4: Production of cement in India [18]

As a consequence, it is critical to address the cement industry's growing challenges, such as conservation of materials, energy resources, and CO_2 emission. According to the International Energy Agency, the use of alternative materials and energy efficient process are the main levers for cement industries. In recent years, many attempts have been made to increase the incorporation of alternative materials, but potential for further exploration in this area still exists. Subsequently, there are limitations of traditional cement constituent's material availability. For that reason, new alternative materials might replace cement constituents in the coming years. *Amin et al.* [19] studied pozzolanic cement blends containing burnt clay with and without silica fume. The 10 % bunt clay with OPC shows enhancement in compressive strength. The DSC and XRD studies indicated the formation of CSH and CASH with CH products. The electric arc furnace slag with and without silica fume was found useful for the fabrication of blended cement paste [20]. A similar approach is explored with lime sludge for cement fabrication.

The lime sludge is mainly composed of calcium carbonate with some silica and alumina. The lime sludge is primarily composed of calcium carbonate with some silica and alumina. The main crystalline phases (**Fig. 1.5**) present in lime sludge are calcite and kaolinite. Calcite is a calcium carbonate mineral while kaolinite is made up of hydrous aluminum silicate ($2H_2O.Al_2O_3.2SiO_2$). Both chemical and physical qualities of kaolin influence its utilization. Calcination of lime sludge produces metakaolin ($Al_2O_3.2SiO_2$) that is highly reactive and can be used as an additive material in cement. The mineralogy of lime sludge shows its potential as raw material for yielding a product with pozzolanic activity, hence for the manufacture of a cementitious binder. Therefore, the cementitious binder is an ideal target for lime waste utilization.

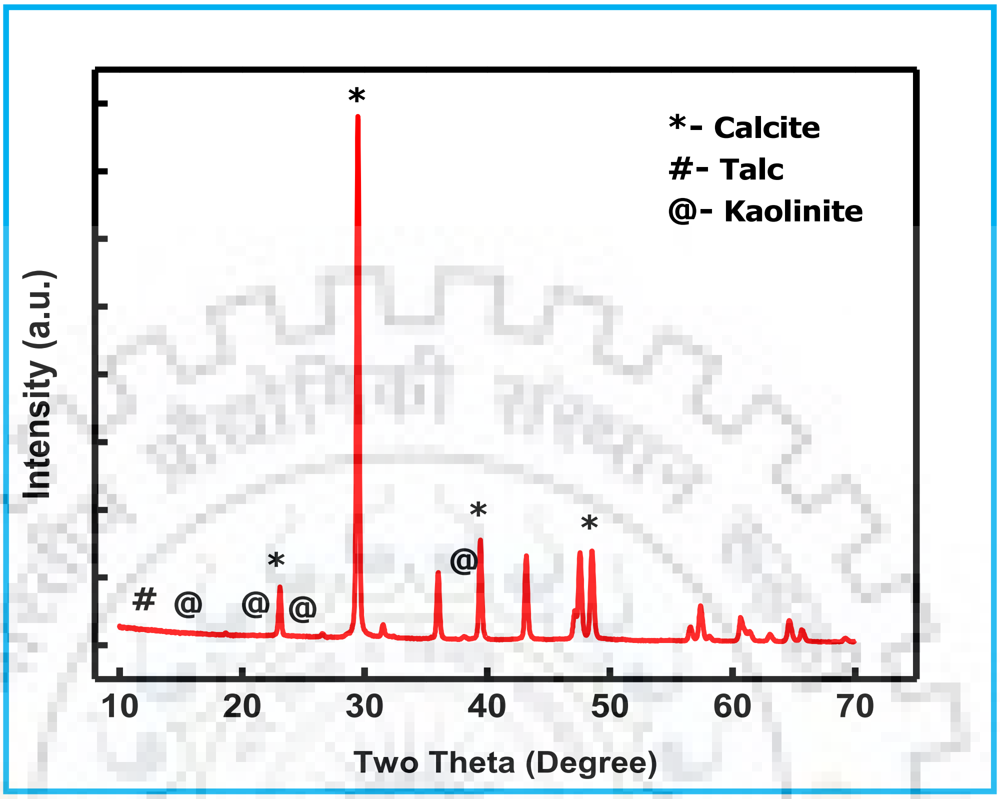

Fig. 1.5: XRD of lime sludge

Table 1.1 represents various studies conducted on lime sludge utilization in cement production. *Schneider et al.* [21] provided an overview considering all possibilities of lime sludge use in the production of cement. *Garg et al.* [22] conducted an experimental study for the tile's fabrication with fertilizer industry lime sludge, in which various pozzolana was mixed in blended cement, such as calcinated clay, fly ash and silica fume with some amount of gypsum. Pozzolana content in OPC was found to be varying from 5 % to 20 %, and better results were observed up to 20 % of pozzolana than compared to conventional cement based tiles. *Wei et al.* [23] had undertaken a study on dried lime sludge utilization in cement production. In the presented research, the viability of amalgamating lime sludge with cement kiln and its influence on the sintering of cement was investigated. The results indicated that the lime sludge addition improved the burning ability of clinker, which in turn reduced the temperatures for calcium carbonate ($CaCO_3$) decomposition and liquid phase formation.

Further, the presence of phosphorus and other trace elements increased the liquid phase and decreased the viscosity, making it favorable for tricalcium silicate (C_3S) formation in cement clinker. *Maheswaran et al.* [24] investigated the synthesis of belite from paper mill lime sludge and nano-silica. Belite or β-dicalcium silicate (β-C_2S, Ca_2SiO_4), is the component of Portland cement clinker which constitute 20 % of it, whereas alite is the main component which comprises

80 % of cement clinker. In the presented research belite was synthesized by using lime sludge and nanosilica in a ratio of 2: 1 at a relatively lower temperature of 850 °C through the solid-state reaction, while Portland cement clinker is was produced conventionally by sintering raw materials on a higher temperature, i.e. 1200 °C, with naturally occurring raw materials like limestone and quartz. In another extended work by *Maheswaran et al.* [25] lime sludge was used with silica fume for the synthesis of belite. *Leire et al.* [26] had undertaken a study on the production of the binder with the application of paper mill waste. Different blends of lime sludge, biological sludge, and fly ash were prepared and then sintered at a relatively lower temperature of 1350 °C in comparison to conventional clinker synthesis temperature, which is 1450 °C, to develop belitic and Portland clinkers. Blend with 49 % lime sludge, 20 % fly ash and 30 % biological sludge produced the maximum amount of belite was also used to prepare the belite cement-based mortar that produced satisfactory mechanical strength and did not reveal signs of deterioration or durability weakness. *Simao et al.* [27] tried to use lime sludge, coal-biomass ash, and wastewater treatment process sludge for the manufacture of clinkers, named eco clinkers. Different formulations were prepared mixing three raw materials in various ratios and fired at the temperature ranged between 1350 to 1450 °C. The study revealed that the formulation with 69 % lime sludge, 29 % biomass ash and 2 % wastewater process sludge at 1450 °C showed the main crystalline phases commonly found in commercial cement and therefore was considered as eco clinker. Besides, this eco clinker was chosen to produce the eco-cement (95 wt% of eco clinker and 5 wt. % of gypsum). Furthermore, the produced eco-cement was used to produce eco mortar. Functionalization of eco-cement in mortar showed compression strength of ~21 MPa after 28 days curing time.

With the recent advancement, researchers also worked on the role of lime sludge in geopolymer concrete. *Adesanya et al*. [28] in an experimental study used lime sludge as an activator in geopolymer cement CEM IIIC and type 32.5 N class under the European standards EN-197 fabrication. The lime sludge was pretreated with sodium hydroxide and then mixed with blast furnace slag to make one part geopolymer cement. Additionally, non-reacted lime sludge worked as filler in the mortar preparation. Cement showed increasing compressive strength by increasing the amount of lime sludge. It was observed that the maximum compressive strength (42 N/mm^2) was attained with 18 % application of lime sludge. In addition to the strength properties of the mortars, the heat of hydration and setting time of cement was also analyzed. In case of the heat of hydration, cumulative heat release from the lime sludge cement was found equal to the OPC cement. It was also observed that setting time of the mix increased with the increasing amount of the lime sludge in the cement due to the formation of carbonate salts such as calcite and pirssonite. These salts increased the setting time of the cement.

Utilization of lime sludge in environmentally and economically sustainable manner in cement fabrication can be a favorable solution to the industries for lime sludge disposal problem. The application of lime sludge in the process of cement manufacturing also reduces the consumption of naturally available mineral soil and at the same time reduces the carbon emission due to less energy consumption [24, 26].

Table 1.1: Lime sludge application in cement fabrication

S. N.	Materials used with lime sludge	Product prepared	Parameter studied	Reference
1.	Nano silica	Clinker	Mineralogical studies	*Maheswaran et. al., 2015a*
2.	Silica Fume	Clinker	Mineralogical studies	*Maheswaran et al. 2015b*
3.	Fly ash and biological sludge	Clinker	Mineralogical, hydration and compressive strength studies	*Leire et. al. , 2014*
4.	-	Cement	Lime sludge addition in cement kiln improved sintering of cement	*Wei et. al., 2014*
5.	Sodium hydroxide and Ground granulated blast furnace slag (GGBS)	Geopolymer cement	Mineralogical, heat of hydration and compressive strength	*Adesanya et al., 2018*

1.3 APPLICATION OF LIME SLUDGE IN CEMENT MORTAR

Mortar, a workable paste of cement and sand, is used in construction activities in masonry work. Lime sludge has been utilized in mortars as the replacement material for cement and fine aggregates by several researchers. It is utilized in mortars in different forms (calcined and as received) and combinations with other materials. **Table 1.2** summarizes the work of various researchers on the effect of lime sludge in mortars. The calcination of lime sludge between 650 °C and 800 °C enhances the reactivity of the lime sludge. The lime obtained after decomposition of $CaCO_3$ is hydraulically reactive and stable for making binders. Besides, active CaO reacts with available SiO_2 in matrices to make secondary C-S-H products. However, the presence of excessive CaO may have an adverse effect on durability. *Bouamrane et al.* [29] used incinerated lime sludge for mortar preparation. Lime sludge treated at different temperatures was used to replace 25 % of cement in mortars preparation. The compressive strength of the mortars after 90 days of curing was found more than conventional concrete. The compressive strength development at the later stage of curing might be due to the conversion of calcium carbonate of the lime sludge into the calcium oxide on the heat treatment which helps in the formation of more calcium silicate hydrate in late-stage of curing. Calcination of the lime sludge consumes an immense amount of energy that vague the point of the economy. For the economical point of view, lime sludge should be utilized in its as-received condition. In agreement with the reason stated above, *Modolo et al.* [30] worked on as received lime sludge utilization. Lime sludge was used as a filler material in mortars preparation and compared them with the mortars prepared with the use of standard filler (commercial filler) application. Lime sludge was used after ball milling with reduced particle size. Mortars were prepared after replacing 6, 12 and 18 % of total aggregates by lime sludge by weight, resulting in 10 %, 17 % and 23 % increase in compressive strength respectively in comparison to the reference mortar. This effect might be associated with filler and binder effect of lime sludge, due to the presence of ball milled small particles in the matrix of the concrete. After this outcome, some studies have also focused on the replacement of fine aggregates with lime sludge. *Sahu et al.* [2] have studied two types of mortars with four lime sludge binder combinations. Binder 1 was prepared with lime sludge (30 %) and fly ash (70 %) whereas Binder 2 was prepared with the same proportioning having 1 % gypsum. The addition of gypsum showed a positive effect on the compressive strength of mortars due to accelerated pozzolanic reaction. *Bras et al.* [31] worked on producing eco materials for construction applications by the application of as received paper mill lime sludge and fly ash. The mortars were prepared with and without lime sludge and fly ash. Maximum compressive strength and flexural strength were achieved by replacing 10 % of total cement by lime sludge; however, strength was decreased if cement replacement with lime sludge exceeded 10 %. *Kumar et al.* [32] made experimental investigations on the application of fly ash and paper mill lime sludge in a mortar. Lime sludge was used in as a received condition. The optimum compressive strength of 25 N/mm^2 was found in mortars with 12.5 % replacement of cement by lime sludge and 12.5 % replacement by fly ash. Mortar prepared with higher lime sludge and fly ash content showed a significant decrease in compressive strength. *Oliveira et al.* [33] developed a cement adhesive with lime sludge, fly ash, and Portland cement. Maximum 20 % of lime sludge & fly ash were used then these cement pastes were used in the grounding of the mortars. Fluidized bed reactor sand was used to replace fine aggregates in mortar preparation. The research concluded that fly ash application with lime sludge increased the yield stress and viscosity of cement paste. Mortars showed best compressive strength with the 10 % application of lime sludge and 10 % application of fly ash in cement paste.

S. N.	Material replaced	Material used with lime sludge	% replacement with lime sludge	Optimum Replacement (%)	Fine Aggregates particle range (mm)	Parameter studied	Effect on compressive strength in respect to optimum replacement	Reference
1.	Cement	Fly ash, Gypsum	80-100	80	0.15-4.75	Compressive strength	27% increased	*Sahu et. al., 2014*
2.	Fine aggregate	-	10-30	30	_	Compressive strength	1.34% increased	*Modolo et. al., 2014*
3.	Cement	-	10-30	25	_	Compressive strength	3.1% increased	*Bouamrane et al., 2014*
4.	Cement	Fly ash	10-20	10	_	Compressive strength, flexural strength	6% decreased	*Brás et. al., 2016*
5.	Cement	Fly ash	12.5	12.5	0.15-4.75	Compressive strength	4.1% increased	*Kumar et. al., 2016*
6.	Cement and Fine aggregate	Fly ash	10	10	_	Compressive strength	37% decreased	*Oliveira et al., 2017*
Note: Authors have recommended the optimum % of replacement based on the maximum compressive strength with lime sludge application								

Table 1.2: Application of lime sludge in mortar

Based on research work carried out, lime sludge shows a significant potential for replacing cement or fine aggregates in concrete and mortar. Researchers worked on the different grades of concrete, but in the study of these innumerable researches, it is concluded that compressive strength of concrete and mortars remains same as that of reference maximum up to 30 % replacement of total cement and afterward start decreasing with an increase in replacement of cement by lime sludge. Some research works have optimized this limit of lime sludge application between 10-20 %. In case of replacement of fine aggregates by lime sludge, no significant effect on compressive strength of mortars and concrete was observed up to 25-30 % application of lime sludge. Utilization of other industrial by-products with lime sludge in mortar resulted in better mechanical strength properties**.**

1.4 APPLICATION OF LIME SLUDGE IN CONCRETES

Concrete is a composite material made up of fine and coarse aggregates bonded together with cementitious binders that hardens over time. Researchers across the globe are trying for the utilization of various types of wastes such as sugarcane bagasse ash, fly ash, recycled aggregates, rubber waste, ground granulated blast furnace slag, silica fume, ceramic waste, waste glass sludge, agro waste and hydrated lime from different industries for cost-effective and sustainable production of concrete. These materials were deployed either as filler or as pozzolanic materials in the cement-based concrete [34-44]. The wastes from the pulp and paper industries, e.g., lime sludge, deinking sludge, primary sludge, and waste paper fibrous sludge are also being used in building materials like as thermal insulation material in bricks and as filler & pozzolan in cement-based concrete production [13, 45-48] *Cordeiro et al.* [37] used sugarcane bagasse ash in Portland cement and lime-based mortars, it proved the pozzolanic activity and filler effect of the ash. Paper industry deinking sludge has also been utilized in the formation of masonry blocks by *Singh et al.* [48] and in mortar renders by *Yan et al.* [38]. The cellulosic content of deinking sludge proved to be an active set retardant in this study. Similar study with paper primary sludge was performed by *Malaiskiene et al.* [41], it also confirmed the slowdown of exothermic reactions in cement paste with paper sludge application. *Abo-El-Enein et al.* [47] used cement kiln dust and hydrated lime as cementious material in mortars. In another study, *Abo-El-Enein et al.* [42] utilized lime rich sludge with ground granulated blast furnace slag for fabrication of cementious building materials. Apart from this, wastes are also utilized in the preparation of geopolymer cement. *Adesanya et al.* [28] utilized slag and paper industry sludge in the fabrication of geopolymer cement.

The key to gainful utilization of waste materials in concrete depends on their chemical composition [34, 36, 49]. The composition (**Table 1.3**) and fineness (BET surface area 15 m^2/g)

indicates that some of the ingredients used in concrete can be targeted and replaced with lime sludge [11, 31, 49]. **Fig. 1.6** represents the different possible methods of lime sludge application in concrete production.

Table 1.3: Chemical composition of lime sludge [2, 11]

Oxides	Percentage (%) in lime sludge
SiO_2	2.0 - 8.0
Al_2O_3	0.8 - 5.0
Fe_2O_3	0.8 - 2.5
CaO	70.0 - 93.0
MgO	0.2 - 10.0
SO_3	0.2 - 9.0
Na_2O	0.8 - 2.0
NiO	0.01 - 0.02
MnO	0.01 - 0.02
P_2O_5	0.1 - 0.3
CoO	0.01- 0.02
SrO	0.01- 0.02
CuO	0.01-0.02
MoO_3	0.01-0.02
LOI (loss of ignition)	20.0 -50.0

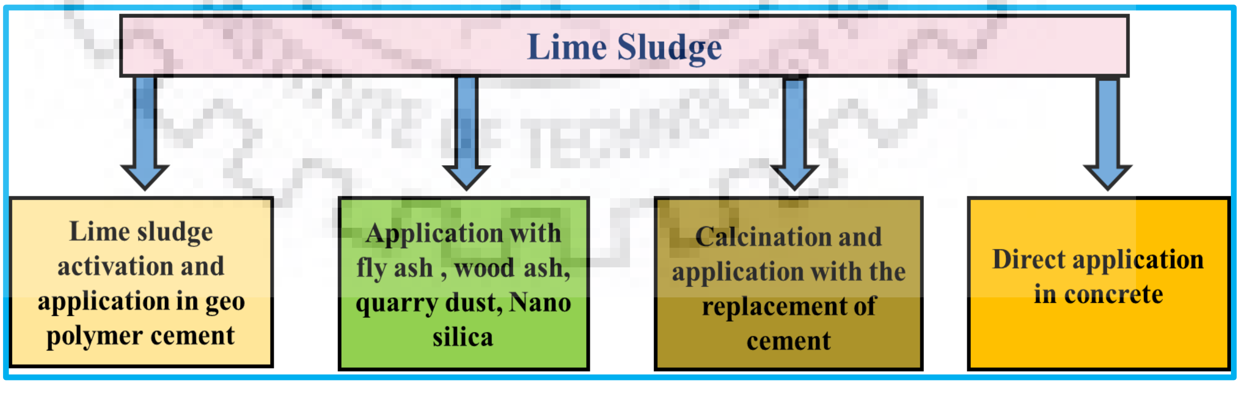

Fig. 1.6: Different methods of lime sludge utilization in concrete

1.4.1 Impact of lime sludge on compressive strength of concrete

Compressive strength is the first parameter for quality assurance of concrete. Therefore, based on its compressive strength and ratio of raw materials used in concrete, the concrete has been defined into different grades. **Table 1.4** represents the proportioning and compressive strength of standard concrete grades [50].

Table 1.4: Compressive strength of different grades of concrete at 7 and 28 days [50]

Grade of Concrete	Compressive strength (N/mm^2) at 7 days	Specified compressive strength (N/mm^2) at 28 days	Ratio (C:FA: CA)
M-15	10.5	15	1:2:4
M-20	13.0	20	1:1.5:3
M-25	17.0	25	1:1:2
M-30	20.5	30	1:1:3
M-35	24.0	35	1: 0.5: 1
M-40	27.0	40	1: 0.3: 0.6
C: Cement, FA: Fine aggregate, CA: Coarse aggregate			

Numerous studies have been conducted to describe the effect of lime sludge on concrete. **Table 1.5** summarizes the work of various researchers on the effect of lime sludge application on different grades of the concrete after 28 days of curing. Researchers have utilized Lime sludge in preparing different grades of concrete. Most of the studies have been conducted on M20, M30 and M40 grades of concrete only one study by *Yousuf et al.* [51] could be found on the M15 grade of concrete. **Fig. 1.7** illustrates the effect of lime sludge in different grades of concrete reported by three independent researchers. However, for a particular grade of concrete, similar trend has been reported by other researchers. The effect on the M15 grade of concrete has not been presented due to single study.

Studies on M20 grade of concrete concluded that 10-20 % replacement of cement by lime sludge resulted in a slight increase in compressive strength in comparison to reference concrete.

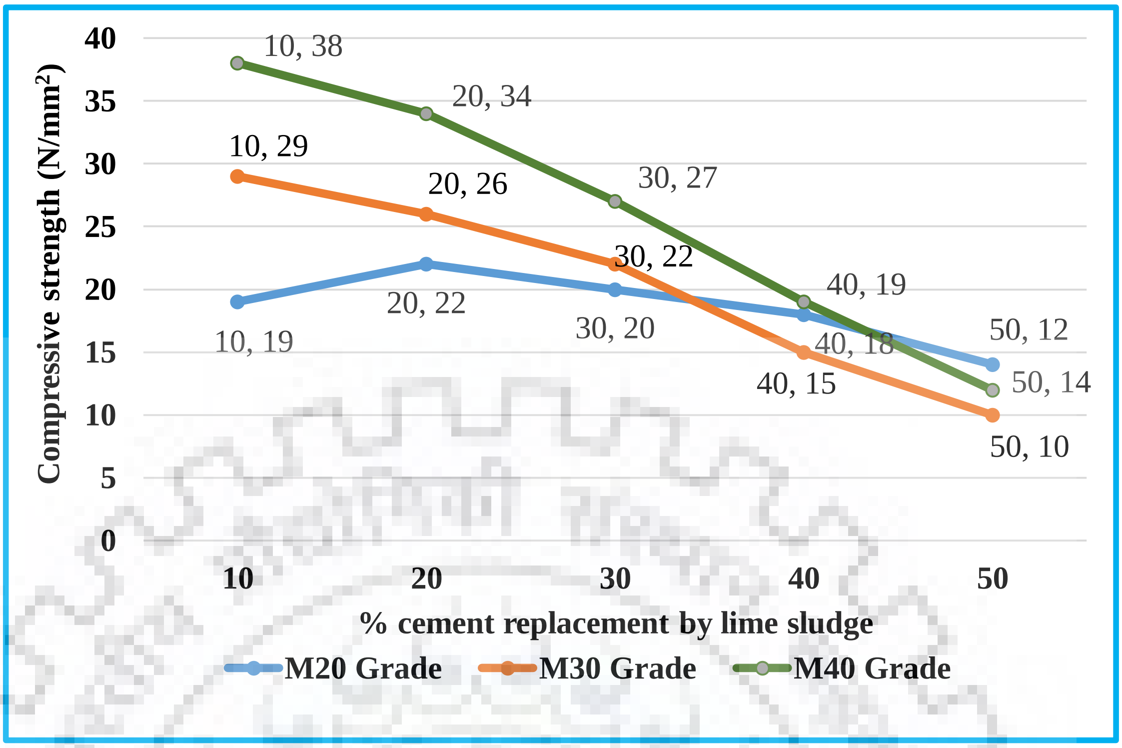

Fig. 1.7: Effect of lime sludge on different grades of concrete after 28 days of curing [49, 52, 62]

However, increasing the replacement further resulted in the reduction of compressive strength. Moreover, at 30 % replacement of cement by lime sludge shows similar compressive strength as that of conventional M20 grade concrete [52-55]. This kind of effect of lime sludge in concrete might be associated with its binder type effect. The negative impact on the higher percentage of lime sludge is might be due to the saturation of lime sludge binding in the matrix. This restricts the bulk utilization of lime sludge in concrete. Therefore, it was needful to utilize lime sludge in large proportions, which led the researchers to employ lime sludge in the upper grade of concrete. Many researchers tried to upsurge the utilization of lime sludge in M30 grade of concrete blocks. However, none of the researchers has reported a trend similar to the published in case of M20 concrete. *Srinivasan et al.* [56] reported a decrease in compressive strength with lime sludge and restricted replacement of total cement with lime sludge up to 30 %. Since beyond this limit of replacement, the compressive strength decreased drastically below the M30 grade of concrete. *Maheswaran et al.* [49] also observed a similar trend in compressive strength reduction. It was inferred by the study that lime sludge can only work as filler material, and only 20 % of cement replacement was acceptable in M30 grade of concrete. Excessive use of lime sludge is reported to have a negative impact on strength properties of the M30 grade of concrete. There is no literature describing the reason and mechanism of these contradictory results of M20 and M30 grade concrete compressive strengths. Although, this kind of contradiction is might be linked to

Table 1.5: Application of lime sludge in concrete

S. N.	Material replaced	% replacement by lime sludge	Grade of concrete	Optimum % replacement of lime sludge	Aggregates particle size range (mm)		Parameter studied	Effect on compressive strength in respect to the optimum replacement by lime sludge	Reference
					Fine aggregates	Coarse aggregates			
1.	Cement	10-70	M30	30	0.15-4.75	4.75-80	Compressive strength	4% increased	*Srinivasan et al. 2010*
2.	Cement	10-30	M20	30	0.3-1.30	_	Yield stress, viscosity, fluidity, cohesion	1.34% decreased	*Modolo et. al. 2011*
3.	Cement	10-40	M40	10	0.15-4.75	4.75-20	modulus of elasticity	_	*Pitroda et. al. 2013*
4.	Cement	10-20	M15	15	0.15-4.75	4.75-80	Compressive strength	16.6 % increased	*Yousuf et al. 2014*
5.	Fine aggregates	10-25	M25	25	0.15-4.75	4.75-20	Compressive strength	5% decreased	*Soni et. al. 2015*
6.	Fine aggregates	10-40	M30	20	_	_	Compressive strength	3.7% increased	*Shermale et al. 2015*
7.	Cement	10-30	M20	30	0.15-4.75	4.75-20	Compressive strength	6.2% decreased	*Alam et. al. 2015*
8.	Cement	10-40	M20	30	0.15-4.75	12.5-20	Compressive strength	8% increased	*Manchriyal et al. 2016*
9.	Cement	10-40	M20	30	0.075-4.75	4.75-20	Compressive strength	_	*Abhishek 2017*
Note: Authors have recommended the optimum dosage based on comparable strength for a particular grade of concrete.									

the materials proportioning of the M20 grade of concrete. This can be a future perspective of the researchers, to find out the reasonable mechanism out of this contradiction.

A few Researchers also focused on the cost-benefit of lime sludge in concrete selected higher grade of concrete for study [57, 58]. Exponentially increasing high landfill costs have driven the attention of researchers to focus on the cost viability of lime sludge application in concrete. *Rashad et al.* [57] concluded in a study that 50 % replacement of cement by lime sludge reduced the cost of M 40 mortar by 34.59 % but with the use in low strength application. *Khan et al.* [58] prepared a low-cost M40 grade of concrete of different dimensions using lime sludge. However, in both studies, the resultant products were unable to attain adequate compressive strength as M40 grade. These concretes could only be utilized in low-cost temporary structures. Although in terms of lime sludge effect on compressive strength of M40 grade concrete, *Pitroda et al.* [59] suggested up to 10 % replacement of cement by lime sludge without a reduction in its strength.

Besides the use of lime sludge in cement replacement, some studies have also focused on the replacement of fine aggregates with lime sludge. *Shermale et al.* [60] have reported that replacement of 20 % fine aggregates with lime sludge in M30 conventional concrete found no significant differences in the compressive, tensile, and split tensile strength. Contributing to the novelties in lime sludge utilization, in a study *Kumar et al.* [61] concluded that after replacing fine aggregate with lime sludge, the strength of concrete reduces, however, this reduction is not signed up to 25 % replacement of fine aggregate. The reported decline in compressive strength can be due to a decrease in workability of concrete. The coarser particle size of fine aggregate helps in maintaining the workability of the concrete matrix while its replacement with comparably lesser particle size lime sludge. The presence of excess water in the concrete matrix ultimately leads to a reduction in compressive strength.

Lime sludge in concrete affects rheological properties of concrete such as fluidity, plastic viscosity, yield stress, and cohesion between particles [62-64]. *Modolo et al.* [62] reported that an increase in lime sludge content lowered the fluidity and plastic viscosity of matrix, while enhanced the yield stress and cohesion between particles in the fresh state. The apparent porosity of concrete decreased on increasing lime sludge application, about 30 % application of lime sludge reduced the apparent porosity by 6 % in comparison to the reference concrete. Based on the outcome of rheological tests, the study suggested up to the 30 % the replacement of the lime sludge. *Ferreira et al.* [63] also supported the assessment and concluded in research that yield stress of mortar increased and plastic viscosity decreased with the increasing percentage of lime sludge. It was also concluded that lime sludge application resulted in the decrement of the fluidity of mortar and increment of cohesion between particles and water. *Pitroda et al.* [64] reported the effect of cement replacement by lime sludge on the modulus of elasticity. Research could use lime sludge up to 10 % in M40 grade concrete without affecting the modulus of elasticity, beyond this limit elasticity of concrete decreased significantly. In general, this effect of lime sludge on the rheology of concrete is due to the small particle size of the lime sludge, which causes the reduction of the free water content. Hence, workability, modulus of elasticity of the concrete decreases while the cohesiveness, viscosity, and yield stress increases with application of lime sludge.

1.4.2 Lime sludge application with other waste materials

Lime sludge has also been utilized with other pozzolanic supplementary cementitious materials to maintain the desired quality of the concrete. Pozzolanic materials are siliceous or siliceous and aluminous compounds that reacts with calcium hydroxide to form cement. Incorporation of pozzolanic materials in lime sludge based binders has been proved to be highly beneficial, Binary blended cement concrete with pulverized fly ash and metakaolin with various combinations of the cementitious system in conventional curing and air curing showed enhanced strength and durability. It is reported that chloride ions ingress is reduced which led to safeguarding reinforcement. The ternary blended concrete with cement, fly ash, and silica fume provides an increased strength and enhanced durability compared to the control mix. Long-term resistance to sulphate attack for ternary blended concrete shows excellent chemical resistance.

Durability is also one of the crucial aspects of lime sludge based concrete and mortar. Many papers reveal that fly ash and silica fume when used as a partial replacement in certain combinations with lime sludge enhances the durability of concrete. Many supplementary cementitious materials (SCM's) like fly ash, slag cement, rice husk ash, metakaolin, palm oil fuel ash, silica fume are being used extensively [65-70]. *Kumar et al.* [70] have studied the chemical resistance of lime sludge based cement concrete by exposing it to 5 % HCl and 5 % H_2SO_4. Acid mass loss factor was more in the case of H_2SO_4 as compared to HCl, which indicates that the concretes are more susceptible to sulfate attack.

Initially, different types of fly ash were used in cement mortar to influence the pozzolanic activity of the cement [71]. Based on this, researchers extended the research and used different pozzolanic materials with paper industry lime sludge in mortar and concrete [72, 73]. Several studies reported the application of lime sludge with fly ash in concrete. **Table 1.6** summarizes the work of various researchers on the effect of lime sludge and other waste materials on different grades of the concrete at 28 days. The sludge used by *Solanki et al.* [74] was generated from the deinking and repulping of the paper and contains a high lime percentage. This lime sludge was used with fly ash to prepare concrete of M20 grade. Lime sludge and fly ash used in the proportion of 1:1 and 20 % replacement of blend increased the flexural strength by 11.08 %. Use of fly ash with this type of lime sludge improves the workability of the concrete due to the similarity of fly ash particle size and shape (spherical) with Portland cement. This property of fly ash causes the requirement of less amount of water for mixing and placing, which can be translated into better workability and improved strength properties of the concrete. Lime sludge application in combination with fly ash and quarry dust showed a positive effect on the compressive strength due to the similar impact of quarry dust as fly ash in concrete [75]. *Pal and Mahela* [72] studied the mechanical properties of 30MPa concrete made by using lime sludge as replacement of fine aggregates and silica fumes as replacement of cement respectively. Also, the studies were carried out for a combination of lime sludge and silica fume. It was observed that the replacement of 20 % fine aggregate with lime sludge and 20 % of cement with silica fume resulted in similar compressive strength as of control concrete at 28 days. *Vashistha et al.* [76] used nanosilica with paper mill lime sludge to replace cement and concluded that with use of 4 % nanosilica and 30 % dried and pestle lime sludge, compressive strength remained same as conventional concrete of M30 grade. The nanosilica used in the process was synthesized from boiler ash through the sol-gel method with particle size ranges from 10-25 nm and with a specific surface area of 450 m^2/g. Application of silica fume and nanosilica with lime sludge improved the compressive strength but at the same time process should also be checked for the economic feasibility of the concrete. *Kumar et al.* [73] used fiber of jute and glass in addition to deinking and repulping generated paper mill lime sludge. Cement was replaced by a combination of sludge and lime sludge for the M30 grade of concrete. Concrete did not attain much compressive strength, and only 10 % application of sludge was acceptable with the fiber of jute and glass. *Rudrawar et al.* [77] reported the combined application of lime sludge and wood ash for concrete production. This study suggested the application of lime sludge in concrete for the minimization of sludge disposal and reduction of carbon dioxide and greenhouse gasses.

Table 1.6: Application of lime sludge with supplementary/other materials in concrete

S. N.	Materials used with lime sludge	Material replaced	% replacement of lime sludge	Grade of concrete	Max. recommended %	Aggregates particle range (mm)		Parameter studied	Effect on compressive strength with respect to the max. recommended %	Reference
						Fine aggregates	Coarse aggregates			
1.	Fly ash	Cement	10-30	M20	10	0.15-4.75	4.75-80	Flexural strength, workability	*8.91% Increased*	*Solanki et al. 2013*
2.	Silica fume	Fine aggregates	5-20	M30	20	_	10-20	Compressive strength	*6.09% Decreased*	*Pal et al. 2016*
3.	Quarry sand	Cement	10-40	M20	20	0.15-4.75	Upto 20	Compressive strength	*12.5% Decreased*	*Dhananjaya et al. 2016*
4.	Nano silica	Cement	10-40	M20	30	0.15-4.75	4.75-20	Compressive strength	*1.37% Decreased*	*Vashistha et al. 2017*
5.	Fibre of jute and glass	Cement	10-40	M30	30	0.15-4.75	10-20	Compressive strength	*2.13% Increased*	*Kumar et. al. 2017*

Note: Authors have recommended the optimum dosage based on comparable strength for a particular grade of concrete.

1.5 LIME SLUDGE APPLICATION IN BRICKS AND CERAMICS

Burnt clay bricks are used as building construction material in India. The clay castoff to concoct good quality burnt clay bricks is generally procured from the river basin, ponds, and coastal areas because of its suitability for molding and high plasticity. In central as well as in southern parts of India, the soil is not suitable for bricks production. This soil being gritty, sandy in nature and having low plasticity property, which makes it difficult for molding. The two options available with the brick manufacturers are either to make the bricks transported from the good brickfield which makes it costlier or to make substandard bricks from low-quality local clay. The reserves of alluvial soil, suitable for making bricks are depleting day by day with the continuously rising demand for clay-based bricks in the country. It also presents a bigger concern as the highest share of agricultural production in India comes from alluvial soil. Therefore, the Ministry of Environment & Forests, Government of India [78] formulated new guidelines for soil use in brick production in 2013. The clay borrowing/excavation activity is now restricted to a maximum depth of 2 m below the general ground level. At the sites where the groundwater level is very high, the borrowing/excavation activity is restricted to 2 m above the groundwater table [79]. The immense need to conserve the traditional building construction materials that are facing depletion has attracted the attention of researchers to look for alternative materials. Thereby, use of industrial waste materials in the brick making will not only help industries in managing their solid waste but will also meet the construction industry's increasing demand for bricks without degrading good quality agriculture soil. Several research on the utilization of recycling paper mill waste, craft pulp residue, marble industry sludge, rice husk waste, sugarcane bagasse, waste glass sludge, agro waste, sawdust and urban waste in the production of burnt bricks has been going on [80-84]. Some recent studies also depict different combinations of these waste materials are also being tried in the fabrication of burnt clay bricks [85-90]. *Raut et al.* [14] have provided an overview of the utilization of these waste materials in burnt clay bricks production.

Table 1.6 summarizes the work of various researchers on the effect of lime sludge in burnt clay bricks and ceramics. *Cultrone et al.* [91] proposed the mechanism of the reaction between calcium and silicate phase during brick firing. Additionally, XRD (X-ray diffraction spectroscopy) studies concluded that firing temperature is the most critical factor in brick formation and development of strength in the bricks. Temperature more than 1000 ºC causes significant phase changes leading to better brick fabrication. Based on calcium and silicate phase and reaction mechanism, lime sludge utilization in bricks production is illustrated in **Table 1.7**. *Jahagirdar et al.* [92] developed a method to use textile mill sludge in dried condition with red, white, and black soil for the production of burnt clay bricks. The composition of the used soils in the study revealed silica content shorted by 10-15 % as good soil for good quality brick production [93]. To fulfill the required percentage of silica and other minerals in the soils, sludge was used with soils for brick production and resulted in better physical and mechanical properties. Samples were prepared with 0-35 % sludge in clay bricks. 800 ºC firing temperature with 24 hours firing time was found optimum for best compressive strength of the bricks. Bricks with 15 % lime sludge content yielded acceptable compressive strength of 4.5 N/mm^2, but bricks with more than 15 % lime sludge content were reported to endure compressive strength lower than minimum acceptable limit of 3.5 N/mm^2 for burnt clay bricks [94].

Furthermore, studies on lime sludge application also demonstrated its use in the fabrication of ceramics. A study by *Qin et al.* [95] highlights the reuse of the paper industry's lime sludge and fly ash, for the fabrication of anorthite ceramic by the action of solid-state reaction. Raw materials were directly mixed in mortar mixture. Preliminary investigation suggests that both lime sludge content and sintering temperature influenced the synthesis of anorthite phase ceramic. Besides, experiments were performed with different combinations of lime sludge and fly ash content at different sintering temperature. It was determined that the anorthite phase was mostly present in all samples at 1100 °C but it was synthesized prominently in the sample having 36 % or more lime sludge. *Qin et al.* [96] further worked on ceramsite synthesis by direct mixing of as received lime mud, fly ash and different additives (sawdust, shale, diatomite, and perlite) by the process of pelletizing and sintering. In this study, the additive's effect on the synthesis of anorthite was also analyzed. It was observed that with the addition of diatomite additive, use of lime sludge in the mixture was increased to 40 % whereas sintering temperature declined to 1050 °C. Therefore, the reuse of lime mud in the form of ceramsite is also considered an effective way to reduce solid waste generated from paper industries.

Table 1.7: Lime sludge application in burnt bricks fabrication

S. N.	Max. % of replacement by lime sludge	% Replacement (Max. Comp. strength)	Material used with lime sludge	Material prepared	Parameter studied	Effect on compressive strength Effect on compressive strength in respect to the max. comp. strength gain	Reference
1.	40	20	Clay, fly ash	Burnt and unburnt bricks	Compressive strength	4.1% Decreased	*Sarkar et al., 2017*
2.	60	36	Fly ash	Anorthite ceramic	Mineralogy and compressive strength	_	*Qin et al., 2015a*
3.	60	40	Fly ash, additives	Ceramsites	Mineralogy and compressive strength	_	*Qin et al., 2015b*
4.	4	3	Fly ash	Laterite bricks	Compressive strength	2.3% Decreased	*Khaleel et al., 2015*
5.	35	15	Red, white and black soil	Bricks	Compressive strength	50% Decreased	*Jahagirdar et al., 2013*
6.	20	20	Fly ash	Tiles	Compressive strength	_	*Garg et al., 2006*
Note: Authors have recommended the optimum % of replacement based on the maximum compressive strength with lime sludge application.							

1.6 APPLICATION OF LIME SLUDGE IN OTHER BUILDING MATERIALS

Utilization of waste lime sludge is a potential source for making low-cost housing material several studies on lime sludge innovative utilization in manufacturing of unburnt bricks and tiles are reported. *Singh and Garg* [97] tried to use burned lime sludge from the fertilizer industry to make floor tiles and utilized burned lime-fly ash mixture for mortar preparation. *Khaleel et al.* [98] used lime sludge for making laterite soil based brick. Lime sludge and cement were added in 3 % and 4 % respectively. This proved to be an economical option for producing laterite bricks. *Sarkar et al.* [99] tried to use lime sludge and fly ash for preparing unburned bricks. The bricks were made using lime sludge, fly ash and soil in the ratios of 15:10:75, 20:10:70, 25:10:65, 30:10:60, 35:10:55, and 40:10:50 respectively. However, compressive strength of unburnt bricks was found to be less than 2 N/mm^2, due to the presence of pozzolanic materials in very less quantity. Therefore, it failed to fulfill the minimum Indian standards' compressive strength criteria of unburned bricks.

1.7 APPLICATION OF BOILER ASH FOR NANOSILICA SYNTHESIS

Sustainable development is one of the major global concerns in the present era. It demands elimination of unsustainable trends and practices and efficient use of alternative resources. Reduction in waste generation and its effective utilization is a major concern nowadays. Rapid industrialization in sectors such as sugar, pulp and paper, Iron/steel etc. has resulted in the generation of huge quantity of wastes. All these industries produces bulk of fly ash, boiler ash and slag [2]. Despite their utilization in building materials, these wastes are generally dumped on land or discharged into water bodies, without adequate treatment. Thus becoming a large source of environmental pollution and health hazard. In the consequence of this researchers are finding more significant ways for the valorization of generated wastes. The value addition to these wastes can be done through the synthesis of nanoparticles. These wastes can work as a precursor for the synthesis of nanosilica, titanium nanoparticles and Iron nanoparticles etc. The demands of nanosilica has increased due to their increasing applications. Nanosilica can be utilized as an additive for rubber and plastics, as a strengthening filler for concrete and other construction composites and as a stable, non-toxic platform for biomedical applications such as drug delivery and theranostics [100].

Nanosilica can be synthesized from many waste materials. Several researchers have successfully produced nanosilica from silica rich agro waste materials like rice husk ash and bagasse ash. *Liou and Yang* [101] utilized rice husk ash for the synthesis of nanosilica from alkali extraction method. *Thuadaij and Nuntiya* [102] synthesized nanosilica from rice husk ash through precipitation method. *Hassan et al.* [103] used surfactant free sol gel method for the synthesis of nanosilica with high surface area. Application of nanosilica in building materials is also an exciting research area. Lime sludge and nanosilica has been utilized to synthesize belite based clinker at a relatively lower temperature [24].

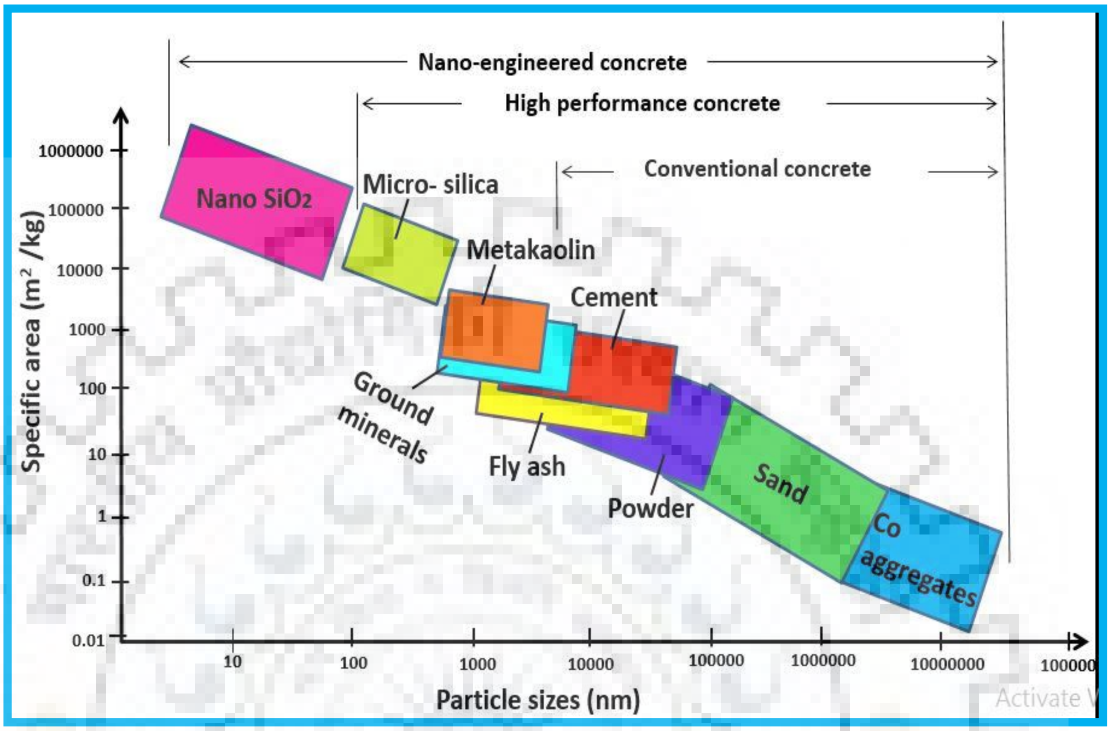

Fig. 1.8: Particle size range and specific surface area of concrete ingredients [14]

Application of nanosilica in concrete is also advantageous as application of it enhances the compressive strength significantly. Nanosilica in concrete works on two different levels. The first effect is chemical effect, pozzolanic reaction of nanosilica and calcium hydroxide forms more C-S-H hydrates and the second effect is related to its physical activity in concrete, because of its very small size nanosilica can fill the remaining voids in partially hydrated cement paste (**Fig. 1.8**). Hence, nanosilica based concrete imparts better compressive strength [104, 105].

1.8 APPLICATION OF ETP SECONDARY SLUDGE FOR METHANE GENERATION

Large quantities of wastewater are generated during the production of pulp and paper. The waste water has to be treated for purification to escape severe environmental threats [106,107]. The purification of wastewater in Pulp and Paper industries involved many techniques, e.g. sedimentation, chemical precipitation, flotation, and biological treatments. The combination of these techniques also applied depending on the local conditions. The wastewater purification results in the generation of solid waste in large volumes. The generated waste contains high water content, that is why its applications are limited as biofuel, and it is creating disposal problems for paper industries [108]. The use of the secondary sludge for other applications like methane production from anaerobic digestion (AD) can provide a sustainable solution. AD is three stage phenomena which can be classified as (i) Hydrolysis (ii) Acidogenesis and (iii) methanogenesis. In the first step of hydrolysis, all macromolecules like proteins, polysaccharides, and lipids are hydrolysed into micro molecules like amino acids, carbohydrates, and fats. These micro molecules broken down further during the second step of acidogenesis, in the result of which acetate is formed with hydrogen and carbon dioxide.

The products of acidogenesis function as the precursor of methanogenesis, the final step of AD process. At this stage, two types of microorganisms-based mechanism function for the production of methane. One group of microbes' splits acetate into methane and carbon dioxide and another group works based on electrochemical reactions to produce methane.
But, due to the reason of substrate imbalance in the ETP secondary sludge of the paper industry, anaerobic digestion of it is still in its infancy. Many studies on methanogenesis from ETP secondary sludge have been published which would involve substantial costs for pre-conditioning prior to anaerobic digestion in terms of the addition of macronutrients, trace elements, vitamins and caustic for pH adjustment.

1.9. OBJECTIVES

In view of the above discussion the following objectives are formulated for the present study:

[1] Preparation of belite based clinker by lime sludge and boiler ash synthesized nanosilica at relatively lower temperature and product development through the clinker, in the form of cementitious binder.

[2] Direct utilization of lime sludge in concrete:

- **(i)** Cement and fine aggregates substitution through lime sludge application.
- **(ii)** Lime sludge application with synthesized nanosilica for bulk utilization.

[3] Low temperature calcination of lime sludge and valorization of it by application in concrete.

[4] Anaerobic co-digestion of Paper Industry ETP sludge with cow manure at uncontrolled temperature.

Hence, an effort has been made to cover all the objectives in the following four chapters. Suitable experiments have been planned, data generated, analyzed, and results have been discussed with possible reasoning.

Chapter 2 covers, the utilization of lime sludge with boiler ash synthesized nanosilica for production of belite based clinker at a relatively lower temperature. Lime sludge was also used in combination with fly ash and boiler ash to check the synthesis of compounds at varying temperatures. Nanosilica was synthesized from pretreated boiler ash through alkali treatment and acid precipitation. The synthesized nanosilica has been characterized for specific surface area, crystallinity, surface functional groups and size. Three different mixtures, containing lime sludge with nanosilica, fly ash, and boiler ash are fired at temperatures ranging from 900°C to 1200°C and characterized for the synthesis of belite. Conventionally, belite is synthesized above 1200°C, whereas the combined application of lime sludge and nanosilica reduces the temperature of belite synthesis to 900°C without pre calcination or addition of any chemical stabilizer. In the case of lime sludge and boiler ash blend, belite formation takes place at a higher temperature (1100 to 1200°C). Anorthite synthesis takes place in case of lime sludge and fly ash blend, due to the high percentage of alumina present in fly ash. Lime sludge and nanosilica based belite clinker are used to develop newer cementitious binder. Hydration and strength properties of developed binder proved worthy as building materials. This study will present alternatives for sustainable utilization of lime sludge, fly ash, and boiler ash in construction.

Chapter 3 focuses on the fly ash utilization for nanosilica synthesis, because of the presence of silica precursor in very high amount. Nanosilica was synthesized with the alkali treatment of ash and acid precipitation. The produced nanosilica was characterized for crystallinity, specific surface area, size, and morphology. Lime sludge was utilized for the partial substitution of cement and fine aggregates in concrete, but concrete only attained appropriate compressive strength on the application of plasticizer with lime sludge. The synthesized nanosilica was also used with lime sludge in cement-based concrete. Concrete blocks were evaluated for compressive strength after 7 and 28 days of curing. It was observed that the compressive strength of concrete blocks with only lime sludge decreased up to 50% with the replacement of cement by lime sludge from 10-40 %. Concrete blocks produced with the addition of 0.3, 0.6 and 1.0 % nanosilica and different proportions of lime sludge attained up to 30 % more compressive strength in comparison to the blocks without nanosilica. The morphological study of concrete block also showed the FESEM micrograph of uniform and compact microstructure on the addition of Nano-SiO_2.

Chapter 4 covers the application of lime sludge in concrete directly after the calcination. In this study, calcination of lime sludge was performed at a low temperature of 650 °C, which consumes less energy as compared to the industrial process of calcination. The M25 grade of concrete was prepared, with substitution of cement by as received and calcined lime sludge in the range of 10 %, 20 %, 30 % and 40 % by weight. Compressive strength of concrete mixes was evaluated at 7 days and 28 days of curing and compared with concrete control specimens. Compressive strength of concrete fabricated with 10 % substitution of cement by as received lime sludge was approximately similar to control concrete after that it reduces with increase in lime sludge substitution. Concrete blends with calcined lime sludge achieved the same compressive strength of M25 up to 30 % substitution. Lime sludge after low-temperature calcination produces better compressive strength and morphology of concrete than as received lime sludge due to the presence of reactive lime and metakaolinite which worked as a pozzolana. The heat of hydration of cement and calcined lime sludge blends were also found more than blends with cement and as received lime sludge, which confirms the reactivity of the lime sludge calcined at a low temperature of 650 °C. This study will help in developing sustainable utilization of paper industry lime sludge in construction.

Chapter 5 covers the biogas production from anaerobic digestion (AD) process of ETP sludge and cow manure. It can stabilize the sludge with energy production at the same time. The AD process was performed at uncontrolled temperature in mesophilic range, which can be effective for small and medium scale of industries. The aim of the study was to utilize the Paper ETP sludge (PSS) for the AD process and to Co-utilization of PSS with cow manure to check the effect of codigestion. The reactor containing PPS only was started to generated biogas on 5th day of the reaction with 7.8 % of methane. The cumulative methane yield attained to 13.5 ml/g volatile solid (VS) until day 30. The second reactor containing PPS and cow manure produced methane 134 ml/g VS until day 30. This study presents a more optimized process of anaerobic digestion of paper sludge and co-digestion of paper sludge with cow manure.

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CHAPTER - 2

SUSTAINABLE UTILIZATION OF PAPER MILL SOLID WASTES VIA SYNTHESIS OF NANOSILICA FOR PRODUCTION OF BELITE BASED CLINKER

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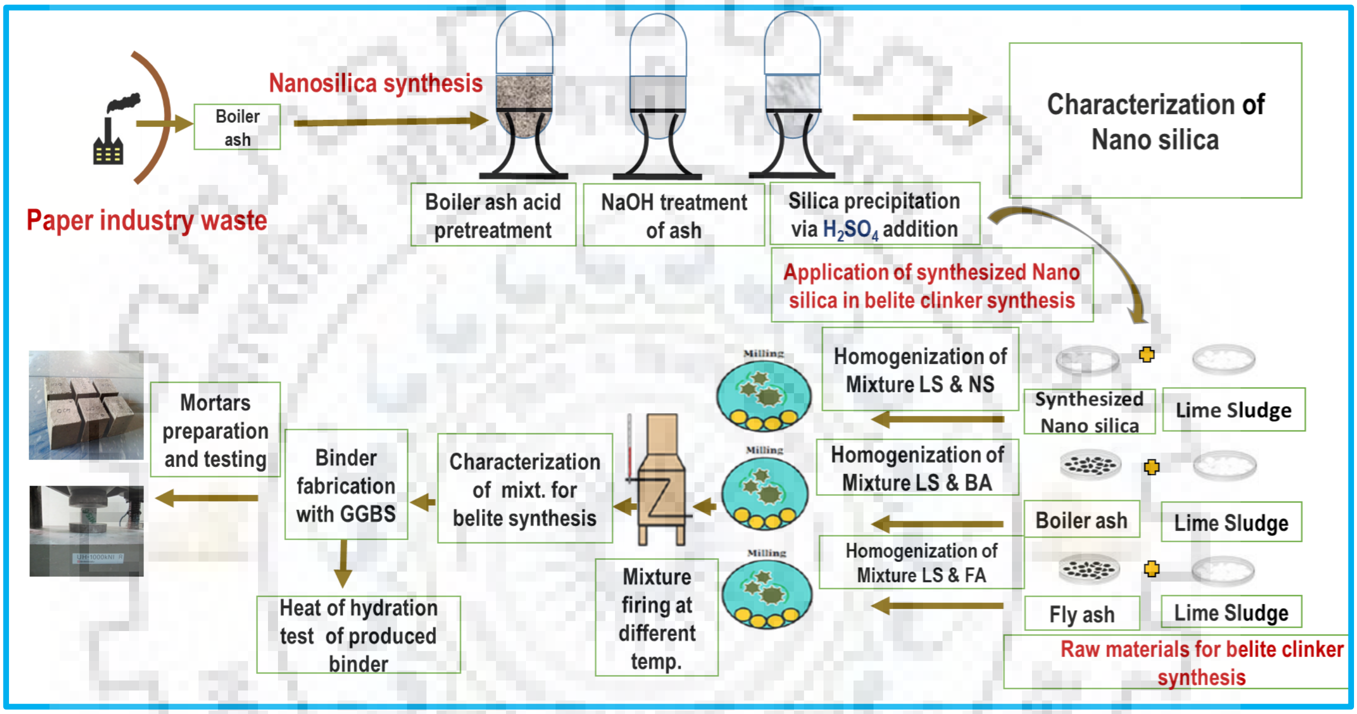
CHAPTER 2

SUSTAINABLE UTILIZATION OF PAPER MILL SOLID WASTES VIA SYNTHESIS OF NANOSILICA FOR PRODUCTION OF BELITE BASED CLINKER

GRAPHICAL ABSTRACT



2.1 INTRODUCTION

The aim of present chapter is gainful utilization of lime sludge and boiler ash for the development of belite based newer cementitious binder. In this, Boiler ash used for the synthesis of nanosilica whereas lime sludge was used as different blends with (i) nanosilica, (ii) boiler ash, and (iii) fly ash for synthesis of belite based clinker at low temperature. Several researchers have successfully produced nanosilica from silica-rich agro waste materials like rice husk and bagasse ash [1, 2]. But no attempts were made for the synthesis of nanosilica from paper industry boiler ash. Boiler ash contains sufficient amount of silica along with other salts of potassium, calcium and magnesium. Therefore, fly ash from paper industry can be used for the production of nanosilica. The binder was also prepared for the product development from synthesized clinker. In addition, ground granulated blast furnace slag (GGBS) was also used for development of binder. GGBS was incorporated to help in early strength development of developed newer cementitious binder. Belite based clinker are known for slower rate of strength development. The developed binder was studied for hydration and strength properties. Lime sludge based developed binders instead of conventional OPC help in reducing in global warming caused by carbon dioxide emission, ozone layer depletion etc. [3, 4]. This study is intended to explore the possibility of large-scale utilization of solid waste materials.

2.2 MATERIALS AND METHODS

2.2.1 Materials

Lime sludge (LS), boiler ash (BA), and fly ash (FA) were procured from M/s Ruchira paper industry, Kala Amb (India). BA and FA ash used in the study are generated from the co-combustion of coal and agricultural residue. Ground granulated blast furnace slag (GGBS) used in the preparation of binder, was purchased from Ecogen industries private limited in powder form. Raw materials were stored in a clean and dry storage area and were used in their as-received conditions. **Fig. 2.1** illustrates the experimental procedure implemented for the study.

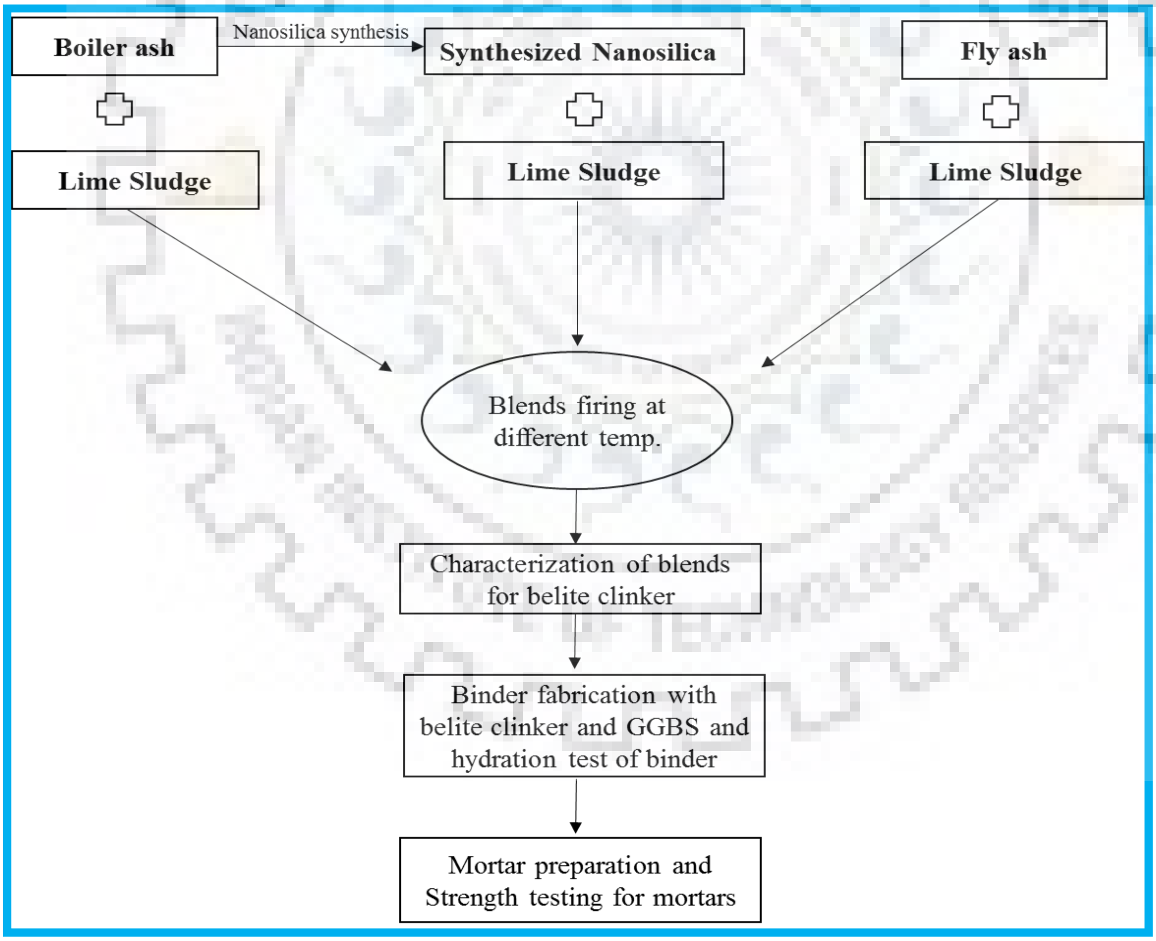


Fig. 2.1: Experimental flow chart

2.2.2 Nanosilica Preparation

Nanosilica was synthesized from BA through precipitation method. The detailed schematic procedure for nanosilica synthesis is illustrated in **Fig. 2.2**. First of all, the dry-ash was pretreated with 1N H_2SO_4 for 2 hours to remove metallic compounds, as these compounds can harm the quality of nanosilica by decreasing its surface area [5, 6]. In the process of nanosilica preparation, 50 g of pretreated ash was refluxed in 150 mL of 2N NaOH for 2 -3 hrs.

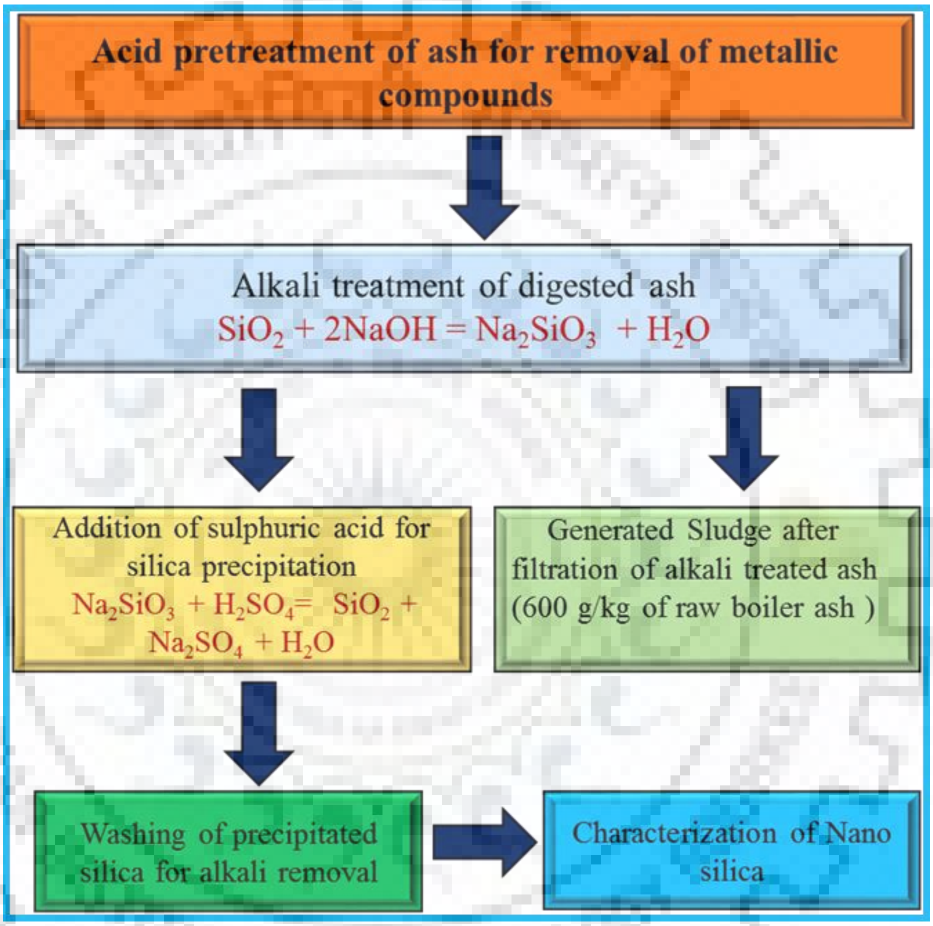


Fig. 2.2: Synthesis of nanosilica through boiler ash

The refluxed ash was filtered to obtain the solution of sodium silicate. Then it was titrated with 6N H_2SO_4 to get precipitated silica. During the titration, approx. 15 mL of H_2SO_4 was added drop wise to achieve the anticipated chemistry of reacting mass as the bulk accumulation of H_2SO_4 can change the size and morphology of reacting mass [5]. The precipitated silica was washed repeatedly with warm distilled water for the complete removal of alkali and then dried for 12 hours in the oven [5-8]. The total amount of nanosilica synthesized from the fly ash by using precipitation method was 20 % (by weight) of the raw fly ash. It means 200 kg of the nanosilica can be synthesized from 1 ton of the boiler ash. The amount of sludge produced from this process was the 60 % of the raw fly ash. It means 600 kg sludge might be produce on the application of 1 ton of fly ash in nanosilica preparation method. The produced sludge was characterized for its composition and its major constitutes were Al_2O_3 - 48.64%, SiO_2- 20.72 %,Na_2O - 15.53%, CaO- 4.35% .The utilization of nanosilica synthesis process generated sludge in concrete is one of the future perspective of this research. The utilization of nanosilica synthesis process generated sludge in concrete is one of the future perspective of this research.

2.2.3 CLINKER AND BINDER PREPARATION

Lime sludge blends with nanosilica, boiler ash and fly ash is denoted as F1, F2, and F3 respectively. Blends were prepared according to the stoichiometry of the reactions (2.1) and (2.2).

$$CaO + SiO_2 \rightarrow CaO.SiO_2 \qquad (2.1)$$

$$CaO.SiO_2 + CaO \rightarrow 2CaO.SiO_2 \quad (\text{Belite}) \qquad (2.2)$$

It presents a molar ratio of $CaO/SiO_2 = 2$ for the synthesis of belite based clinker. The mass ratio of the prepared blends is presented in **Table 2.1**.

Table 2.1: Composition of the prepared blends

	Lime sludge (g)	Nanosilica (g)	Boiler ash (g)	Fly ash (g)
F1 blend	130	34	-	-
F2 blend	130	-	78	-
F3 blend	130	-	-	85

Initially, dried raw materials were mixed to make a homogeneous mixture. Mixing was carried out in the ball mill for 60 minutes with the 10:1 ball and powder ratio at 400 rpm. DTA/TGA of these homogenized mixtures of different blends was performed to check the phase transition temperature of the materials. The test was performed up to 1000 °C. Parallel to this, pellets of these homogenized blends were also prepared by using hydraulic press and applied pressure of 9000 kg/cm^2. Pellets were then kept in a furnace at elevated temperatures between 900 °C to 1200 °C for 1 hour to allow solid-state reactions. The reacted pellets were then crushed, and the fine powder was stored in airtight containers for characterization to investigate the extent of belite based clinker formation. The blend characterized by belite synthesis (F1 fired blend) was further used for binder preparation. 80 % belite based clinker and 20 % GGBS (by weight) was applied for the fabrication of the binder. The fired powder (clinker) was milled and sieved, then mixed with 20 % of powdered GGBS, to get the binder. GGBS was used in binder preparation due to its pozzolanic nature with cementitious value.

2.2.4 Hydration analysis and mortar preparation

In this study, Hydration analysis of developed binder was performed by using isothermal conduction calorimeter (Modal: ICal 2000H) at 27°C. Only one formulation of clinker and GGBS were prepared due to the experimental limitations in producing a large amount of clinker. Clinker synthesis was performed with very small-scale instruments. Raw materials pellets of 5 mm diameter size were used to sinter in furnace, which took immense amount of time and furnace heat energy for the production of clinker. The mortars were prepared by using the binder. The prepared mortars were tested for compressive strength and density after 7, 28 and 56 days as per *Indian Standard* IS: 2250-1981 (First Revision) [9].

2.2.5 Characterization techniques

In order to accomplish the synthesis of nanosilica and belite, raw materials were characterized. Chemical & mineralogical characterization were carried out through X-ray fluorescence (XRF) and X-ray diffraction (XRD) analysis. The non-destructive analytical technique, X-ray fluorescence (XRF, Bruker S4 Pioneer spectrometer) is used to determine the elemental composition by measuring the fluorescent (or secondary) X-ray emitted from a sample when it is excited by a primary X-ray source. The XRD (X-ray diffractometer Bruker AXS D8 advance) with Cu source (Kα = 154 À) was used to analyze the presence of different minerals phases in raw materials and synthesized nanosilica. The X-ray patterns were acquired using Bragg's law (nλ=2dsinθ) with a scanning rate of 1°/min from 5° to 80°. The room temperature was kept at 25°C. The average particle size and its particle size distribution of raw material were determined by a laser particle size analyzer (Horiba LA-950V2). The synthesized nanosilica was characterized for the morphology, crystallinity, surface functional groups, specific surface area and size to determine its suitability for clinker synthesis process. Transmission electron microscopy (TEM, FEI Tecnai G^2 20 S-Twin model) was used to determine the particle size and morphology of the synthesized nanosilica. FTIR was used to identify the functional groups present in the synthesized nanosilica. Nicolet 6700 Fourier Transform Infrared system with Omnic Software version 9 was used for the spectroscopic study. Initially, 0.1 mg of the sample was mixed with KBr in the ratio of 1:8 and compressed into a fine and uniform pellet by using a hydraulic pressure pelletizer with approximately 5-ton load capacity. The transparent pellet was then scanned in the range of 400 to 4000 cm^{-1} at a resolution of 4 with 32 scans per spectrum. Textural properties (surface area) of nanosilica were studied by N_2 sorption analysis (Autosorb-iq/mp®-xr). Surface area is an important parameter to determine the reactivity of nanosilica in the reactions. More is the surface area, more will be the reactivity. The differential thermal analysis and Thermo gravimetric analysis (DTA/TGA) of ball milled and homogenized powder blends were carried out with Thermal Gravity Analyzer (TGA Model No: Netzsch STA with Proteus software) to check the synthesis of new phases, the powdered samples were taken in alumina crucible fitted with pierced lids. Thermal gravimetric analysis is related to the change in mass of the sample when it imposed to the heat with increasing temperature. TG measures mass changes in a material as a function of temperature (or time) under a controlled atmosphere. While in DTA, the material under study and an inert reference are made to undergo identical thermal cycles, (i.e., same cooling or heating programme) while recording any temperature difference between sample and reference For performing both studies, samples were heated with the uniform heating rate of 10°C min^{-1} in air atmosphere from room temperature to 1000°C to determine the phase transition temperature of the blends. Textural properties (surface area) of nanosilica were studied by N_2 sorption analysis (Autosorb- iq/mp®-xr). Surface area is an important parameter to determine the reactivity of nanosilica in the reactions.

2.3 RESULTS AND DISCUSSION

2.3.1 Raw materials characterization

In order to accomplish the synthesis of nanosilica and belite, raw materials are characterized to determine their chemical, thermal, and mineralogical properties. The chemical characterization of raw materials was conducted using the non-destructive analytical technique, X-ray fluorescence (XRF, Bruker S4 Pioneer spectrometer). It is used to determine the elemental composition by measuring the fluorescent (or secondary) X-ray emitted from a sample when it is excited by a primary X-ray source. **Table 2.2** illustrates the chemical composition of the raw materials and it also reflects their generation process.

Table 2.2: Chemical composition of the dried wastes obtained by XRF

Raw materials	Oxide content (% weight)										
	Al_2O_3	SiO_2	CaO	Fe_2O_3	MgO	SO_3	MnO	NiO	Na_2O	P_2O_5	LOI (%)
Lime sludge	0.25	2.74	52.10	0.27	0.02	0.23	0.02	0.02	0.88	0.29	43.18
Boiler ash	6.18	43.22	8.11	0.33	0.25	1.12	0.04	0.15	0.29	0.21	40.10
Fly ash	25.13	41.11	13.19	6.05	0.15	1.11	0.02	0.05	0.45	0.39	12.35
Note: LOI= Loss of ignition at 1000° C											

The LS is generated in the recovery circuit via the conversion of calcium oxide into the calcium carbonate. This is the reason, XRF of LS imputes 52.10 % calcium oxide with loss of ignition (LOI) of 43.10 %. Loss of ignition is the result of calcium carbonate ($CaCO_3$) decomposition into calcium oxide (CaO) and carbon dioxide (CO_2). FA and BA are generated in the boiler through the combustion of organic materials like coal, agriculture waste, etc. The main constituents of FA are silicon dioxide (SiO_2, 41.11 %) and aluminum oxide (Al_2O_3, 25.13 %) with 12.35 % loss of ignition (LOI) [10, 11]. The LOI of the FA largely refers to the presence of moisture in the sample. While BA comprises more silicon oxide (43.22 %) with less aluminum oxide (6.18 %) in comparison to FA, this is the foremost reason for the selection of the boiler ash as nanosilica precursor. The LOI (loss of ignition) of BA is more due to the incomplete combustion of coal and agricultural waste in the boiler. Calcium from LS and silica from FA and BA are major targeted elements pertaining to the objectives of this study.

The X-ray diffractometer (Bruker AXS D8 advance) with Cu source (Kα = 154 À) was used to analyze the presence of different minerals phases in LS, BA, and FA and are given in **Fig. 2.3**. The X-ray patterns were acquired using Bragg's law ($n\lambda=2d\sin\theta$) with a scanning rate of 1°/min from 5° C to 80 °C. The room temperature was kept at 25 °C.

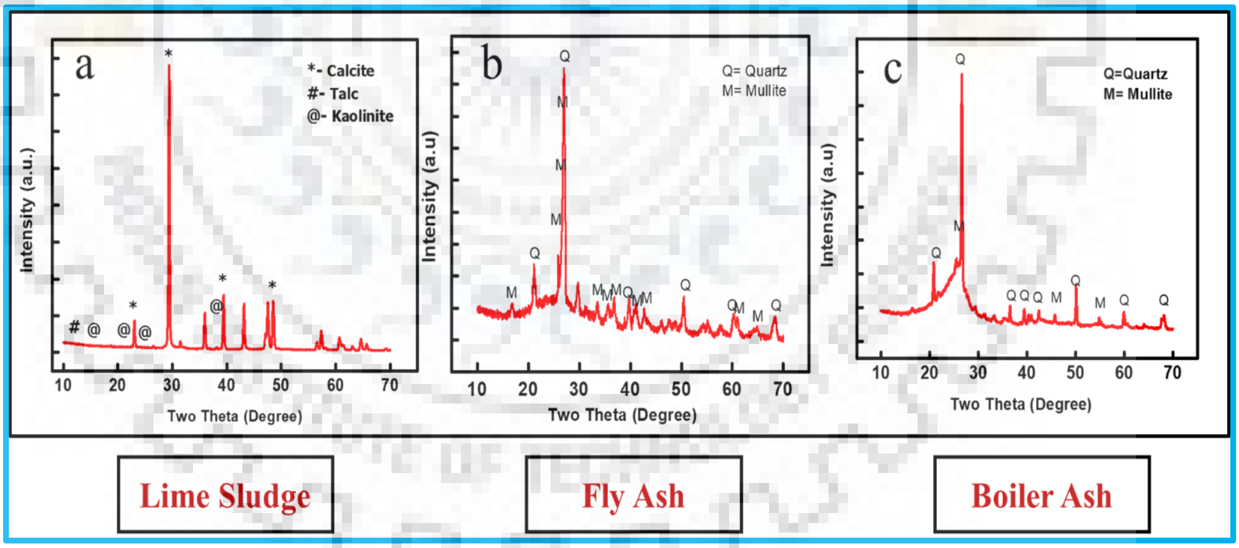


Fig. 2.3: XRD spectrum of lime sludge, boiler ash, and fly ash

The peaks obtained in the XRD spectra of LS shows the presence of calcite and kaolinite, whereas BA and FA show the peaks of quartz and mullite. Quartz is more prominent in BA while mullite is a major phase in FA. Hence, it can be inferred that BA contains the significant amount of quartz than FA and the same has been observed from the results of XRF which confirms that the abundance of silica compounds in boiler ash makes it a perfect raw material for the synthesis of nanosilica. LS contains the significant amount of calcium carbonate, which will work as calcium precursor in the synthesis of the clinker [12, 13]. The cumulative particle size distribution of LS, BA, and FA are illustrated in **Fig. 2.4 to 2.6.** The particle size of LS varies from 5.1 to 262.37 µm with an average particle size range (D50) of 36.65 µm. BA and FA have particle size distribution from 3.9 to 344.2 µm and 4.3 to 260.68 µm with average particle size (D50) of 69.37 and 46.23 µm respectively.

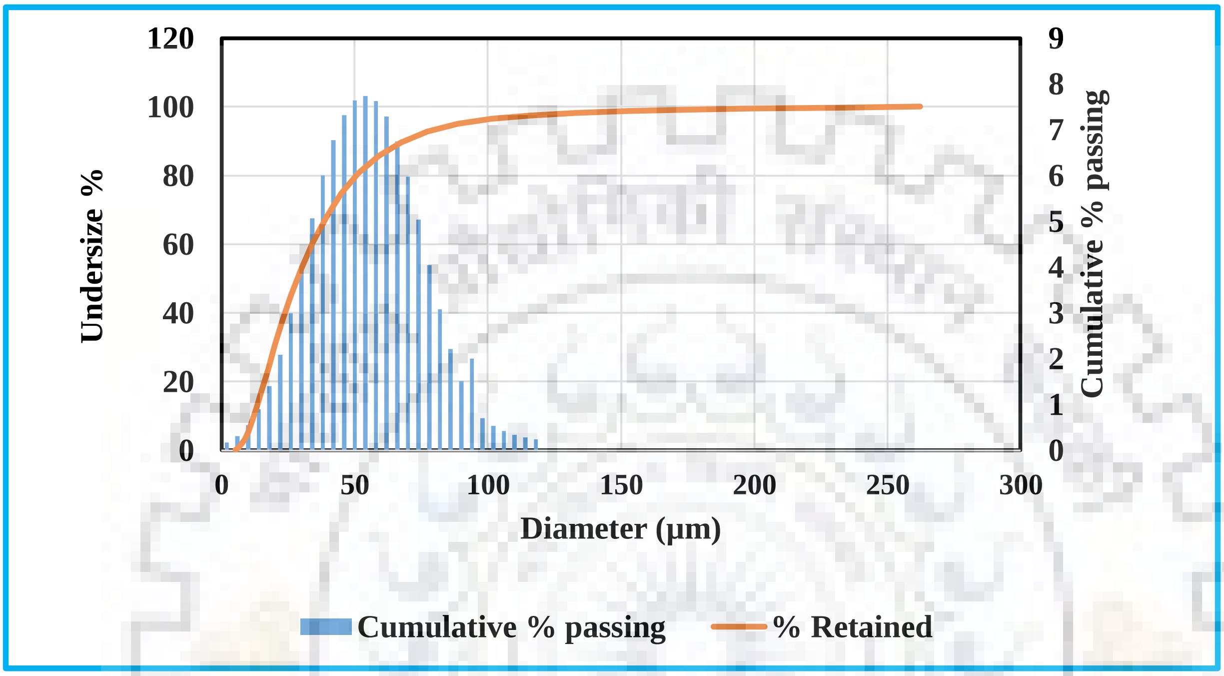


Fig. 2.4: Particle size analysis of lime sludge

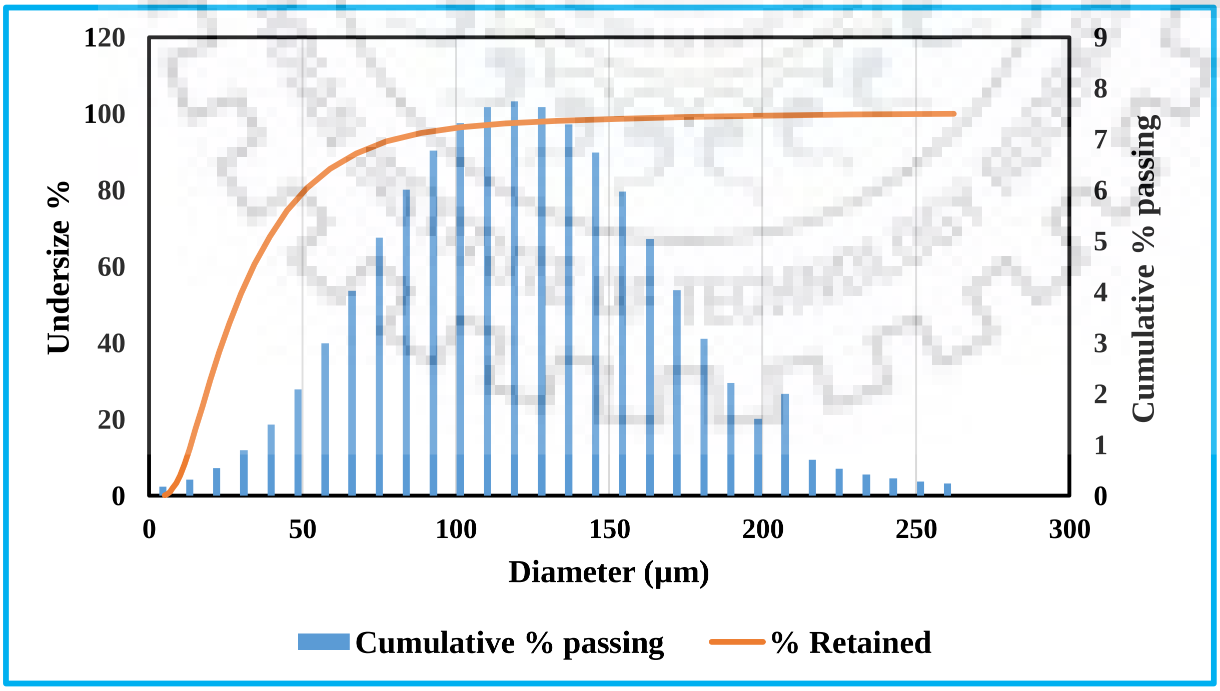


Fig. 2.5: Particle size analysis of boiler ash

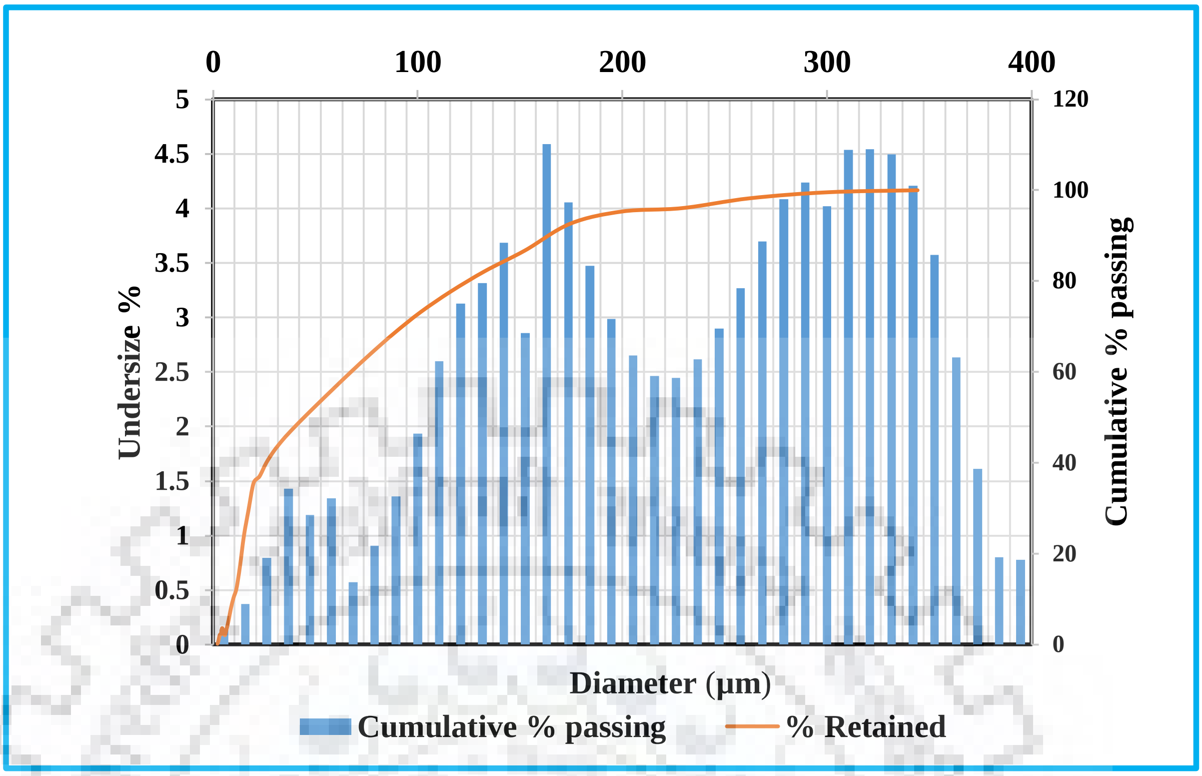


Fig. 2.6: Particle size analysis of fly ash

The thermal behavior of LS, BA, and FA are studied in **Fig. 2.7 to 2. 9.** TGA curve of LS sample indicates the initial mass loss of 7.26%, which is attributed to moisture removal. At temperature 787 °C DTA curve is dominated by a strong endothermic peak, which is characteristic of the decomposition reaction of calcite ($CaCO_3$) to calcium oxide. It reflects a significant mass loss of approximately 40 %. The total mass loss percentage is in consistency with the LOI (43 %).TGA of BA shows moisture removal in the early stage and start of combustion of organic matter from 491 °C. Exothermic Peak at 564 ºC confirms the presence of quartz; in this temperature range (530-580 ºC) quartz polymorphic inversion is observable, which is related to second-order phase inversions. In the case of FA, it suffers less conversion upon heating with a total mass loss of 16.93 %. DTA curve of FA shows exothermic peak at 596 °C due to the presence of quartz, which reflects the relatively inert nature of FA with heat treatment. Mass loss of 43 %, 16.93 % and 41.23 % for LS, FA, and BA respectively are consistent with the loss of ignition (LOI), which is determined through chemical analysis reported in **Table 2.1**.

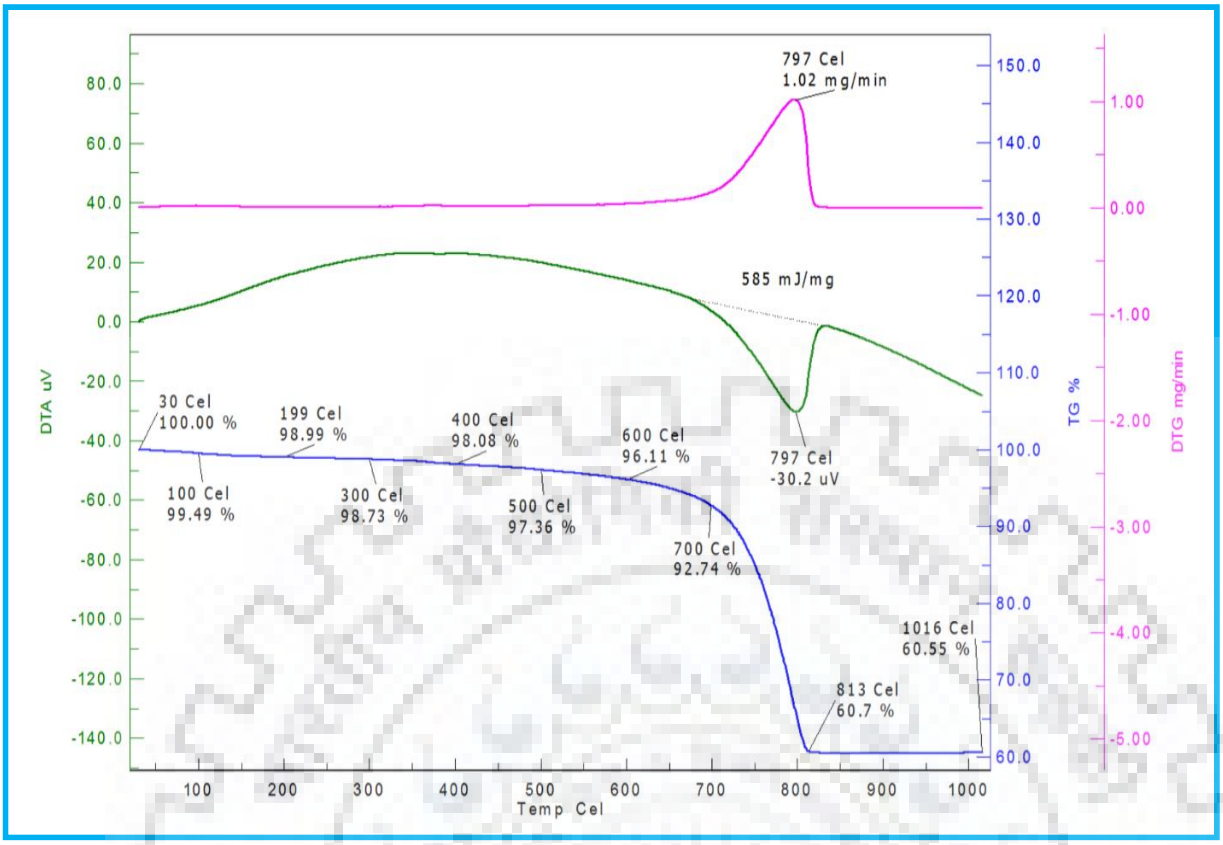


Fig. 2.7: TGA/ DTA of lime sludge

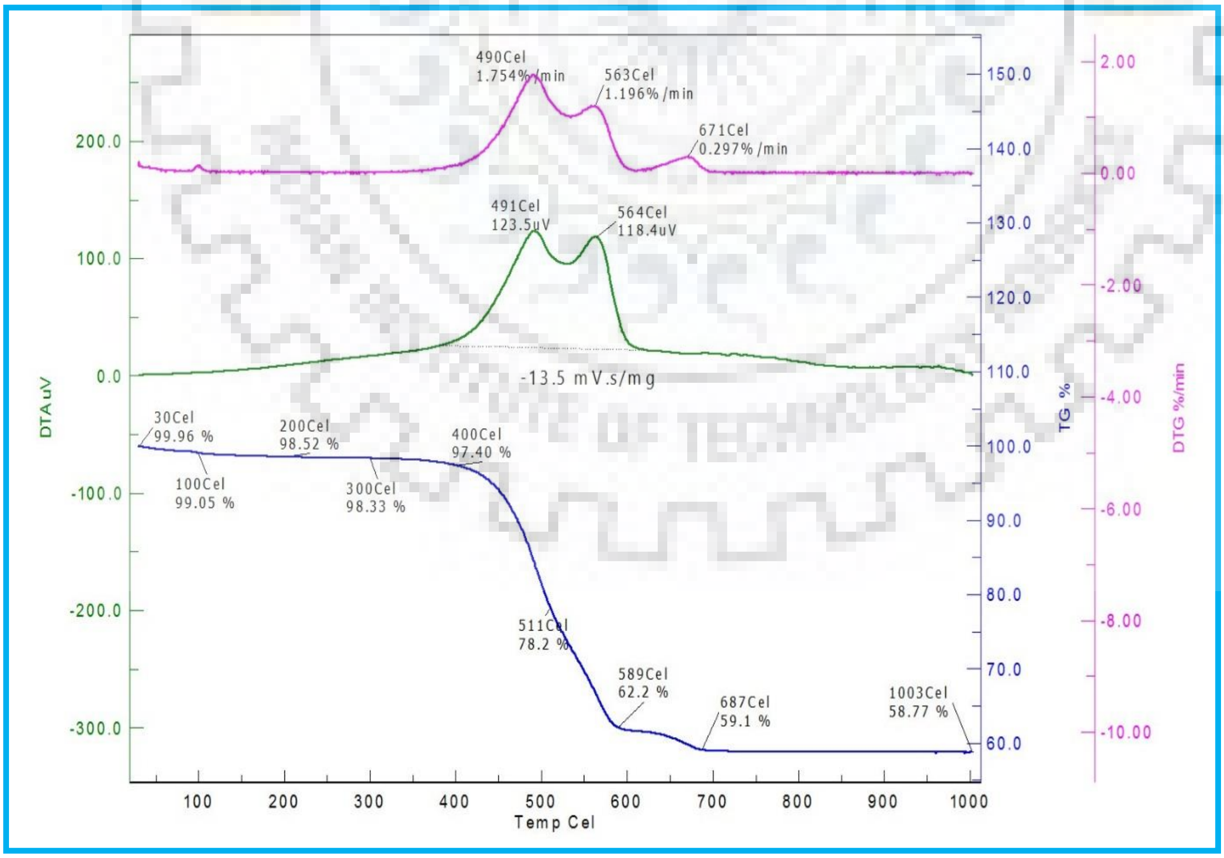


Fig. 2.8: TGA/ DTA of boiler ash

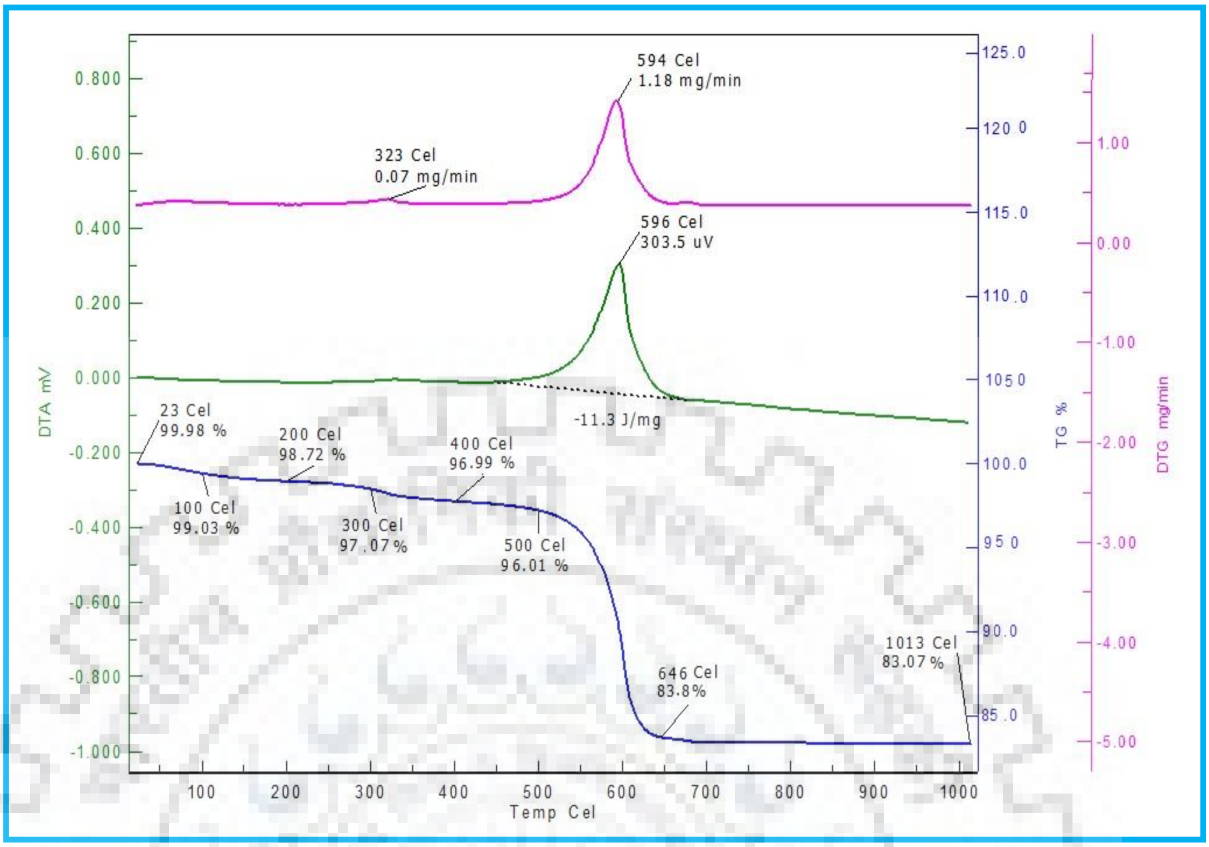


Fig. 2.9: TGA/ DTA of fly ash

2.3.2 Nanosilica characterization

The synthesized nanosilica was characterized for the morphology, crystallinity, surface functional groups, specific surface area, and size to determine its suitability for clinker synthesis process. Transmission electron microscopy (TEM, FEI Tecnai G^2 20 S-Twin model) was used to determine the particle size and morphology of the synthesized nanosilica.

TEM images presented in **Fig. 2.10** show the size and morphology of the synthesized particles. The monodispersed spherical particles in the range of 10-25 nm diameters are seen in the TEM images. The morphology observed is as expected for amorphous silica particles as the sole particles often have a tendency to adopt the spherical shape so as to reach a minimum of interfacial surface area.

The XRD (X-ray diffractometry) and FTIR (Fourier Transform Infrared spectrophotometer) of nanosilica are presented in **Fig. 2.11a and 2.11b** respectively. XRD pattern shows a broad peak from 18° to 36° (2 thetas), which indicates the synthesis of single phase amorphous nanosilica. The amorphous phase of nanosilica implies a more significant pozzolanic activity in comparison to quartz, which has a crystalline structure [8]. No other peaks are seen in the diffractogram which confirms the absence of an ordered crystalline structure in the material.

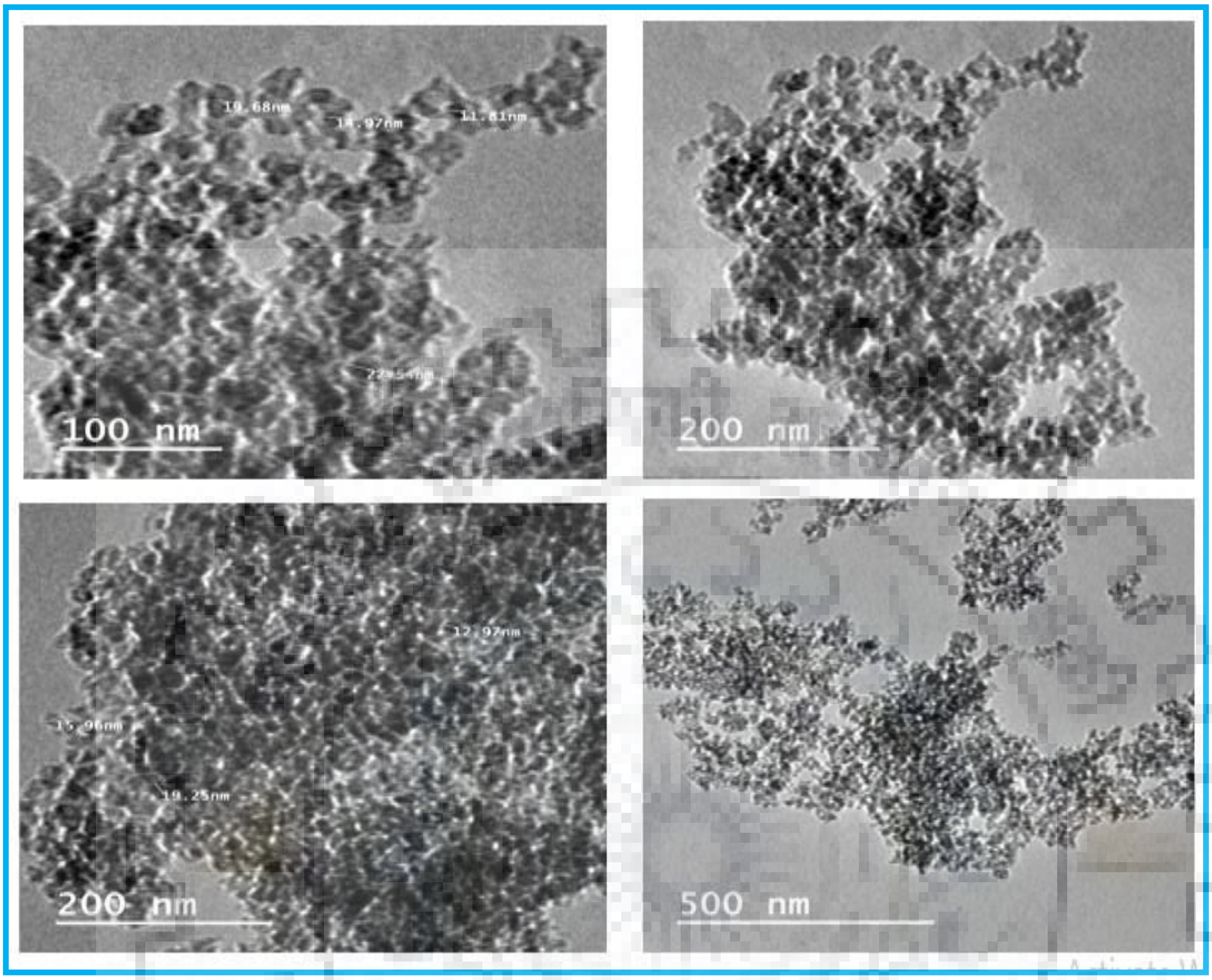


Fig. 2.10: TEM image of nanosilica

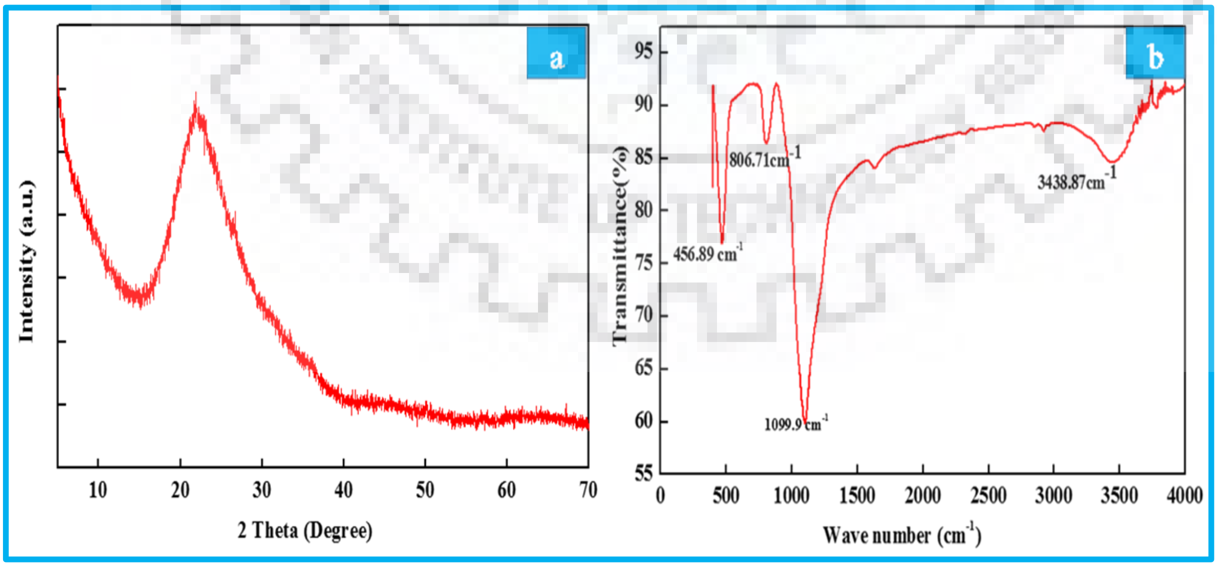


Fig. 2.11: XRD and FTIR of nanosilica

The FTIR spectrum of nanosilica is similar to standard silica spectrum, but the amorphous nature of the nanosilica is the reason for increased line width. The high-intensity band at 1099 and 456 cm^{-1} are due to asymmetric stretching of Si-O and flexural vibrations of Si-O-Si bonds, while that at 806 cm^{-1} could be attributed to the vibrations of (SiO_4) tetrahedrons. Broad bands around 3447 cm^{-1} and 1642 cm^{-1} are attributed to O-H stretching and bending vibrations, respectively of hydrophilic surface silanol groups and water molecules. More is the surface area, and more will be the reactivity. The specific surface areas of nanosilica calculated from the BET equation is found to be 450 m^2g^{-1}.

2.3.3 Phase transition temperature of mixed powder blends

The thermal analysis (DTA/TGA) of ball milled and homogenized powder blends were carried out with Thermal Gravity Analyzer (TGA Model No: Netzsch STA with Proteus software) to check the synthesis of new phases, the powdered samples were taken in alumina crucible fitted with pierced lids. Samples were heated with the uniform heating rate of 10°C min^{-1} in air atmosphere from room temperature to 1000°C to determine the phase transition temperature of the blends. This phenomenon of heat treatment is associated with the formation of new phases, which indicates the formation of calcium silicate (belite) in the case of F1, F2, and F3 blends. **Fig. 2.12** represents the thermal analysis of F1, F2, and F3 blends.

In the case of F1, the initial mass loss of 5.14 % on heating up to 500 °C is due to the removal of absorbed moisture and volatile content. DTA graph shows an endothermic peak at 757 °C due to the decomposition of $CaCO_3$ and CO_2 evolution, while the exothermic peak at the temperature of 866 °C is attributed to the formation of a new phase. The residual mass at the temperature of 1000 °C is about 72.7 % in the whole heating process of TGA-DTA. New phase formation in this process at 866 °C can be the evidence for the synthesis of belite based clinker by LS and NS below 1000 °C [1, 2].

In the case of thermal analysis of blend F2, the initial mass loss of 1.74 % on heating up to 400 °C is attributed to the moisture and volatile matter removal. A sharp mass loss of 31 % on heating the sample between 400 to 565 °C is due to combustion of organic content. It is also observed in DTA graph with an exothermic peak at a temperature of 491 °C and 564 °C. The reduction in mass from 565 °C to 710 °C is due to the evolution of CO_2 from the decomposition of $CaCO_3$ to CaO. After 710 °C, no phase change happened till 1000 °C.

Thermal analysis of blend F_3 followed the same pattern as F_2 with the exothermic peak at temperature 494 °C after that no phase change happened till 1000 °C. It means that in case of blend F2 and F3 phase conversion reactions take place at a higher temperature than 1000 °C. DTA curve of F1 shows clear evidence of new phase formation; the much lesser particle size of NS in comparison to FA and BA is the substantial reason for new phase formation at a much lower temperature.n The reason of shift in the decomposition temperature of calcium carbonate might be associated to the lime sludge ratio in the blends. F1 blend has the maximum quanity of lime sludge amoung other blends F2 and F3. This might be the reason of delayed complete decomposition of calcium carbonate.

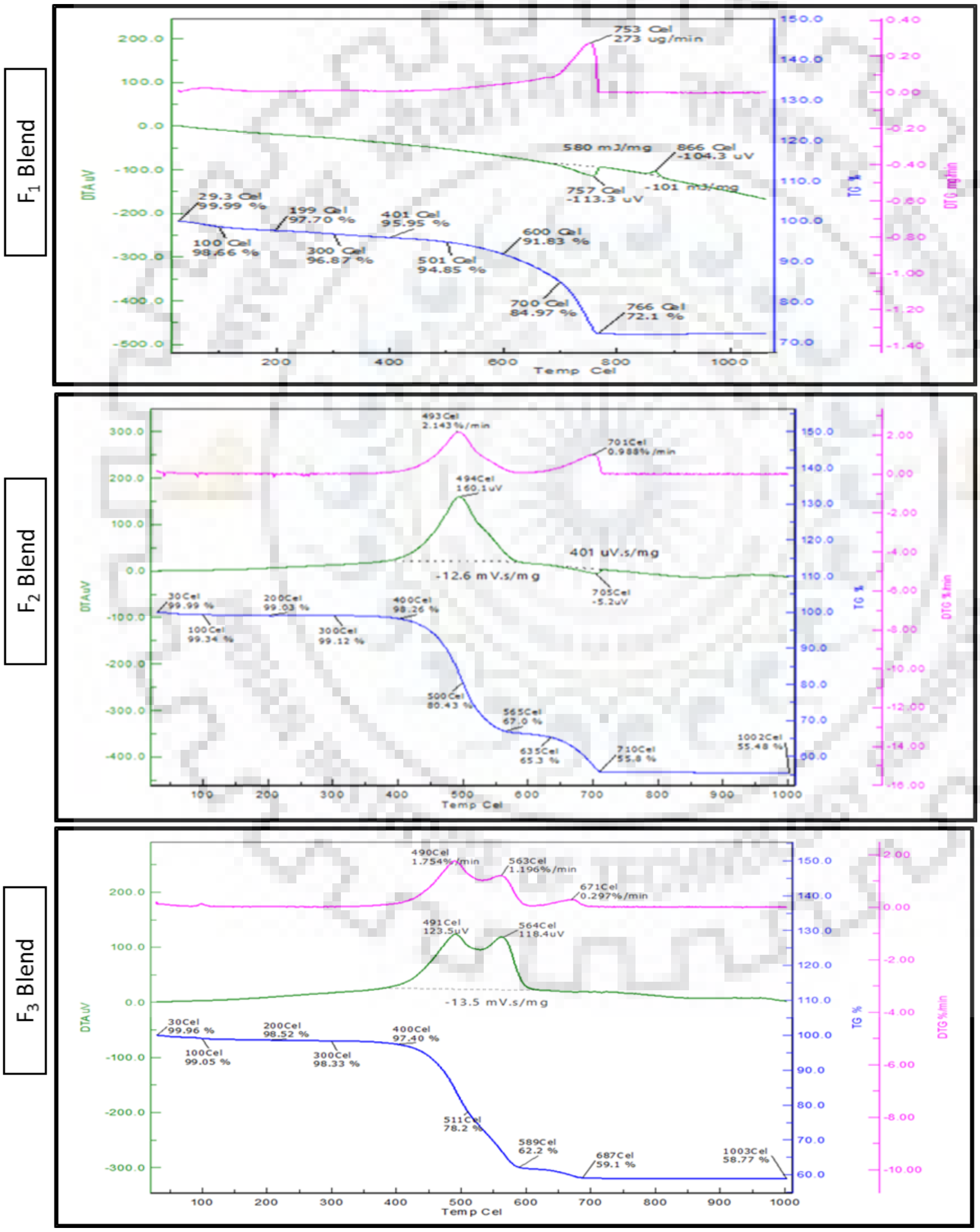


Fig. 2.12: Thermal analysis of the blends

2.3.4 Characterization of fired powder blends

Fig. 2.13 represents the XRD spectrum of the fired blends F1, F2, and F3. According to the spectrum, F1 and F2 blends show belite formation, but F1 is the only blend with belite synthesis at the lower temperature of 900 °C. While, in case of blend F3, belite formation did not take place, but Anorthite is formed on the firing of blend above 1000 °C.

The XRD pattern of F1 fired at the temperature between 900-1200 °C shows the formation of belite. The appearance of the main diffraction peak for belite at 900 °C shows the formation of this phase at a much lower temperature as predicted by *Maheswaran et al.* [14]. The results revealed that the intensity of belite peaks are well emphasized at 1100 °C and then decreases at 1200 °C. The increment in crystallinity of belite phase is due to the nanoparticle size of silica, owing to the reaction of a higher number of atoms with higher surface area. The higher specific surface area and lower particle size of the reactants induce the chemical reaction at a lower temperature with the relatively higher rate of reaction due to the electrostatic attractive forces [15]. On the other hand, the intensity of belite peaks decreased at 1200 °C due to the formation of wollastonite at a higher temperature with the expenses of belite as a reactant in wollastonite formation. Wollastonite is formed from the reaction of two moles of belite. The appearance of belite peaks at 900 °C shows the synthesis of it at lower temperature, which is in the accordance of DTA/TGA of unburnt F1 blend for a phase transition.

It was observed from the synthesis pattern of belite in F1 blend, that the belite based clinker formation takes place in two stages, shown in reactions 2.3 and 2.4.

(i) Carbonate decomposition (550-850°C)

$$CaCO_3 \rightarrow CaO + CO_2 \quad (2.3)$$

(ii) Formation of belite (850-1100 °C)

$$2CaO.SiO_2 + H_2O \rightarrow 2CaO.SiO_2 \quad (2.4)$$

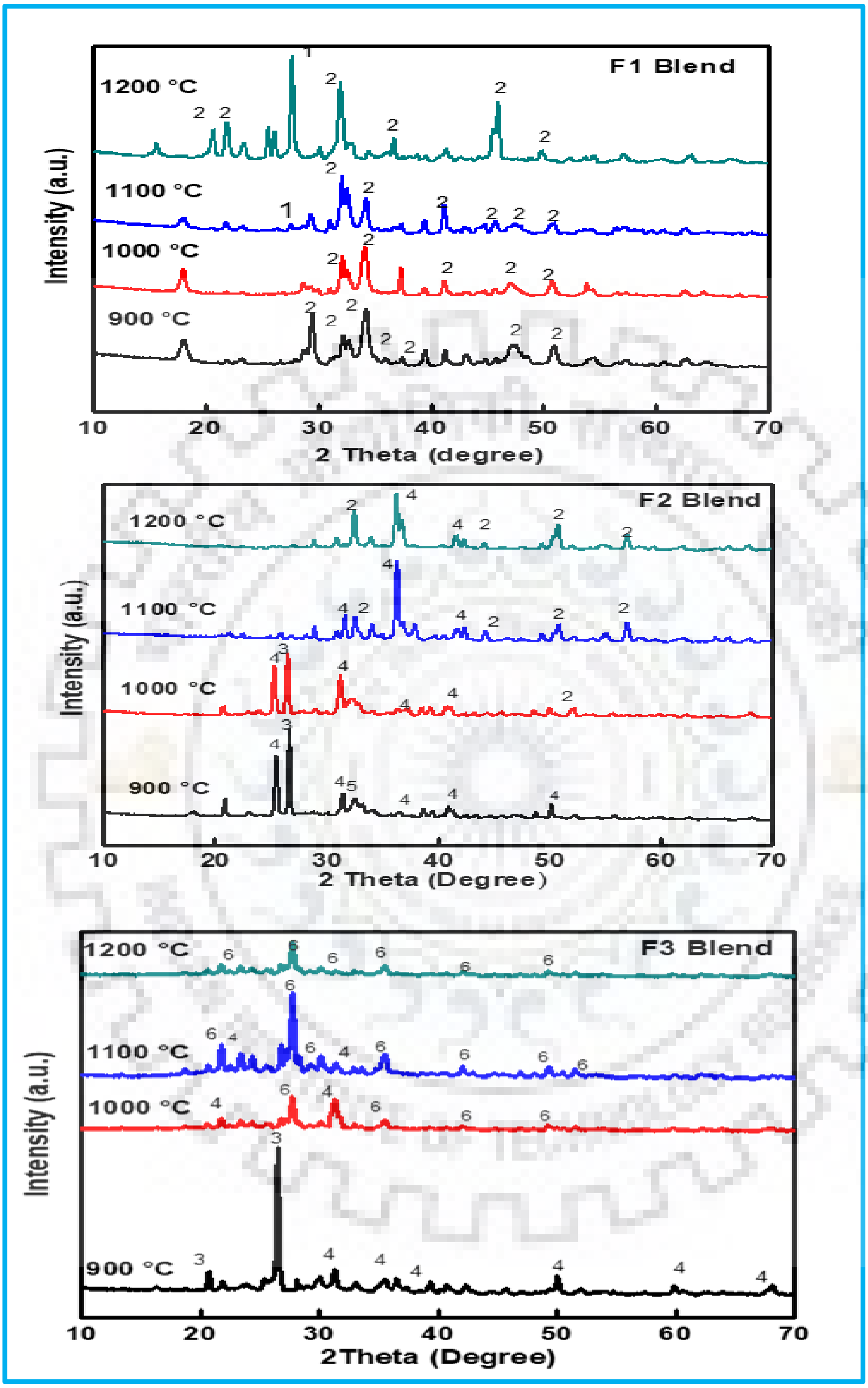


Fig. 2.13: XRD patterns of the blends at different firing temperature (Wollastonite, 2-Belite, 3-Mullite, 4- Gehlenite, 5- Calcium Oxide, 6- Anorthite)

XRD pattern of fired blend F2 (sintered between 900 and 1200 °C) shows the presence of Mullite ($Al_6Si_2O_{13}$), Gehlenite ($Ca_2Al_2SiO_7$), belite ($CaSiO_2$) and calcium oxide (CaO). Characteristic peaks of mullite preset in the BA were detected as the major phase between 900-1000 °C. However, distinct firing behavior was observed above 1000 °C, and gehlenite was a major phase. The intensity of gehlenite decreased with increasing temperature and finally disappears at 1100 °C, indicating that once all aluminum has consumed in the synthesis of gehlenite the remaining silica in the sample reacts with calcium oxide at above 1000 °C to form belite. Therefore, it can be concluded that in the case of blend F2, belite formation takes place at the temperature more than 1100 °C. Following are the two major phase transformation reactions.

$$\underset{\text{(Mullite)}}{Al_6Si_2O_{13}} + \underset{\text{(Quartz)}}{6CaO} + SiO_2 \rightarrow \underset{\text{(Gehlenite)}}{3Ca_2Al_2SiO_7} \quad (2.5)$$

$$CaO.SiO_2 + CaO \rightarrow \underset{\text{(Belite)}}{2CaO.SiO_2} \quad (2.6)$$

Observed phases in the XRD pattern of fired blend F3 (900 and 1200 °C) are Mullite ($Al_6Si_2O_{13}$), Anorthite ($CaAl_2Si_2O_8$), and Gehlenite ($Ca_2Al_2SiO_7$). XRD spectra of a mixture are attributed to the synthesis of anorthite as the major phase at the temperature above 1100 °C.

$$\underset{\text{(Gehlenite)}}{3Ca_2Al_2SiO_7} + \underset{\text{(Mullite)}}{Al_6Si_2O_{13}} + SiO_2 \rightarrow \underset{\text{(Anorthite)}}{6CaAl_2Si_2O_8} \quad (2.7)$$

Gehlenite which is synthesized from reaction between mullite and quartz as per equation 2.5 at a temperature between 900 to 1100 °C, disappeared above 1100 °C indicating that aluminum phase (mullite) present in fly ash further reacted with gehlenite to form anorthite. Equation 2.7 refers to the synthesis of anorthite in case of blend F3. Anorthite formation in blend F3 but not in bend F2 is due to the presence of bulk aluminum (approx.25.13 %) in fly ash as compared to aluminum in boiler ash (6.18 %) (**Table 2.2**).

According to *Juan Q. et al.* 2015 [11], anorthite is synthesized with the mixture of LS and FA above 1100 °C with no belite formation at all. *Buruberi et al*. [13] have synthesized belite by a mixture of LS and low aluminum FA at 1350 °C. Therefore, it is concluded that belite can be synthesized using fly ash with a small aluminum percentage while anorthite synthesis takes place with fly ash having high aluminum content. The variability in the formation of β-C_2S (belite) from different sample mixtures is dependent on aluminum composition, firing temperature, and particle size of the reactants.

2.3.5 Heat of hydration of prepared binder

As mentioned earlier, belite resulted from the firing of F1 blend and GGBS are used for the binder fabrication. This binder is tested for isothermal conduction hydration for 72 hours. **Fig. 2.14a and 2.14b** illustrated the heat flow curve and cumulative heat flow curve of the F1 cement. The calorimetric response of the binder paste shows two peaks, an early dissolution, and a later acceleration peak. The heat flow represents the rate of hydration, whereas cumulative heat evaluation represents the degree of hydration. Wetting and dissolution of the binder particles cause the early dissolution peak. The period of dominance after this phase is followed by an acceleration phase, which is due to the precipitation of the calcium silicate hydrate and calcium hydroxide phases.

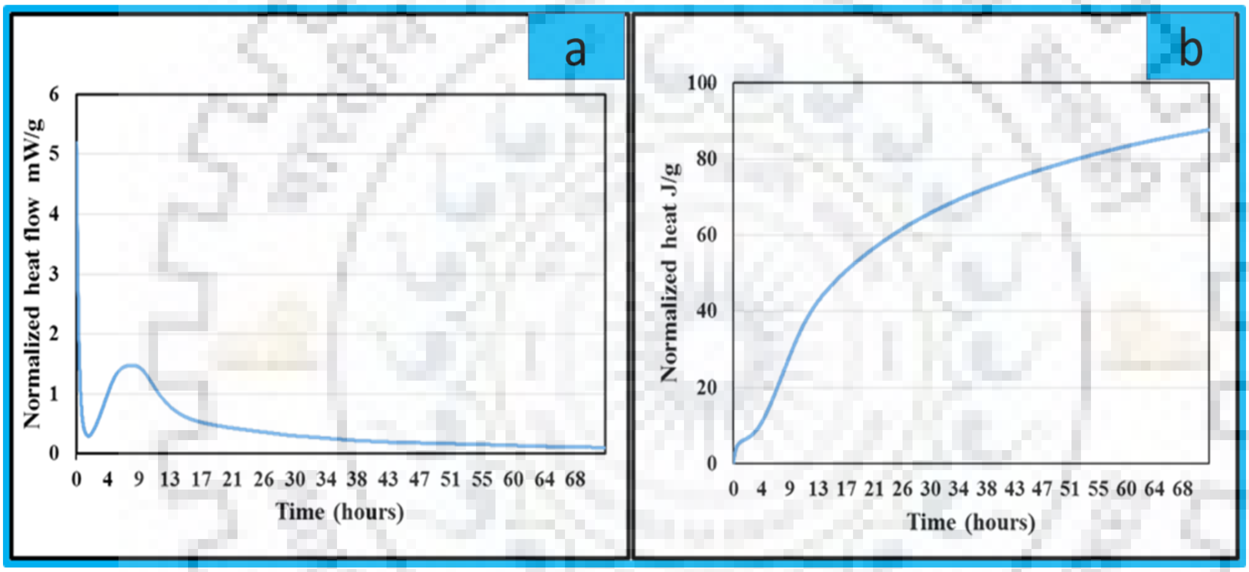


Fig. 2.14: Normalized heat flow (a) and normalized heat (b) of hydration of F1 clinker binder

It is observed that the dormant period of F1 blend based cement is less than the dormant phase of the hydration curve of standard Portland cement, which shows better workability of the F1 blend based binder. Cumulative heat flow curve of F1 based binder shows the lower degree of hydration in comparison to Portland cement [16]. It means that this binder can be applied in the construction where lower heat of hydration is required without adverse impact on strength properties.

2.3.6 Mortar **preparation and characterization**

F1 based binder was used to prepare mortars. The optimal kneading water amount was adjusted by testing the mortars consistency on a slump table, aiming to ensure the desired workability for plastering. The mortars with 11.6 wt. % of water exhibits a slump value of

75±2mm. According to IS: 10262:2009 [17], this value accomplishes the specified slump value requirements for indoor and outdoor plastering applications.

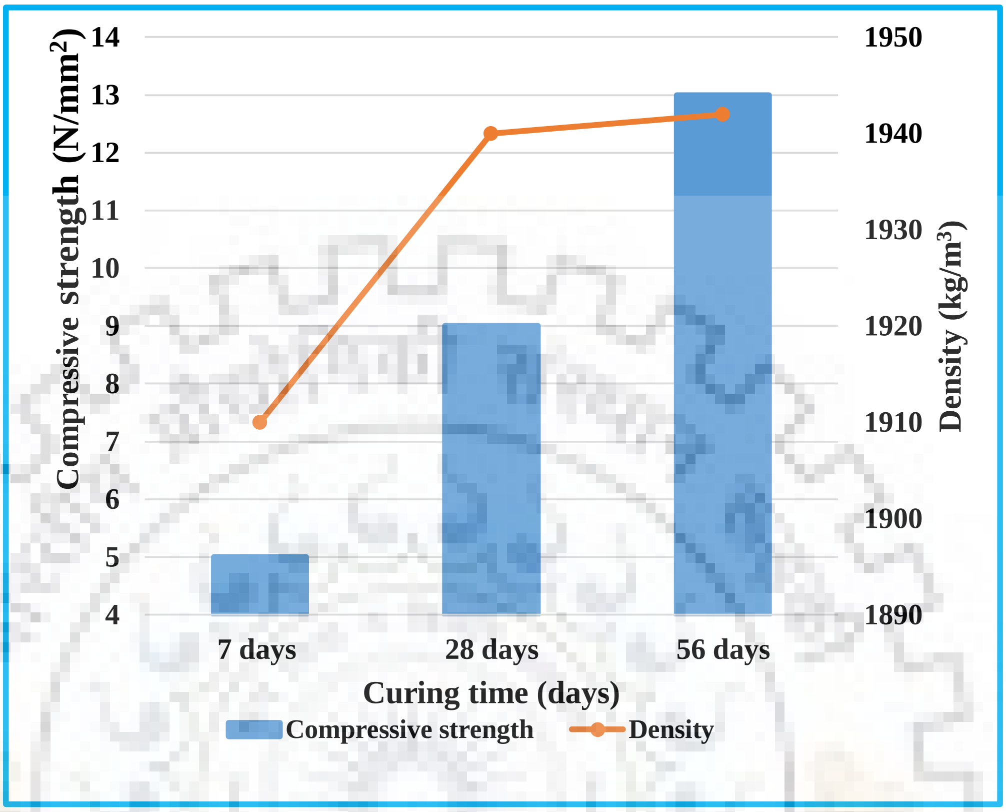


Fig. 2.15: Progression of the compressive strength and density with curing time

The mortars were characterized for compressive strength and density after curing for 7, 28, 56 days. The reaction of cement and water produces hydrated silicates and aluminates, which are accountable for the hardening of the cement paste. **Fig. 2.15** represents the density and compressive strength of the binder. As expected, the compressive strength of the mortars increased with the progression of the curing time. After 7 days of curing, the compressive strength of the material was 5 N/mm^2, which increased to 12 N/mm^2 and 15N/mm^2 at 28 and 56 days of curing. The mortars meet the strength requirements (>7.5 N/mm^2 at 28 days) for masonry mortar according to Indian standard: 2250 [9]. The improvement in strength accompanied by an increment in density for first 28 days of curing, but remain unchanged till 56 days. For the longer period of curing, the reactions responsible for hardening progress without any evident shrinking and blocks remain dimensionally constant. Besides, the visual examination of the mortar did not expose the appearance of efflorescence, or other deleterious signs might be harmful to mortar durability.

2.3.7 Economic consideration of prepared binder

The total amount of nanosilica synthesized from the boiler ash by using precipitation method was approximately 20% (by weight) of the boiler ash. **Table 2.3** represents the cost of production if 1 kg nanosilica from boiler ash. Clinker synthesis can consume 750 g of lime sludge with 250g of nanosilica at low temperature. Clinker was synthesized using only waste from pulp and paper industry as raw materials. The belite clinker synthesized was fired at temperature of 1000°C, which is reasonably less than the temperature employed in cement industry (≈1450°C). **Table 2.4** demonstrates the cost breakdown of binder. The cost of 1kg developed binder is about Rs.8.50 as compared to commercial available cost of OPC 43 grade, which is about Rs.8.00 as mentioned in **Table 2.5**. The cost is comparable. The commercial production of developed binder will reduce in long term. In addition, develop binder is ecofriendly.

Table 2.3: Estimated cost for production of 1 kg nanosilica.

Material	Unit	Quantity	Rate (INR)	Value
Boiler Ash	kg	4	Rs 1.50 /kg	Rs. 6.00
Sulphuric acid (H_2SO_4)	L	0.027	Rs 400.00/lit.	Rs. 10.80
Sodium Hydroxide (NaOH)	kg	0.25	Rs 40.00 /kg	Rs. 10.00
Other expenditure	Lump sum	-	-	Rs. 2.20
Total	-	-	-	Rs. 29.00 /kg of NS

Table 2.4: Cost breakdown for the preparation of 1 kg binder.

Material	Unit	Quantity	Rate	Value
Nanosilica	kg	0.2	Rs. 29.00/ kg	Rs. 5.80
Lime Sludge	kg	0.6	Rs. 1.00/ kg	Rs. 0.60
Ground Granulated Blast furnace slag (GGBS)	kg	0.2	Rs. 8.00/ kg	Rs. 1.60
Other	Lump sum	-	-	Rs. 0.50
Total	-	-	-	Rs 8.50 /kg of binder

Table 2.5: Comparison with commercial cement

	Developed Binder	OPC (Commercial)
Binders (kg)	Rs. 8.50	Rs. 8.00
Low carbon binder	Yes	No
Life Cycle Analysis	High	Low

2.4 CONCLUSION

The work shows that it is possible to use paper mill waste, namely lime sludge, boiler ash, and fly ash in the cement industry with better energy efficiency and better environmental impacts. Synthesis of amorphous nanosilica particles from boiler ash is successfully done with the pretreatment of boiler ash. FTIR, TEM, and XRD studies of the synthesized particles confirmed the formation of nanosilica. The particles have an excellent surface area of 450 m^2/gm. The fine particle size, amorphous nature, and high surface area make it useful for the application in the synthesis of belite based clinker. XRD and TGA/DTA confirmed the synthesis of belite based clinker at low temperature with nanosilica powder mixture. Fly ash and boiler ash mixture with lime sludge is also checked for belite synthesis and found that belite synthesis takes place with boiler ash at much higher temperatures. While belite is not synthesized with the mixture of lime sludge and fly ash. Belite based clinker is used with GGBS for the fabrication of binder. The heat of hydration of binder and compressive strength properties of the prepared mortars have full filled the requirements of indoor and outdoor mortar applications.

It can be concluded from the above findings:

- Boiler ash has enough silica content (43.22 %) for the extraction and synthesis of nanosilica. The fine particle size, amorphous nature, and high surface area make boiler ash based nanosilica an ideal candidate for its application in the low-temperature preparation of belite based clinker. So, synthesis of nanosilica from boiler ash provides a route of value addition and valorization of paper mill boiler ash.
- Conventionally, belite is synthesized above 1,200 °C. But, lime sludge application with nanosilica reduced the temperature of belite synthesis to 900 °C without the addition of any chemical stabilizer and pre calcination of lime sludge.
- In case of lime sludge and boiler ash mixture, belite is synthesized at the much higher temperature than lime sludge and nanosilica combination at 1200 °C as reported in the literature, which is the outcome of higher particle size and presence of alumina in boiler ash. Fly ash and lime sludge mixture lead to the formation of anorthite instead of belite due to the presence of alumina in a much higher percentage in fly ash.
- Belite can be synthesized with lime sludge and fly ash having low aluminum percentage while anorthite synthesis takes place in case of lime sludge blend with fly ash having high aluminum content.
- The heat of hydration of binder, compressive strength and density of the prepared mortars full filled the requirements of indoor and outdoor mortar applications.

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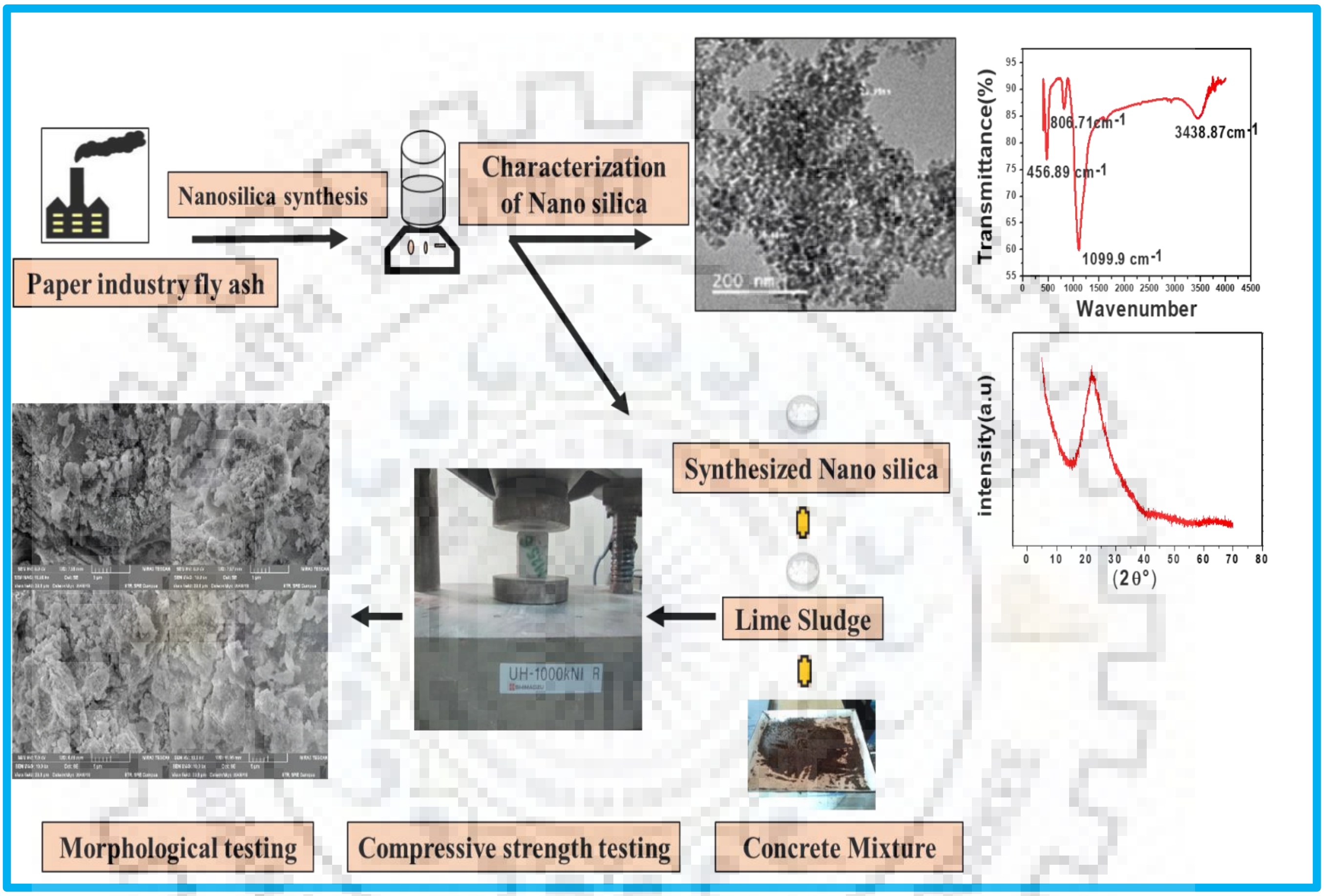
CHAPTER - 3

APPLICATION OF SYNTHESIZED NANOSILICA AND LIME SLUDGE IN CONCRETE

CHAPTER 3

APPLICATION OF SYNTHESIZED NANOSILICA AND LIME SLUDGE IN CONCRETE

GRAPHICAL ABSTRACT



3.1 INTRODUCTION

Alike other waste materials, utilization of lime sludge in cement-based concrete can offer a supplementary source of building construction and a tactic towards reduction of industrial solid waste. As discussed in chapter 1, all the studies utilizing lime sludge in concrete have shown limitation in the bulk use of lime sludge due to reduction in the compressive strength.

One fascinating opening from the previous studies is the absence of lime sludge utilization with nanosilica in concrete. Therefore, in this study lime sludge application in concrete is undertaken in a novel way with boiler ash synthesized nanosilica for the purpose of bulk utilization of lime sludge. The purpose of this chapter is to increase the proportion of lime sludge in concrete making without affecting the compressive strength significantly. On site utilization of paper industry boiler ash for the synthesis of nanosilica and application of synthesized nanosilica with lime sludge in concrete blocks can provide a route of bulk utility of lime sludge. On site production of the nanosilica and concrete blocks will also cut down the transportation expenses of lime sludge and boiler ash disposal or utilization.

Plasticizer is also used with lime sludge to study its impact on strength properties. Lime sludge application in concrete increases the water demand which is one of the reason of compressive strength reduction. The use of Plasticizer facilitate the reduction of water demand in the concrete mix at a great extent. Therefore, application of Plasticizer with lime sludge can improve the compressive strength of the concrete [1, 2]. The current chapter is focused on the application of lime sludge in bulk with co-utilization of synthesized nanosilica and plasticizer in concrete.

3.2 MATERIALS AND METHODS

3.2.1 Materials

The raw materials namely, lime sludge was procured from Ruchira Paper Industry Kalaamb Himachal Pradesh (India). Lime sludge, generated in the chemical recovery subdivision of paper mill and used in work with as received condition. The OPC-43 grade (Vikram) cement (**Fig. 3.1**) was used in the study and was stored properly to avoid environment and moisture effects. The fine aggregates and coarse aggregates (**Fig. 3.2 and 3.3**) used for the experimental investigation were locally available. The colour appearance of the fine aggregate was dark grey. The aggregates were initially dried in natural sunlight and then sieved through 5 mm size sieve to remove the coarser material such as pebble etc. Plasticizer was introduced into the concrete mix to check its effect on the compressive strength of the concrete. In the present investigation, plasticizer, namely Sikament 2002NS was used.

Fig. 3.1: OPC-43 grade


Fig. 3.2: Coarse aggregates

Fig. 3.3: Fine aggregates

3.2.2 Characterization of Cement and aggregates

Cement and aggregates were characterized for their physical and chemical properties. Cement was tested physically and chemically as per *Indian standards IS: 4031* [3] and *IS: 4032* [4], respectively. The cement used in this study was also compared with the cement provisions of *Indian standard IS: 269-2015* [5]. The aggregates were characterized physically as per the *Indian standards IS: 2386* [6]. In this work, sieve analysis of fine aggregates was performed in a mechanical shaker. Fine aggregate was also classified in the different grading zones as *Indian standard IS: 383* [7]. Water absorption, moisture content, and specific gravity tests of fine aggregates were also performed.

3.2.3 Casting of specimens

In this study, concrete of M 25 grade was proportioned in accordance with the *Indian standard IS: 10262-2009* [8]. Besides, the study on lime sludge and Nanosilica-based concrete was made with partial replacement of fine aggregate & cement respectively. The casting procedure is presented in **Fig. 3.4**. Mix proportioning adopted for this study is given in **Table 3.1**. **Table 3.2** and **3.3** represents the lime sludge proportioning in replacement of cement and fine aggregates. While **Tables 3.4** and **3.5** indicate the compressive strength (CS) of different grades of concrete and percentage strength of concrete at different ages, respectively.

For the casting of a specimen, the water was added to mixture. Blocks specimens were prepared by the mixing of materials in concrete mixture. It was ensured that no lump formation takes place in the mixture. All specimens were made of 150 mm x150 mm x 150 mm size respectively. The lime sludge was partially substituted into the concrete mix with the replacement of cement and fine aggregate by 10, 20, 30, and 40 % by weight as mentioned in **Table 3.1 and**

3.2. The mixture of lime sludge, fine aggregate, coarse aggregate, ordinary Portland cement, water was prepared, and specimens cast. Different concrete specimens were prepared with water to binder W/(C+LS) ratio of 0.48 to 0.64. 0.6 % of Plasticizer (Sikament 2002NS) was also used with the same proportion of concrete as mentioned in **Table 3.1 and 3.2** to check its effect on compressive strength.

In the case of nanosilica application with lime sludge to replace cement, the concrete specimen is produced with the replacement of cement by 0.3, 0.6 and 1 % of Nanosilica and 10-40 % of lime sludge. Different blends of concrete were prepared with lime sludge indicated in **Table 3.2**. Further, all these blends were also mixed with different proportions of nanosilica (0.3, 0.6, and 1 %) for replacement of cement in concrete mixture. Thus different proportions of the mixture of lime sludge, nanosilica, fine aggregate, coarse aggregate, ordinary Portland cement, water were prepared with water to binder W/(C+LS) ratio of 0.48 to 0.64.and specimens were casted. **Table 3.4** indicates the compressive strength of different grades (M15 – M40) of concrete after 7 days and 28 days of curing. The grade of concrete is decided by the total compressive strength attained by the concrete for example M15 should attains compressive strength of 15 N/mm^2 while M40 should attains 40 N/mm^2. **Table 3.5** indicates the average compressive strength attain by the concrete after different days of curing.

Fig. 3.4: Schematic diagram of casting and testing of specimen

Table 3.1: Proportioning for M 25 grade of concrete

S. N.	Constituents	Ratio
1.	Cement	1
2.	Fine Agg.	1
3.	Coarse Agg.	2
4.	Water	0.48
5.	Super-plasticizer by wt. of cement	0.06
6.	w/c ratio	0.48
7.	Proportion C : F.A. : C.A.	**1:1: 2**

Table 3.2: Proportioning of concrete with the replacement of cement by lime sludge

S. N.	Cement Replacement with lime sludge (%)	Proportioning of ingredients by weight					
		C	Lime Sludge	F.A	C.A (10mm)	W	W/(C+LS) Ratio
1	0%	1	0	1	2	0.48	0.48
2	10%	0.9	0.10	1	2	0.55	0.55
3	20%	0.80	0.20	1	2	0.60	0.60
4	30%	0.70	0.30	1	2	0.62	0.62
5	40%	0.60	0.40	1	2	0.64	0.64

Table 3.3: Proportioning of concrete with the replacement of fine aggregate by lime sludge

S. N.	Fine aggregate replacement with lime sludge (%)	Proportioning of ingredients by weight					
		C	Lime Sludge	F.A	C.A (10mm)	W	W/(C+LS) Ratio
1	0%	1	0	1	2	0.48	0.48
2	10%	1	0.10	0.90	2	0.55	0.55
3	20%	1	0.20	0.80	2	0.60	0.60
4	30%	1	0.30	0.70	2	0.62	0.62
5	40%	1	0.40	0.60	2	0.64	0.64

Table 3.4: Compressive strength of different grades of concrete at 7 and 28 days

Grade of Concrete	Lowest compressive strength N/mm^2 at 7 days	Specified compressive strength (N/mm^2) at 28 days
M-15	10.5	15
M-20	13	20
M-25	17	25
M-30	20.5	30
M-35	24	35
M-40	27	40

Table 3.5: Percentage strength of concrete at different ages

Age	Strength percentage
1 day	18%
3 days	40%
7 days	65%
14 days	90%
28 days	99%

3.2.4 Properties of concrete

The various methods and techniques were used to determine the specimen's properties.

3.2.4.1 Water absorption

The water absorption of the specimens with different binders was determined according to *ASTM C 20* [9]. The specimens with precise dimensions were entirely submerged in clean water at 25 °C for 24 hours. After removal from the water, specimens were placed on a 10 mm wire mesh and were allowed to drain for one minute. A damp cloth was used to remove the surface visible water, these surface dry and saturated blocks were weighted immediately. After that ventilated oven was used to dry all specimens for not less than 24 hours at 105 °C. The specimens were kept in the oven after 24 hours until two consecutive weighing at intervals of 2 hours show decrement of loss not greater than 0.2 percent of previously measured mass of the specimen. The water absorption is determined as given below:

$$Absorption\ (\%) = \frac{(A-B)}{B} * 100 \quad (3.1)$$

Where A = cube wet mass in kg. and B = cube dry mass in kg.

3.2.4.2 Density

The density of specimens with different proportions of lime sludge were determined according to *Indian standard IS 2185 (Part 1):2005* [10]. The density calculated by dividing mass of the block by overall volume including holes and cavities and end recesses.

3.2.4.3 Compressive strength

Universal Testing machine of 1000kN capacity was used to determine the compressive strength of the specimens. Three specimens of each mixture were evaluated and the average of the compressive strength was considered. Compressive strength was determined as per *Indian standard* IS 516:1959 [11].

3.2.4.4 Morphological study

Scanning Electron Microscopy (QUANTA 200F FEI) was used to study the surface morphology of concrete. The samples were prepared by standard sputtering technique in which samples were coated with gold. SEM images were captured at 5kx, 10kx and 25kx magnifications respectively.

3.3. RESULTS AND DISCUSSION

3.3.1 Lime sludge characterization

The characterization of lime sludge has already been discussed in section 2.3.1 of chapter 2.

3.3.2 Characterization of cement and aggregates

The cement is the most essential components of concrete which provide strength to concrete. Therefore, it should be as per the relevant standards. The cement was supplied in 50 kg weight packet and stored properly to avoid environment and moisture effects. In this study, OPC-43 grade of Ultra Tech cement was used. The physical and chemical properties of cement are presented in **Tables 3.6 to 3.7**. The cement used were found relevant to the provisions of Indian standard IS: 269.

Table 3.6: Physical properties of cement tested as per IS: 4031

Parameter	Test value	IS 269: 2015 Recommendation
Standard consistency (% of water by wt. of cement)	30	28-32
Setting time (Minutes) a) Initial b) Final	 65 290	 30 (Min.) 600 (Max.)
Compressive strength (MPa) 1) 3- das 2) 7 -day 3) 28- day	 27.5 39.2 46.8	 23 (Min.) 33 (Min.) 43 (Min.)
Fineness By air permeability (m^2/kg)	358	225 (Min.)
Soundness(mm)	1.4	10(Max)

Table 3.7: Chemical properties of cement tested as per IS: 4032

S. N.	Test Parameter	Test values	IS 269: 2015 Recommendation
1	Ratio of lime to silica, alumina and iron oxide (Ratio)	0.85	1.02 (Max.) 0.66 (Min.)
2	Ratio of alumina to iron oxide (%)	1.59	0.66 (Min.)
3	Insoluble residue (%)	1.10	2.0 (Max.)
4	Magnesia (%)	2.40	6.0 (Max.)
5	Total Sulphur content (%)	1.10	2.5 (Max.)
6	Total loss on ignition (%)	0.80	5.0 (Max.)
8	CaO :61.7%; SiO_2 :22%; Al_2O_3:6.2%; MgO:2.4%; Fe_2O_3:3.9%; SO_3: 1.1%		

The fine and coarse aggregates generally occupy 65 % to 75 % of the concrete volume (70 % to 85 % by mass) and have a substantial influence on the economy and properties of concrete in the green and hardened state. Therefore, it is necessary to assess the quality of aggregate in terms of its physical and mechanical properties. In this study, in concrete mix proportioning, aggregate density is the main factor which influences the outcome and quantity of aggregate required for a given volume of concrete. For a workable concrete, it is essential aggregate should have well graded.

The fine aggregate used for the experimental investigation was locally available river sand from the nearby supplier. The colour appearance of the fine aggregate was dark grey. The aggregates were initially dried in natural sunlight and then sieved through 5 mm size sieve to remove the coarser material such as pebble etc. The particle size distribution of fine aggregate may be obtained by shaking the sample either manually or by sieve shaker. Sieve analysis of fine aggregate is illustrated in **Table 3.8**. Depending upon the fineness modulus, sand (fine aggregate) is classified into different groups such as coarse, medium and fine sand as given in **Table 3.9.**

Table 3.8: Fineness module of fine aggregate

Type of fine aggregate	Fineness modulus range
Fine	2.2 to 2.6
Medium	2.6 to 2.9
Coarse	2.9 to 3.2

Table 3.9: Sieve analysis of fine aggregate

IS Sieve	Wt. Retained (kg)	Cumulative Wt. Retained (kg)	% Cumulative weight retained	% Cumulative weight passing
20 mm	-	-	-	-
10 mm	-	-	-	-
4.75 mm	0.010	0.010	0.33	99.67
2.36 mm	0.027	0.037	1.23	98.77
1.18 mm	0.666	0.703	23.43	76.57
600 microns	0.566	1.269	42.30	**57.70**
300 microns	0.835	2.104	70.13	29.87
150 microns	0.778	2.882	96.06	3.94
Pan	0.116	2.998	99.93	0.07
			Total = 233.48	
Fineness Modulus = 233.48/100 = 2.34				

Besides, the specific gravity, water absorption, and moisture content tests have been carried out as per the procedure laid in IS: 2386, and the results obtained are given in **Table 3.10**. It is observed from the result obtained from the sieve analysis that the given fine aggregate belongs to grading zone II, which is ideal for making the conventional concrete. A locally available crushed stone aggregates of maximum nominal size of 20 mm were used as coarse aggregate in the present study. Besides, 10 mm and down aggregate were also used. Sieve analysis of coarse aggregates was carried out manually by a set of sieves as per the procedure given in IS: 2386 (part 1). Specific gravity, crushing value, water absorption, and moisture content tests were also carried out as per the procedure laid in IS: 2386. The results are mentioned in the tabular form, as shown in **Tables 3.11** and **3.12** for 20 mm aggregate and in **Tables 3.13** and **3.14** for 10 mm & down aggregate.

Table 3.10: Physical properties of fine aggregate

S. N.	**Physical Properties**	**Tested Values**	**IS: 383:1970 Recommendations**
1.	Specific gravity	2.64	
2.	Fineness modulus	2.34	2.00 – 3.50
3.	Water absorption (%)	1.65	
4.	Moisture content (%)	0.38	
5.	Grading	Zone II	
6.	Appearance	Dark grey	

Table 3.11: Sieve analysis of coarse aggregate (20 mm size)

IS Sieve size (mm)	**Wt. Retained (kg)**	**Cumulative Wt. retained (kg)**	**% Cumulative weight retained**	**% Cumulative weight passing**
20	0.399	0.399	13.3	86.7
10	2.578	2.977	99.23	0.77
4.75	0.0180	2.995	99.83	0.17
2.36			100	0
1.18			100	0
0.60			100	0
0.30			100	0
0.15			100	0
Pan				
			Total = 712.36	
Fineness Modulus = 712.36/100 = 7.12				

Table 3.12: Physical properties of coarse aggregate (20 mm size)

S. N.	Physical Properties	Tested Values	IS: 383:1970 Recommendations
1.	Specific gravity	2.69	2.60-2.70
2.	Fineness modulus	7.12	5.50-8.00
3.	Water absorption (%)	0.56	-
4.	Moisture content (%)	Nil	-
5.	Texture	Rough	-
6.	Crushing value	15%	-

Table 3.13: Sieve analysis of coarse aggregate (size 10 mm & down)

IS Sieve size(mm)	Wt. Retained (kg)	Cumulative Wt. retained (kg)	% Cumulative weight retained	% Cumulative weight passing
20	-	-	-	-
10	1.215	1.215	40.50	59.50
4.75	1.605	2.820	94.00	6.00
2.36	0.114	2.934	97.80	2.20
1.18	0.056	2.990	99.66	0.34
0.6	-	2.990	99.66	0.34
0.3	-	2.990	99.66	0.34
0.15	-	2.990	99.66	0.34
Pan	-	2.99	-	0.34
			Total = 630.94	
Fineness Modulus = 630.94/100 = 6.30				

Table 3.14: Physical properties of coarse aggregate (size 10 mm & down)

S. N.	Physical Properties	Tested Values	IS: 383:1970 Recommendations
1.	Specific gravity	2.69	2.60-2.70
2.	Fineness modulus	6.30	5.50-8.00
3.	Water absorption (%)	0.65	-
4.	Moisture content (%)	Nil	-
5.	Texture	Rough	-
6.	Crushing value	17%	-

3.3.3 Properties of concrete

3.3.3.1 *Density*

Fig. 3.5 indicates the density of the specimens in which cement and fine aggregates were replaced by lime sludge. While **Fig. 3.6** illustrated the density of the specimens with cement replacement by lime sludge and nanosilica specimens. In Fig. 3.6, the density of control (0 % lime sludge) specimen for cement replacement and fine aggregates replacement is found 2.31 and 2.39 g/cc respectively whereas the density of the specimens with 40 % replacement of cement & fine aggregated by lime sludge is found 2.39 and 2.19 respectively. Results show that the application of lime sludge in concrete does not affect the density significantly on replacement of both cement and fine aggregates but on comparison of specimens of cement replacement and fine aggregates replacement , reduction in density is more in case of fine aggregates replacement because cement is more denser material than fine aggregate.

Fig. 3.6 illustrates the density of concrete specimens with application of lime sludge and nanosilica. On addition of nanosilica in the concrete system density increased with increasing proportion of nanosilica. It is happened due to the physical property of the nanosilica, nanosilica is 100 times small in size than cement. Nanosilica can fill the remaining voids in the partially hydrated concrete system. This is the sole reason of density increment with increasing proportion of nanosilica in concrete [14, 15].

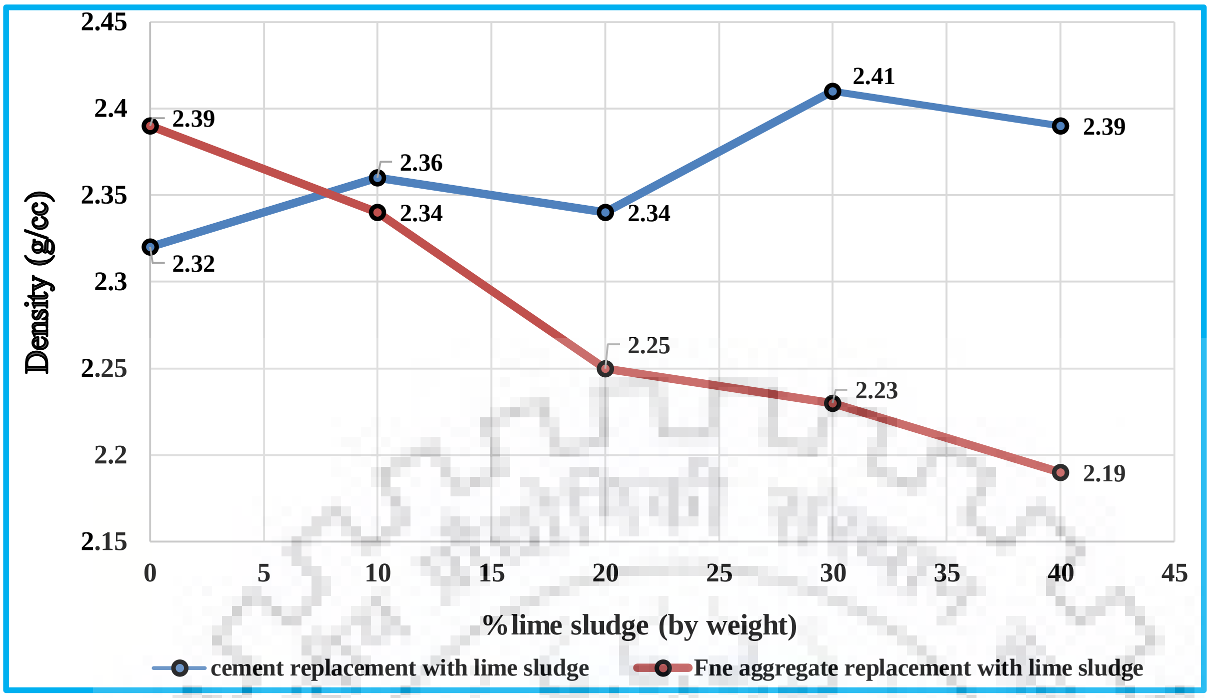


Fig. 3.5: Density of specimens with the replacement of cement and Fine aggregates by lime sludge

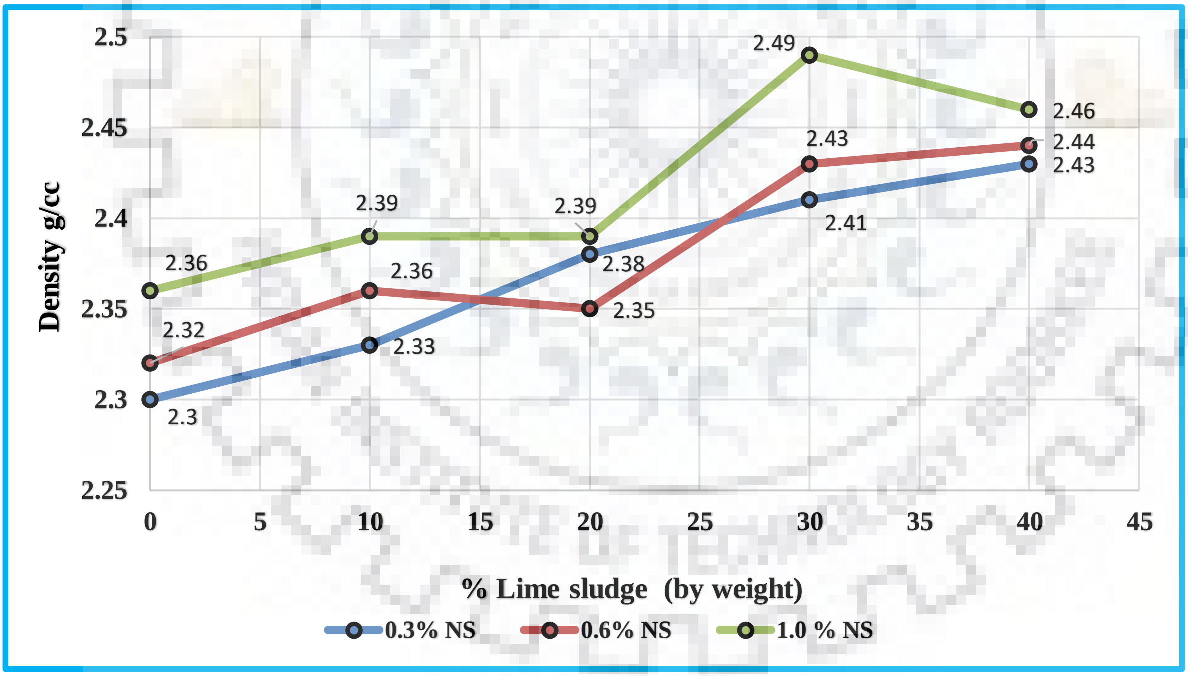


Fig. 3.6: Density of specimens with cement replacement by lime sludge and nanosilica

3.3.3.2. *Water absorption*

Fig. 3.7 indicates the water absorption of the specimens in which cement and fine aggregates were replaced by lime sludge. While **Fig. 3.8** illustrated the water absorption of the specimens with cement replacement by lime sludge and nanosilica specimens. The results show that the specimens with application of lime sludge for fine aggregates replacement show more water absorption than specimens with cement replacement. It reflects that, fine aggregates replacement produces the concrete with more porosity than concrete with cement replacement due to the lesser density of fine aggregates than cement. A similar trend is also observed with cement replacement by lime sludge and nanosilica in **Fig. 3.8**, where lime sludge replacement increases the water absorption but application of nanosilica reduces it. Nanosilica fill the voids and decreases the water absorption the concrete.

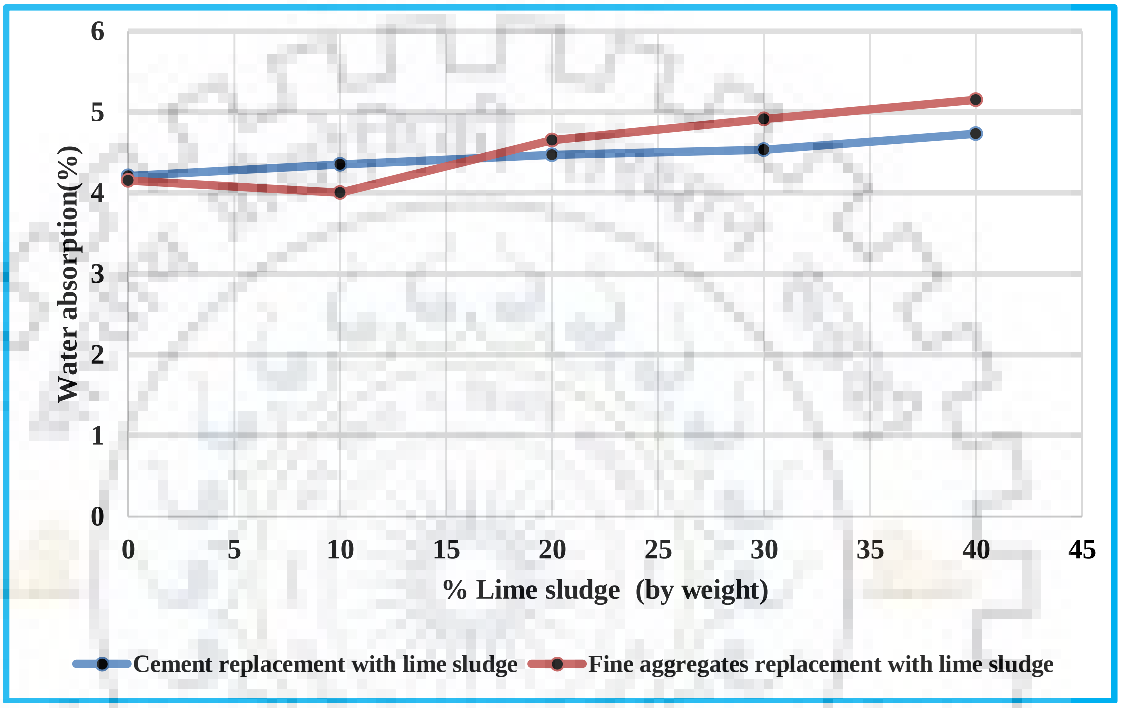


Fig. 3.7: Water absorption of mixtures with the replacement of cement and fine aggregates

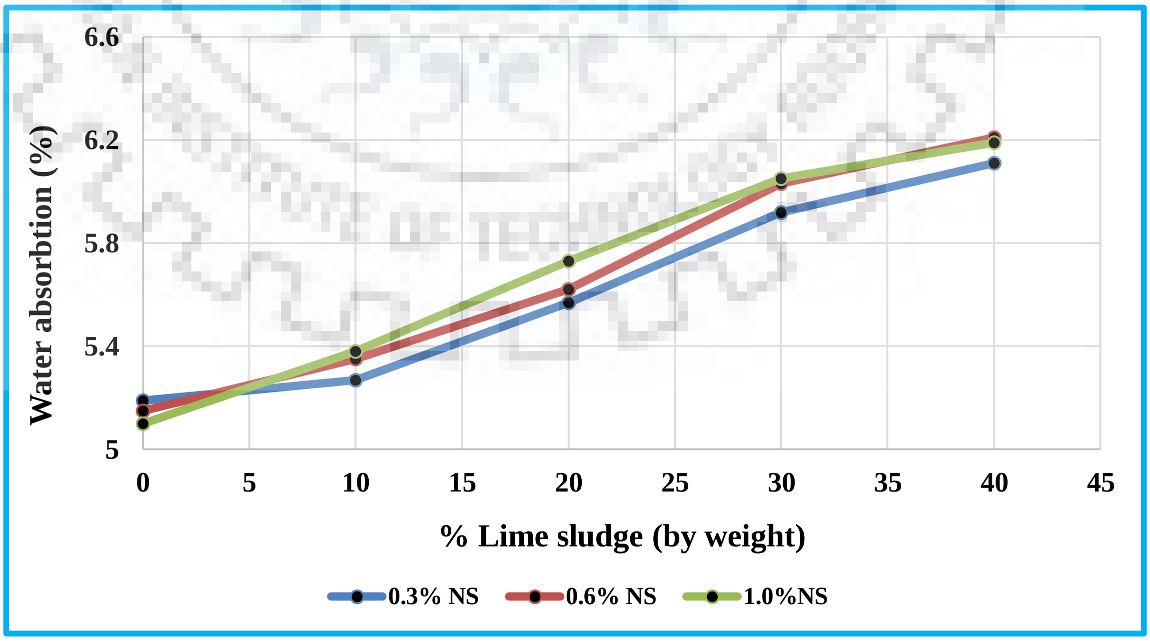


Fig. 3.8: Water absorption of mixtures with the replacement of cement by lime sludge and nanosilica

3.3.3.3 *Compressive strength of concrete*

Fig.s 3.9 and **3.10** show the compressive strength of different specimens of concrete with cement replacement by lime sludge. **Fig. 3.9** shows that the compressive strength of concrete is decreased with increasing application of lime sludge in concrete. Only 10 % replacement of cement by lime sludge can produce enough compressive strength after 28 days of curing. **Fig. 3.10** indicates the concrete with cement replacement by lime sludge and 0.6 % plasticizer. Plasticizer use in concrete enhanced the compressive strength of it and made it effective till 20 % application of lime sludge for M25 grade of concrete.

Fig. 3.11 indicates the compressive strength of the specimens with fine aggregates replacement by lime sludge. The results show that the compressive strength of the concrete specimens decreased with an increasing percentage of lime sludge in concrete and fine aggregates can be replaced up to the 20 % application of lime sludge for M25 grade of concrete. **Fig. 3.12** illustrates the compressive strength of concrete with fine aggregate replacement by lime sludge and plasticizer. Use of plasticizer enhanced the compressive strength of concrete and made the lime sludge use possible up to 30 % replacement of lime sludge, in accordance with 25 grade of concrete.

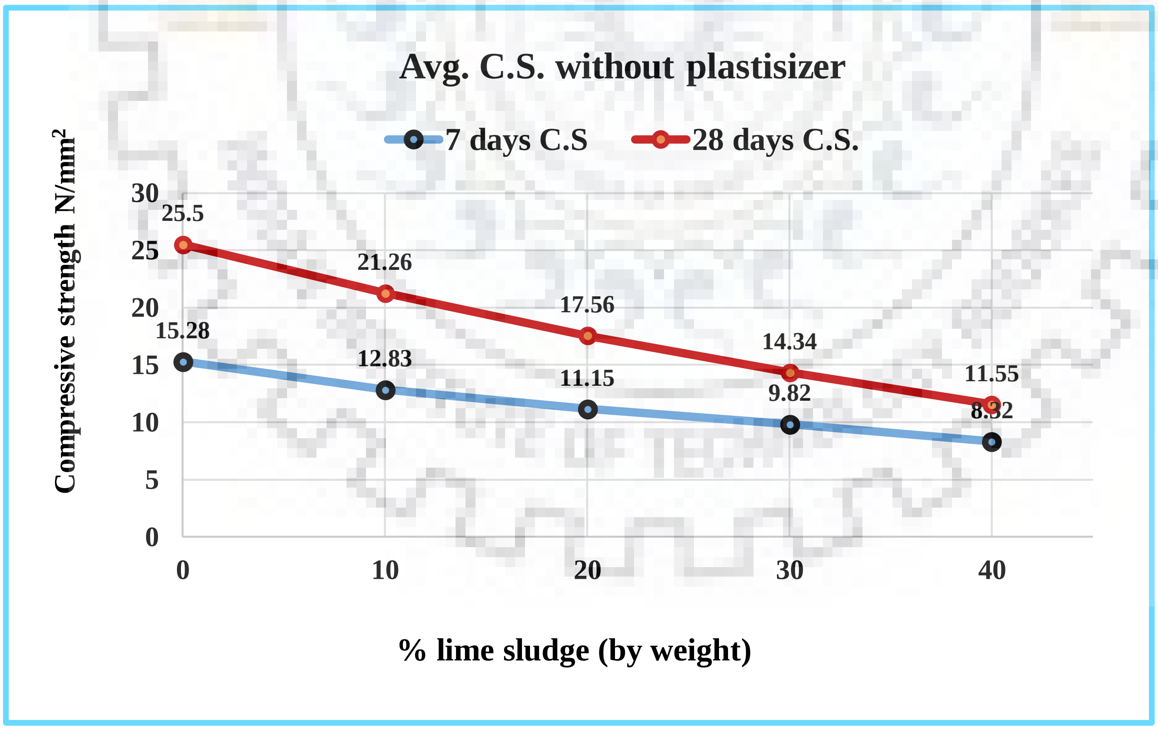


Fig. 3.9: Compressive strength of mixtures with cement replacement by lime sludge

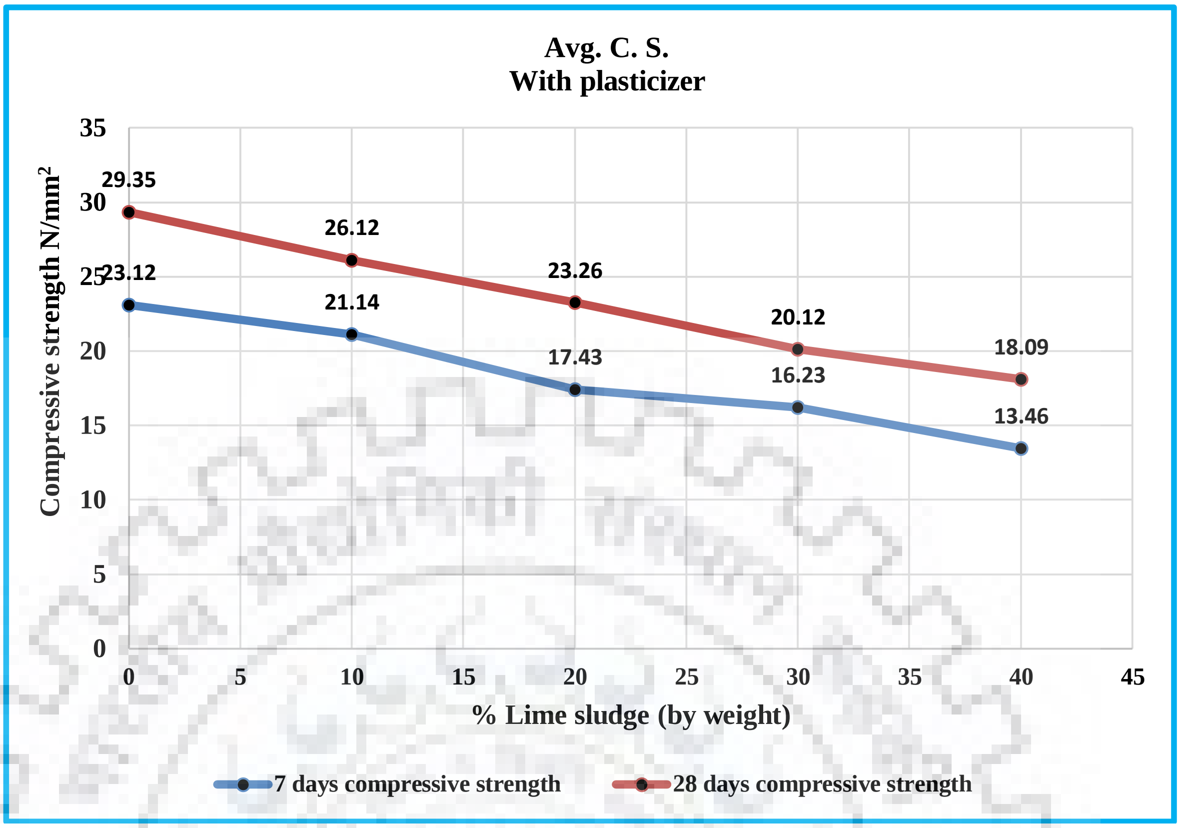


Fig. 3.10: Compressive strength of mixtures with cement replacement by lime sludge with addition of plasticizer

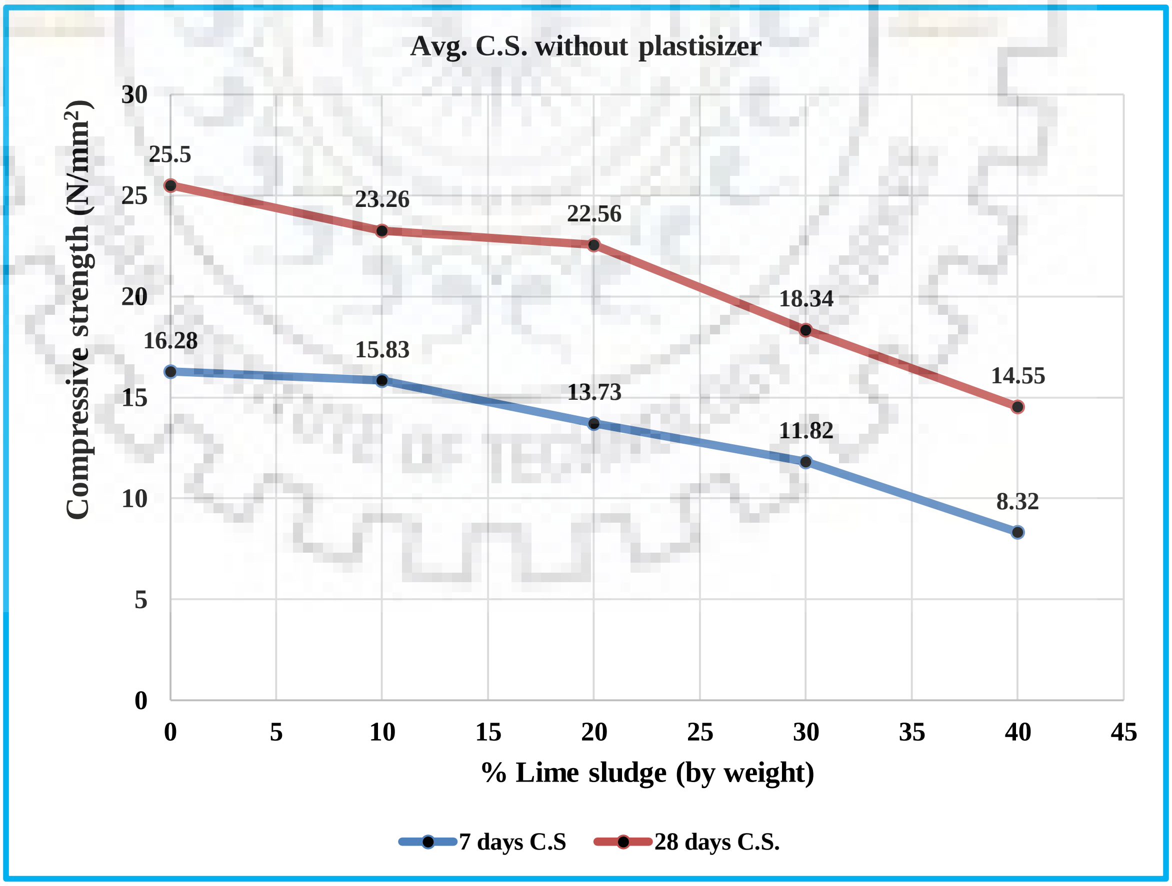


Fig. 3.11: Compressive strength of mixture with fine aggregates replacement with lime sludge

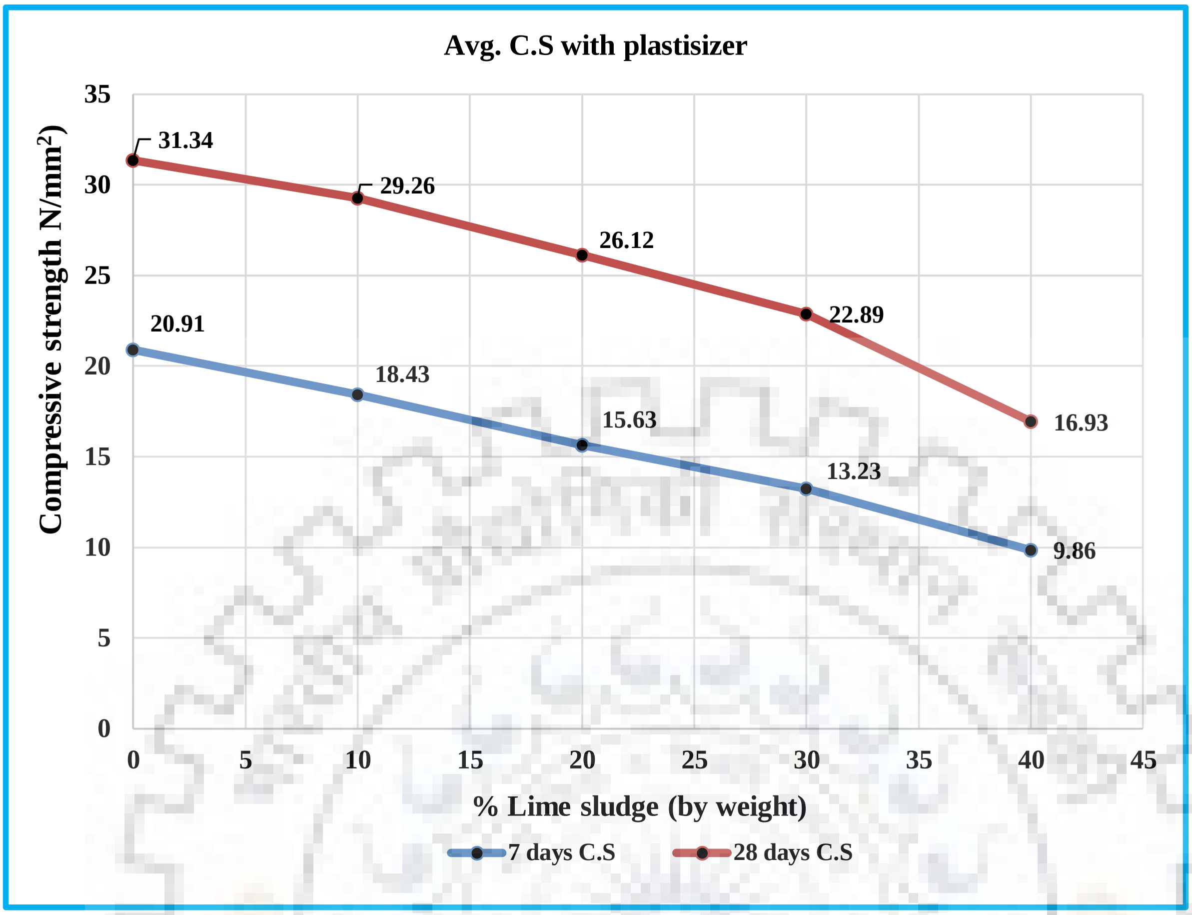


Fig. 3.12: Compressive strength of mixture with fine aggregates replacement by lime sludge with addition of plasticizer

Fig. 3.13 and **3.14** represent the compressive strength of concrete with cement replacement by lime sludge and nanosilica at 7 and 28 days of curing, respectively. It was observed that the use of nanosilica in concrete mixture increased the compressive strength of blends. Lime sludge application with nanosilica increased up to 30 %, without affecting the compressive strength of the concrete in accordance with M25 grade of concrete. Blocks comprising of nanosilica and lime sludge resulted in better compressive strength comparative to ones comprising only of lime sludge. Blocks with 0.3% nanosilica and varying proportions of 10 %, 20 %, 30 %, and 40 % lime sludge were found to have improved compressive strength by, 4.28 %, 4.43 %, and 3.61 % respectively, compared to blocks with lime sludge only. While with application of 0.6 % nanosilica and above indicated proportions of lime sludge, compressive strength improved by 19.19 %, 18.12 %, 15.60 %, and 17.72 % respectively, compared to blocks with lime sludge only. This trend of compressive strength increment remained constant, as blocks with 1 % nanosilica application and above indicated proportions of lime sludge produced improved compressive strength by 32.70 %, 31.80 %, 29.24 %, and 26.52 % respectively, compared to blocks with lime sludge only. It is evident from **Fig. 3.13 and 3.14** that effect of nanosilica on overall compressive strength after 28 days of curing was found less significant compared to ones after 7 days of curing. This is due to the early strength development effect of nanosilica blocks with different proportion of lime sludge and 0.3 %, 0.6 %, 1.0 % application of nanosilica produced approximate increase of 5, 15 and 25 % in their compressive strength. These results of nanosilica application effect on compressive strength of concrete are in accordance with as reported in the literature [12, 13]. It means that application of nanosilica produce better results due to the chemical effect of nanosilica: pozzolanic reaction to form more C-S-H hydrates and also by physical activity of nanosilica, because of its very small size it can fill the remaining voids of the concrete. Both of these effects ultimately increased the compressive strength of concrete [14].

It was observed that compressive strength of the blocks decreases abruptly with increasing proportion of lime sludge but application of nanosilica with lime sludge produce the sustainable concrete blocks with very less reduction in compressive strength. The nanosilica application is limited to 1 % due to the economical point of view as with currently available nanosilica synthesis methods, nanosilica is relatively costlier in-comparison to the other concrete ingredients. Nanosilica application is also kept limited to 1 % for the reason that higher percentage of nanosilica application could resulted in the excessive self-desiccation and cracking in concrete as found in previous studies [16].

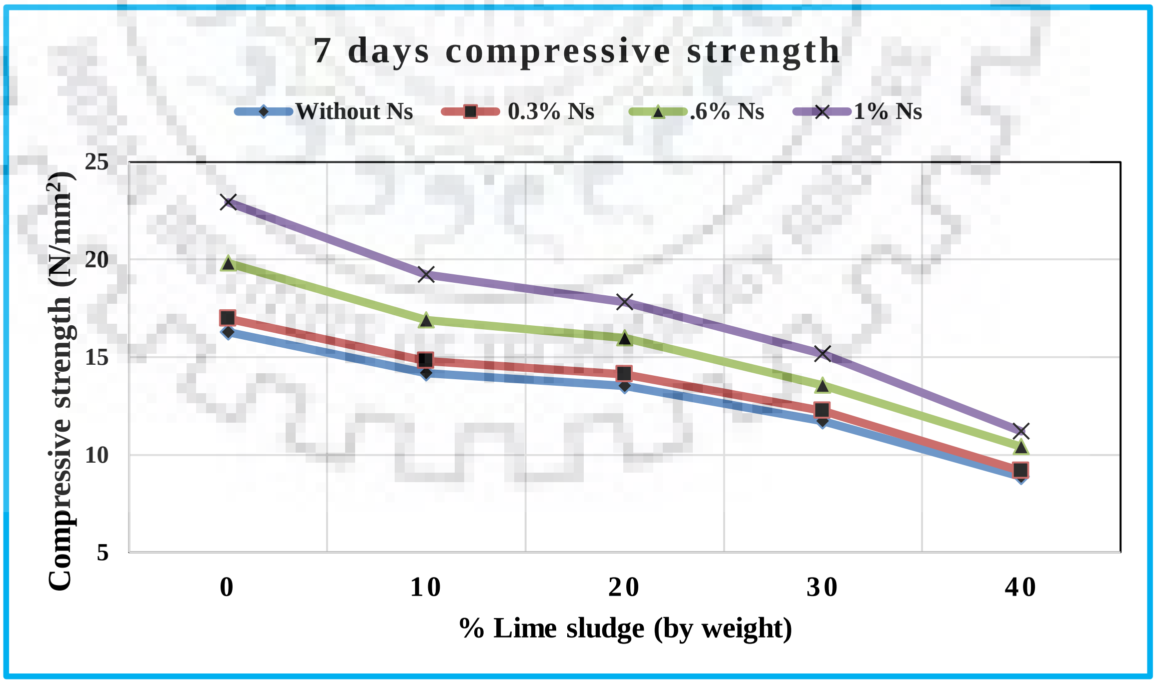


Fig. 3.13: Compressive strength of concrete specimens with different dosage of lime sludge and nanosilica at 7 days

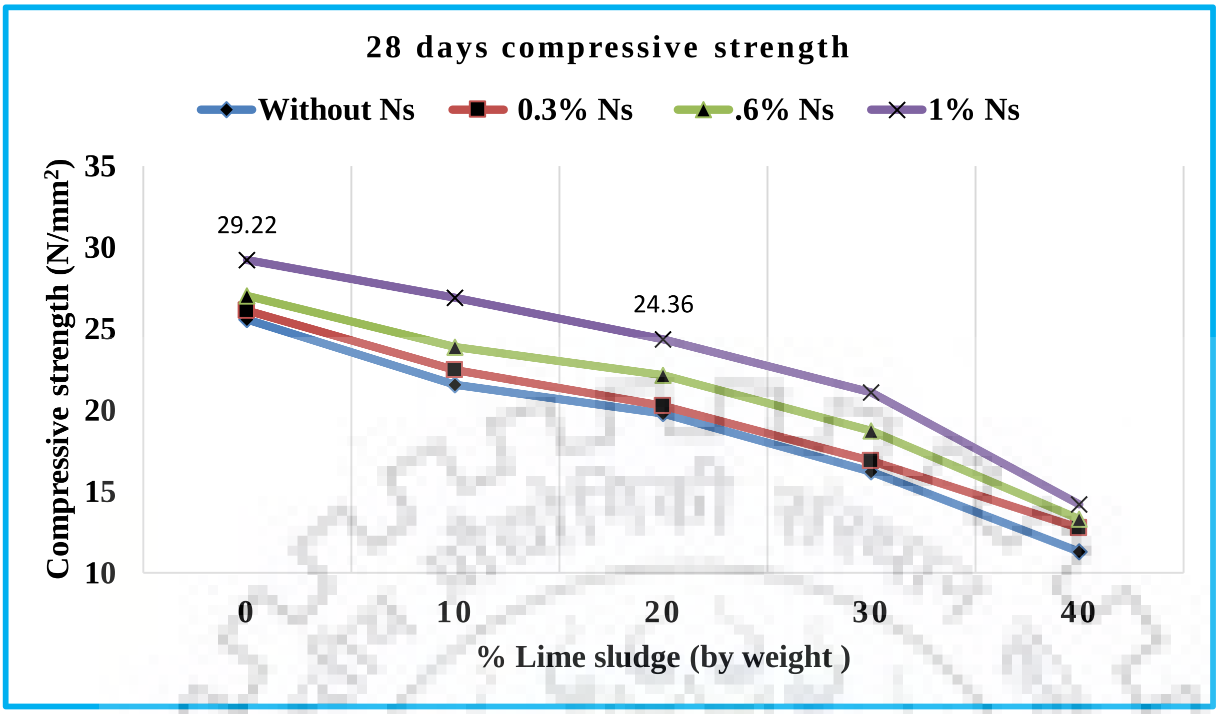


Fig. 3.14: Compressive strength of concrete specimens with different dosage of lime sludge and nanosilica at 28 days

3.3.4. Comparison of FESEM images

Fig. 3.15 illustrates the SEM micrograph of the concrete blocks with 30 % lime sludge and different proportions of nano silica. SEM images reveals that nanosilica acted as an activator to uphold the hydration process and to improve the microstructure of the cement paste. SEM images also reveals that microstructure of concrete with nanosilica was more uniform and compact than normal concrete [13, 16]. SEM images of concrete without nanosilica elucidate that C-S-H (calcium silicate hydrate) bonding in the concrete is not uniform and scattered throughout the micrograph with so many lumps. Calcium silicate hydrate (also shown as C-S-H) is a result of the reaction between the silicate phases and water. This reaction typically is expressed as,

$$2Ca_3SiO_5 + 7H_2O \rightarrow 3CaO.SiO_2.4H_2O + 3CaO(OH)_2 + 173.6\ kJ$$

(Calcium Silicate) (Calcium Silicate hydrate)

The lumps appeared in concrete can be $CaCO_3$ and $Ca(OH)_2$ of lime sludge which weakens the bonds and that directly affect the compressive strength of the concrete. These lumps started to disappear with increasing application of nanosilica in lime sludge based concrete blocks. This happened due to reactivity of the nanosilica in the concrete mixture. Nanosilica reacts with remaining $Ca(OH)_2$ and form more C-S-H hydrate which is the sole reason behind the increased compressive strength and uniformity in the SEM micrographs. SEM micrographs of concrete blocks with 0.3 % nanosilica illustrates better images with packed microstructure in comparison to micrographs without nanosilica, but still large lumps are presents. The particles of nanosilica occupied the pores in C-S-H bonds but still not in enough amount to react with $Ca(OH)_2$ and form more C-S-H bonds. While, in case of .6 % application of nanosilica, micrographs are more uniform with very less space between them. It indicates that nanosilica has reacted with $Ca(OH)_2$ and converted most of it in C-S-H bonds. Concrete with 1.0 % nanosilica shows very compact and dense microstructure images which represents the agglomeration of nanosilica particles and it is the reason of increased compressive strength.

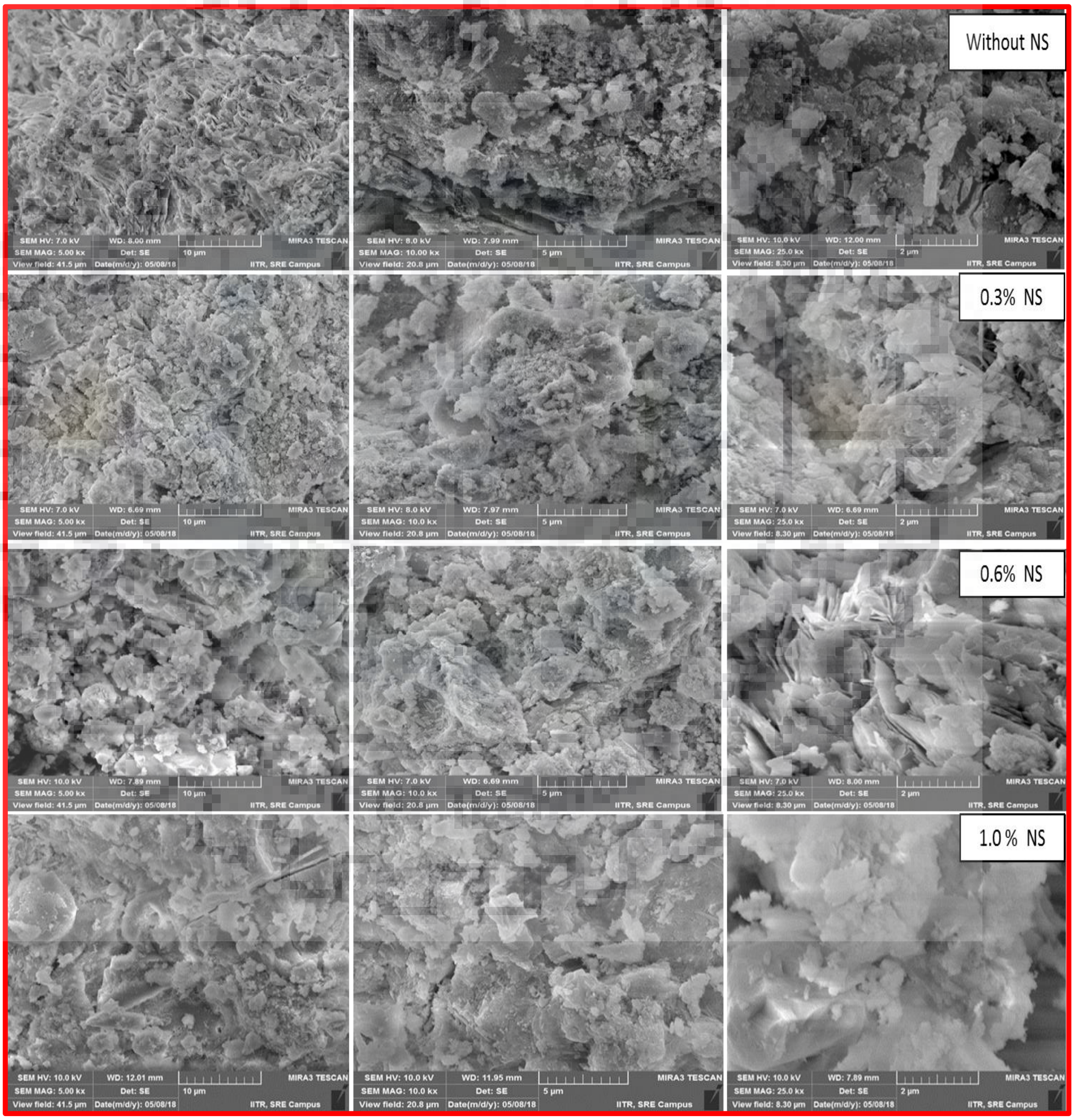


Fig. 3.15: SEM micrograph of concrete with 30 % lime sludge and different proportion of nanosilica

3.3.5 Economic consideration of lime sludge application with and without additives

The lime sludge application cost in concrete is reasonably less. Lime sludge is a waste material which can be procured very inexpensively from industries. This is the biggest benefit of lime sludge application from economical point of view. **Table 3.15** illustrates the capital saving analysis of the lime sludge application with and without additives for the cement and fine aggregates replacement in concrete. The commercial use of lime sludge with nanosilica is recommended for better economic benefits. In addition, lime sludge application is ecofriendly.

Table 3.15: Capital saving analysis of lime sludge application in concrete

S. N.	Material replaced with lime sludge	Optimum% Replacement	Saving of materials on /kg use		Capital Savings/ kg of cement) *(Cost of cement/ fine aggregate saving - lime sludge cost + additive cost) (INR)*
			Saving of cement (kg)	Saving of FA (kg)	
1.	Cement	10	0.10	-	0.85- 0.10 = 0.75 (approx.)
2.	Fine aggregates	20	-	0.20	0.40- 0.20= 0.20 (approx.)
3.	Cement replacement with plasticizer addition	20	0.20.	-	1.70 - (0.20+ 0.30) = 1.20 (approx.)
4.	Fine aggregates replacement with plasticizer addition	30	-	0.30	0.60- (0.30 + 0.30) = 00 (approx.)
5.	Cement replacement with 1% nanosilica	30	0.30	-	2.55- (0.30 + 0.30) = 1.95 (approx.)
Note: Cost of applied plasticizer was approximately 50 Rs/kg. Cost of Cement used- 8.5 Rs/kg Cost of nanosilica used- 29 Rs/kg Cost of Fine aggregates (FA) used- 2 Rs/kg					

3.4 CONCLUSION

Based on this experimental study, there is a possibility for partial substitution of fine aggregate. The compressive strength of concrete blocks found in accordance with M25 grade of concrete with the 10 % substitution of cement and 20 % substitution of fine aggregate with lime sludge. Use of plasticizer in concrete mixture enhanced the compressive strength and made it possible to replace cement the fine aggregate up to 20 and 30 % respectively without affecting their compressive strength significantly. Nano silica application with lime sludge found suitable. Application of 1 % nanosilica in lime sludge-based concrete can enhance the lime sludge application up to 30% without affecting the compressive strength comprehensively.

Based on the findings of this experimental study, the observations are as under regarding:

1. Density and water absorption of the concrete did not affect significantly on the addition of lime sludge in the concrete mixture.
2. Compressive strength of concrete decreased with the replacement of cement and fine aggregates by lime sludge.
3. Use of plasticizer is advantageous up to an extent of lime sludge application.
4. The FESEM micrograph shows a uniform and compact microstructure on the addition of Nano-SiO_2.
5. The utilization of lime sludge waste in the commercial market will help toward sustainable constructions.
6. The minimization of cement usage in the construction of building component can be achieved.

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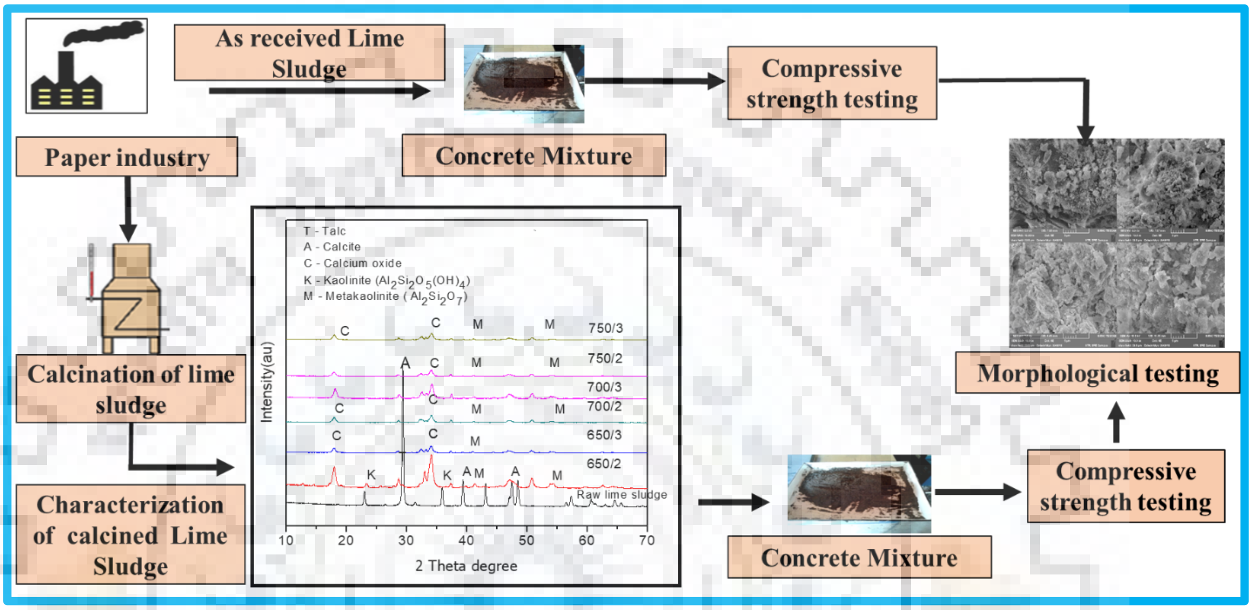
CHAPTER - 4

APPLICATION OF LOW TEMPERATURE CALCINED LIME SLUDGE IN DEVELOPING SUSTAINABLE CEMENTITIOUS BINDER

CHAPTER 4

APPLICATION OF LOW TEMPERATURE CALCINED LIME SLUDGE IN DEVELOPING SUSTAINABLE CEMENTITIOUS BINDER

GRAPHICAL ABSTRACT



4.1 INTRODUCTION

As discussed in chapter 1, as received lime sludge has been utilized in concrete [1-4]. However, the resulting products did not attain adequate compressive strength and could be applicable only in the construction of low-cost impermanent structures. In addition, Chapter 3 reported that lime sludge application in concrete requires addition of some additives like Plasticizer and nanosilica to attain adequate compressive strength with bulk use of lime sludge. This chapter covers the bulk use of lime sludge without addition of any additive material, through the process of low temperature calcination.

Pera J. and Amrouz [5], *and Frias et al*. [6] reported that Metakaolin can be produced from paper industry generated lime sludge. Metakaolin is pozzolanic material and produced on the calcination of the lime sludge [7]. The process of calcination covered the heating of raw lime sludge in the furnace at various temperatures which can transmuted kaolinite ($Al_2Si_2O_5(OH)_4$) into the pozzolanic metakaolinite. Equation 4.1 shows the chemical reaction of kaolinite conversion into metakaolinite with thermal treatment from 450-700 ^{0}C. The MK (metakaolinite-

$Al_2O_3.2SiO_2$) can make the lime sludge more reactive which makes it perfect raw material to use as cement additive [8, 9].

$$Al_2Si_2O_5(OH)_4 \xrightarrow{400-700°C} Al_2Si_2O_7 + 2H_2O \quad (4.1)$$

(Kaolinite) (Metakaolinite)

The utilization of lime sludge indicates its potential as pozzolana for the manufacture of cementitious binder. It is also promising for reducing the environmental wallop of cement industry. This study presents sustainable application of paper industry lime sludge through the process of calcination with less energy input. In present study, calcined lime sludge is utilized in the fabrication of cementitious binder and application of this prepared binder in production of M25 grade concrete. The microstructural behavior of concrete is also studied. The objective of this chapter is to develop a cementitious binder from lime sludge and cement without addition of any additive materials.

4.2 MATERIALS AND METHODS

4.2.1 Calcination of lime sludge

The calcination of lime sludge was performed to increase the reactivity. As received lime sludge was heated at different temperatures. It was done in programmable furnace at 650 ^{0}C, 700 ^{0}C, and 750 ^{0}C for 2h and 3h respectively. **Fig. 4.1** represents typical calcination process of the lime sludge in the laboratory type muffle furnace for a temperature of 650 °C for 2 hours. The rate was kept 2 °C/minute upto 200 °C and it was increased to 4 °C/minute from 200-400 °C

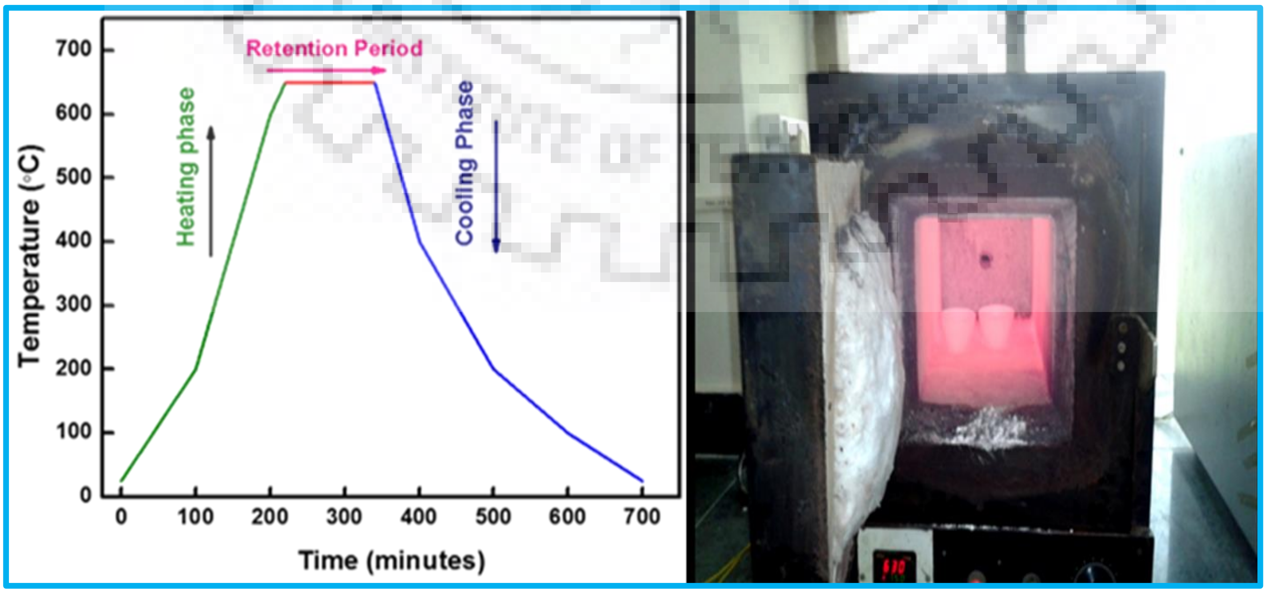


Fig. 4.1: Typical heating profile curve of lime sludge, and view of muffle furnace

after that rate of 5 °C/minute was maintained beyond 400 °C. The sample was retained for 2 hours at the maximum required temperature, after that samples were naturally cooled at room temperature which has taken 6 hours in case of calcination at 650 °C. The calcined lime sludge was grounded by using ball mill and then characterized and used in fabrication of concrete.

4.2.2 Binder fabrication

Lime sludge calcined at relatively lower temperature and characterized for metakaolinite and calcium oxide (calcined at 650 °C for 2 hours) was used with cement for binder preparation. **Table 4.1** demonstrates the different blends of binders formed with the different ratio of calcined lime sludge and cement. The calcined lime sludge was milled and sieved, then mixed with cement to prepare the binder. The same blends of raw lime sludge and cement were also formed and demonstrated in **Table 4.2** to compare the performance of binder prepared with lime sludge calcined at lower temperature.

Table 4.1: Binder fabrication with calcined lime sludge

Binders	**Calcined Lime Sludge (%)**	**Cement (%)**
Control	0	100
CLB 10	10	90
CLB 20	20	80
CLB 30	30	70
CLB 40	40	60
CLB: Calcined Lime Sludge Binder		

Table 4.2: Binder fabrication with raw lime sludge

Binders	**Raw Lime Sludge (%)**	**Cement (%)**
Control	0	100
RLB 10	10	90
RLB 20	20	80
RLB 30	30	70
RLB 40	40	60
RLB: Raw Lime Sludge Binder		

4.2.3 Specimens preparation

Concrete of M 25 grade was proportioned in accordance with the Indian standard *IS: 10262-2009* [11] (Method of concrete mix proportioning). In addition, the study on lime sludge-based binders was made with application of binders in the concrete. The casting procedure of calcined and raw lime sludge-based binders is presented in **Fig. 4.2**. **Table 4.3** represents the mix proportioning adopted for calcined and raw lime sludge-based binders this study.

Table 4.3: Proportioning of concrete with and without lime sludge

S. N.	Proportioning of ingredients by weight			
	Binder	Fine Aggregate (FA)	Coarse Aggregates (CA)	W/ Binder Ratio
1	Control	1	2	0.48
2	CLB10	1	2	0.55
3	CLB20	1	2	0.60
4	CLB30	1	2	0.62
5	CLB40	1	2	0.64

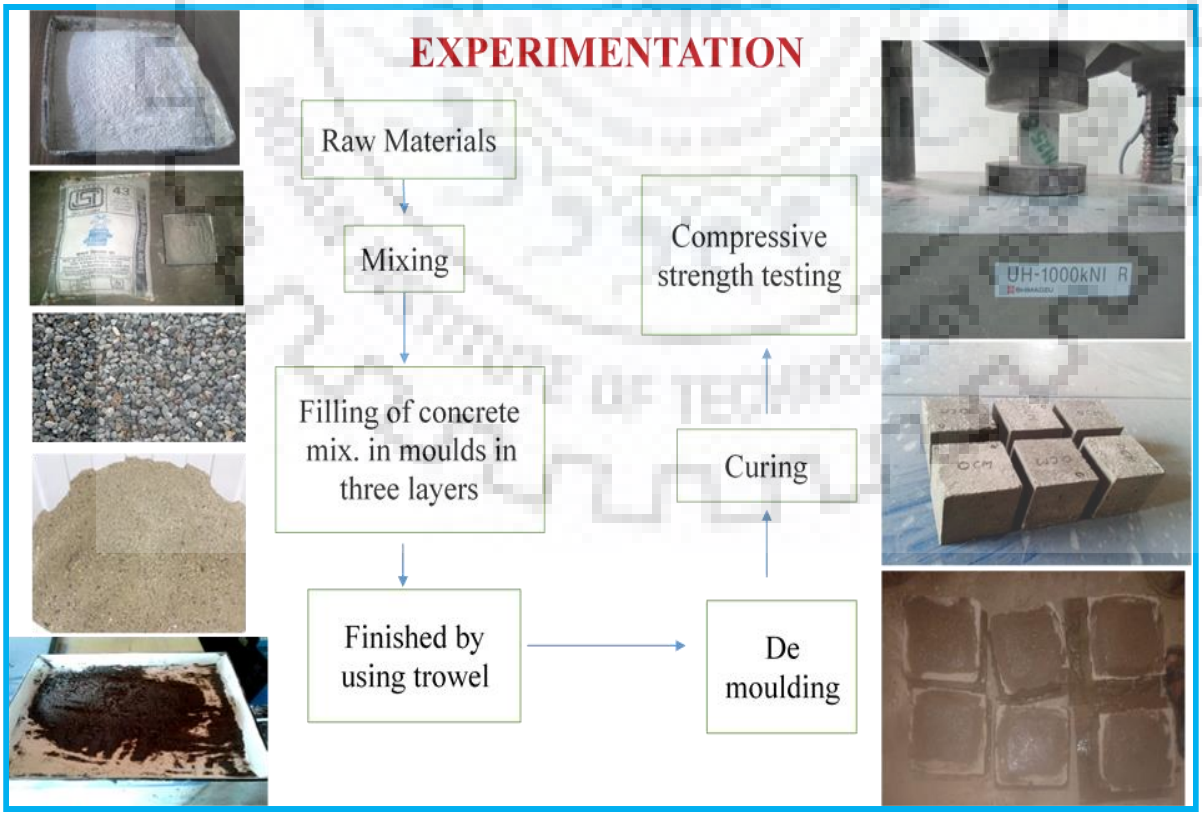


Fig. 4.2: Schematic diagram of casting and testing of cubes specimens

For the casting of specimen, the water was added to mix. Cubes specimens prepared by the mixing of materials in concrete mixture. It was ensured that no lump formation takes place in the mixture. All specimens were made of 150 mm x150 mm x 150 mm size respectively. Binder and other raw materials were applied into concrete mixture. The mixture of cement, course and fine aggregates, water with binders was prepared and specimens of given dimensions were caste. Concrete mixture was casted with 0.48 to 0.64 water to cementitious binder w/binder ratio for concrete mixture. Same proportions of concrete mixture were also prepared with the calcined lime sludge also.

4.2.4 Properties of concrete

Water absorption and compressive strength of the specimens were determined by the methods discussed in chapter 3.

4.2.5 Hydration analysis of binder

Isothermal conduction calorimeter (Modal: TAM Air Isothermal Calorimeter) was used for hydration analysis of cementitious binders. The hydration test was performed at 25 °C. Normalized heat flow and normalized heat of hydration were determined through hydration analysis. Different blends of cement with 30 % as received and 30 % calcined lime sludge were prepared to carry out hydration test. The test was performed to check the increment in heat of hydration of binder prepared with calcined lime sludge incomparison to the binder prepared with as received lime sludge.

4.3 RESULTS AND DISCUSSION

4.3.1 Characterization of as received lime sludge

The characterization of lime sludge has already been discussed in section 2.3.1 of chapter 2.

4.3.2 Characterization of calcined lime sludge

Fig. 4.3 illustrates the XRD pattern of lime sludge calcined at different temperatures of 650 ^{0}C, 700 ^{0}C and 750 ^{0}C for 2 and 3 hours. The heating of as received lime sludge in the furnace at various temperatures has transmuted the calcium carbonate and kaolinite into non-crystalline calcium oxide and metakaolinite respectively. Calcite and kaolinite peaks are most prominent in the as received lime sludge, while lime sludge treated at the temperature from 650- 750 ^{0}C prominently indicates the peaks of calcium oxide and metakaolinite. It is also indicative from the **Fig. 4.3** that lime sludge heated at different temperature for different time illustrates the similar peaks with different intensities. It was the sole reason that lime sludge heated at 650 ^{0}C for 2 hours was chosen for the application in the concrete.

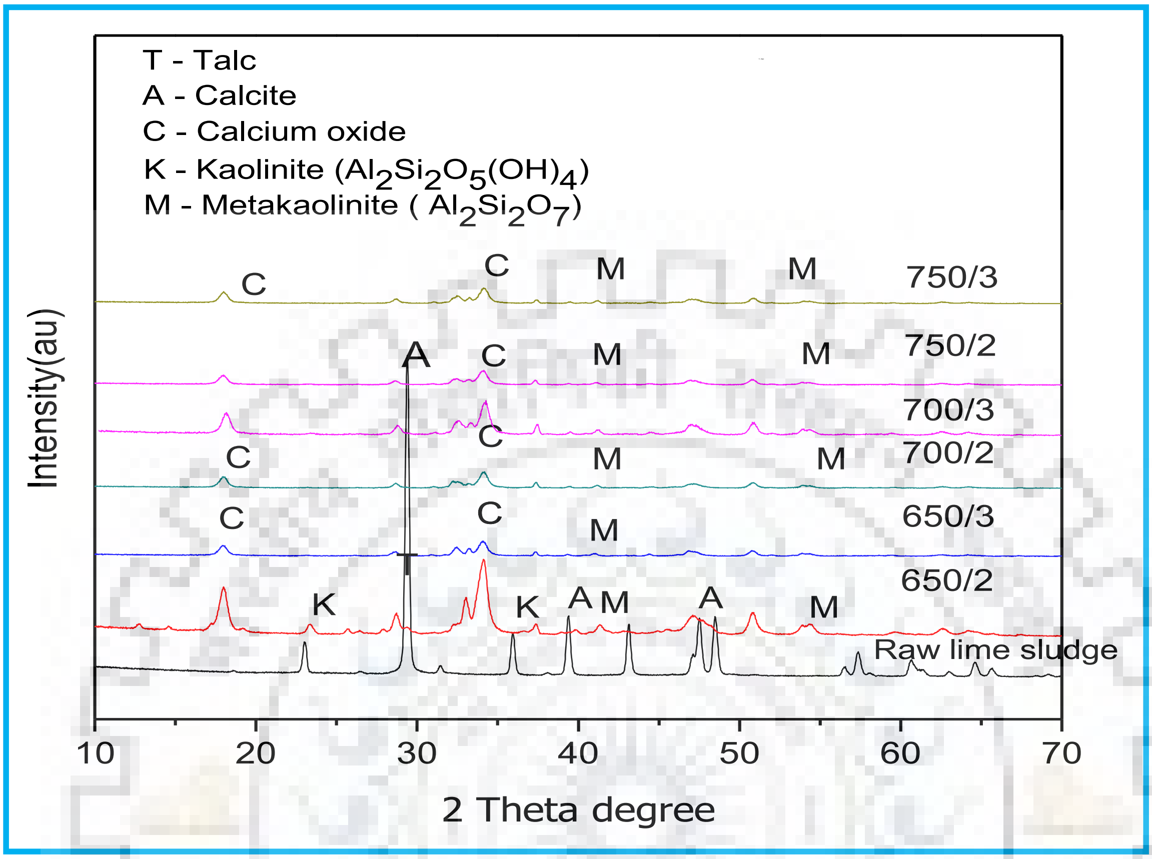


Fig. 4.3: XRD patterns of raw and calcined lime sludge

4.3.3 Properties of concrete

4.3.3.1 Water absorption

Water absorption is an important constraint that is significantly responsible for the durability of the concrete specimens. This parameter is an indicator of open porosity. The specimens with lower water absorption were usually denser and durable. **Fig. 4.4** shows water absorption of concrete specimens as function of binder type and content in mixes. In case of RLB, it was found varying from 3.37 % to 4.26 % with increasing application of lime sludge in RLB, while CLB Binders with calcined lime sludge produced water absorption varying from 3.37 % to 5.1 %. The water absorption with CLB might be the outcome of the hydration reaction of calcined lime sludge which consumes water for the formation of calcium hydroxide from calcium oxide.

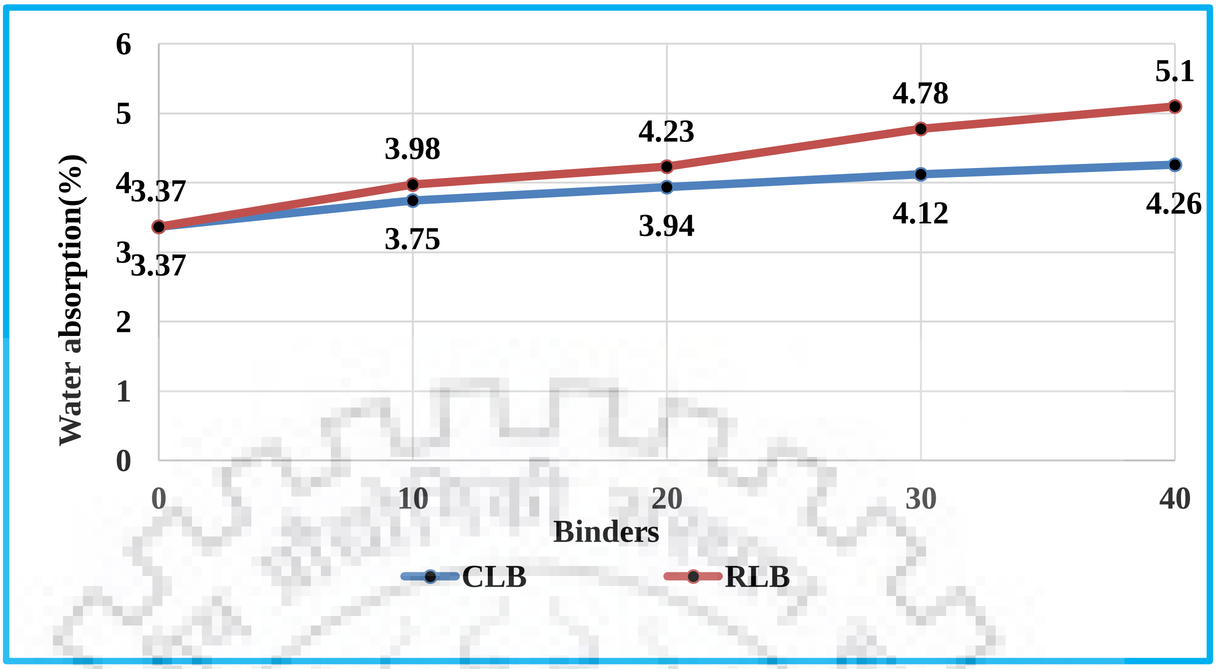


Fig. 4.4: Water absorption of specimens

4.3.3.2 Compressive strength

Specimens comprising of CLB resulted in better compressive strength comparative to ones comprising of RLB. Specimens with 10, 20, 30, and 40 of CLB were found to have improved compressive strength by, 4.28 %, 4.43 %, and 3.61 % respectively, compared to blocks with RLB. It is evident from **Fig. 4.5** that Compressive strength of the blocks decreases abruptly with increasing proportion of as received lime sludge binders but application of calcined lime sludge binders produced the sustainable concrete blocks with very less reduction in compressive strength. **Fig. 4.6** illustrates the effect of calcined lime sludge binders on overall compressive strength after 28 days of curing was found significant compared to ones after 7 days of curing. The increment in compressive strength of concrete might be allocated to pozzolanic activity of calcined lime sludge. The calcination process makes lime sludge reactive and calcium hydroxide of it reacts with the metakaolinite, which make two types of products after reaction i.e. hydrates of calcium silicate (CSH) and hydrates of tetra calcium aluminates (TAH) [12,13]. Equation 4.2 shows the reaction of calcium oxide with water. The hydration resulted in the formation of calcium hydroxide, which further reacts with the metakaolinite. Equations 4.3 and 4.4 show the reactions of metakaolinite with calcium hydroxide which form the calcium silicate hydrate along with calcium aluminate hydrate and calcium aluminum silicate hydrate [8]. These reaction products are the reason for increased compressive strength of concrete in comparison to application of as received lime sludge.

$$CaO \quad + \quad H_2O \quad \rightarrow \quad Ca(OH)_2 \tag{4.2}$$

(Calcium hydroxide)

$$4Al_2O_3.2SiO_2 + 8Ca(OH)_2 + 4H_2O \rightarrow 4\,CaO.Al_2O_3.H_2O + 4\,CaO.SiO_2.2H_2O \tag{4.3}$$

(Metakaolinite) (Tetra calcium aluminate hydrate) (Calcium silicate hydra)

$$Al_2O_3.2SiO_2 + 2Ca(OH)_2 + 2H_2O \rightarrow CaO.Al_2O_3.SiO_2.3H_2O + CaO.SiO_2.H_2O \tag{4.4}$$

(Calcium aluminum silicate hydrate) (Calcium silicate hydrate)

It is also possible that, compressive strength of concrete with calcined lime sludge did not affect significantly in comparison to the concrete without lime sludge up to replacement of 30 % cement by lime sludge, but after that compressive strength of the concrete started to decrease rapidly due to the presence of access calcium hydroxide. It means that application of calcined lime sludge produced better results due to the chemical effect of lime, Pozzolanic reaction to form more C-S-H hydrates up to the limit of 30 %.

The prepared binder of cement and calcined lime sludge has limitation of 30 % lime sludge application, due to presence of free lime content in the concrete after this limit.

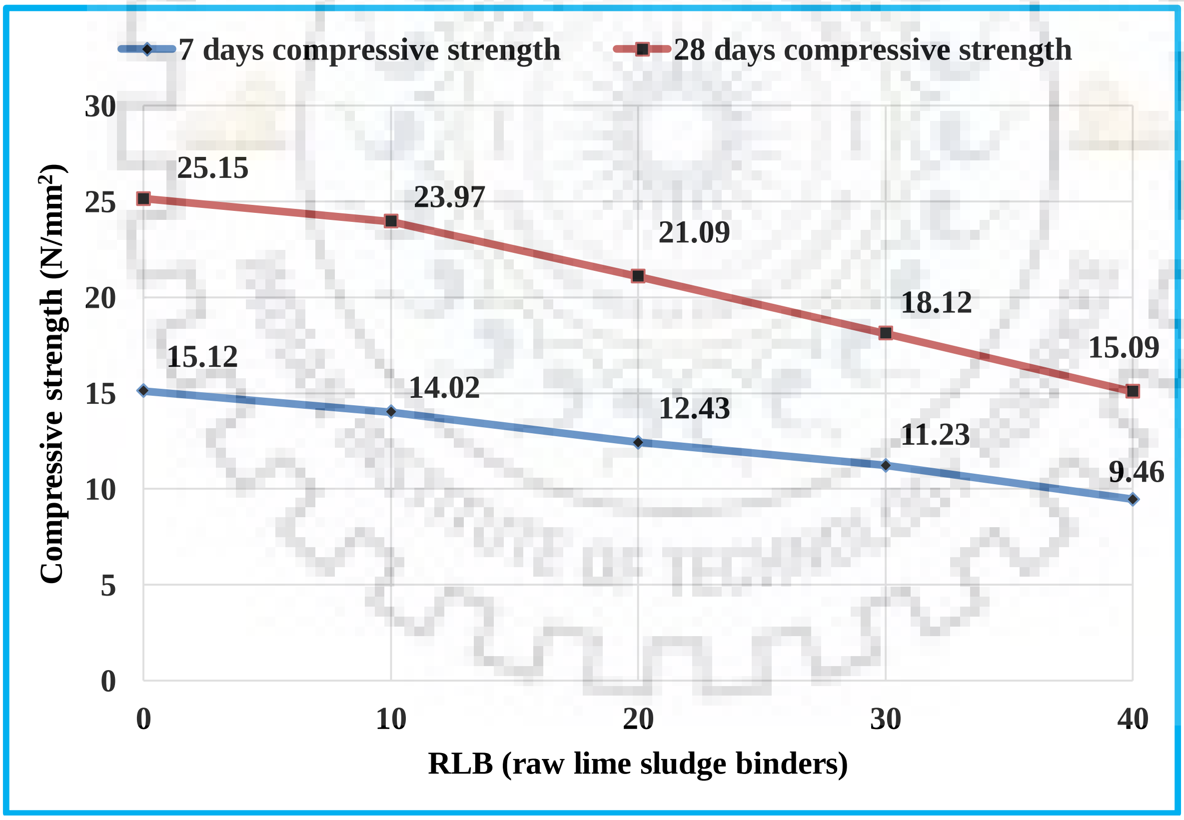


Fig. 4.5: Compressive strength of mixtures with cement replacement by RLB

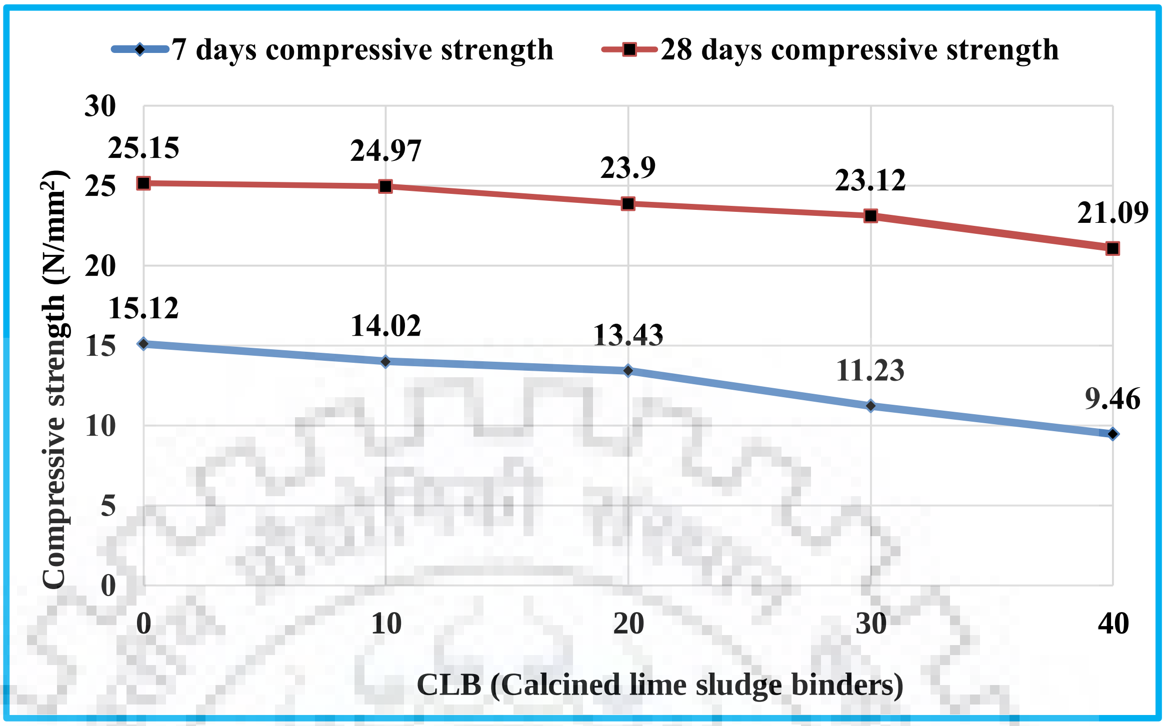


Fig. 4.6: Compressive strength of concrete with CLB

4.3.4 Morphological study

Fig. 4.7 illustrates the SEM micrograph of the concrete specimens of RLB30, CLB30 and concrete without lime sludge-based binders after 28 days of curing of specimens. SEM images reveals that calcined lime sludge binder acted as an activator to uphold the hydration process and to improve the microstructure of the cement paste. SEM images also reveals that microstructure of concrete with calcined lime sludge binder was more uniform and compact than the concrete with as received lime sludge binder [14, 15]. SEM images of concrete with RLB elucidate that C-S-H (calcium silicate hydrate) bonding in the concrete is not uniform and scattered throughout the micrograph with so many lumps. The lumps appeared in concrete can be $CaCO_3$ of lime sludge which weakens the bonds and that directly affect the compressive strength of the concrete. These lumps started to disappear with increasing application of CLB based concrete blocks. This happened due to reactivity of the lime in the concrete mixture. Reactive lime reacts with the silica and formed form more C-S-H hydrate which is the sole reason behind the increased compressive strength and uniformity in the SEM micrographs.

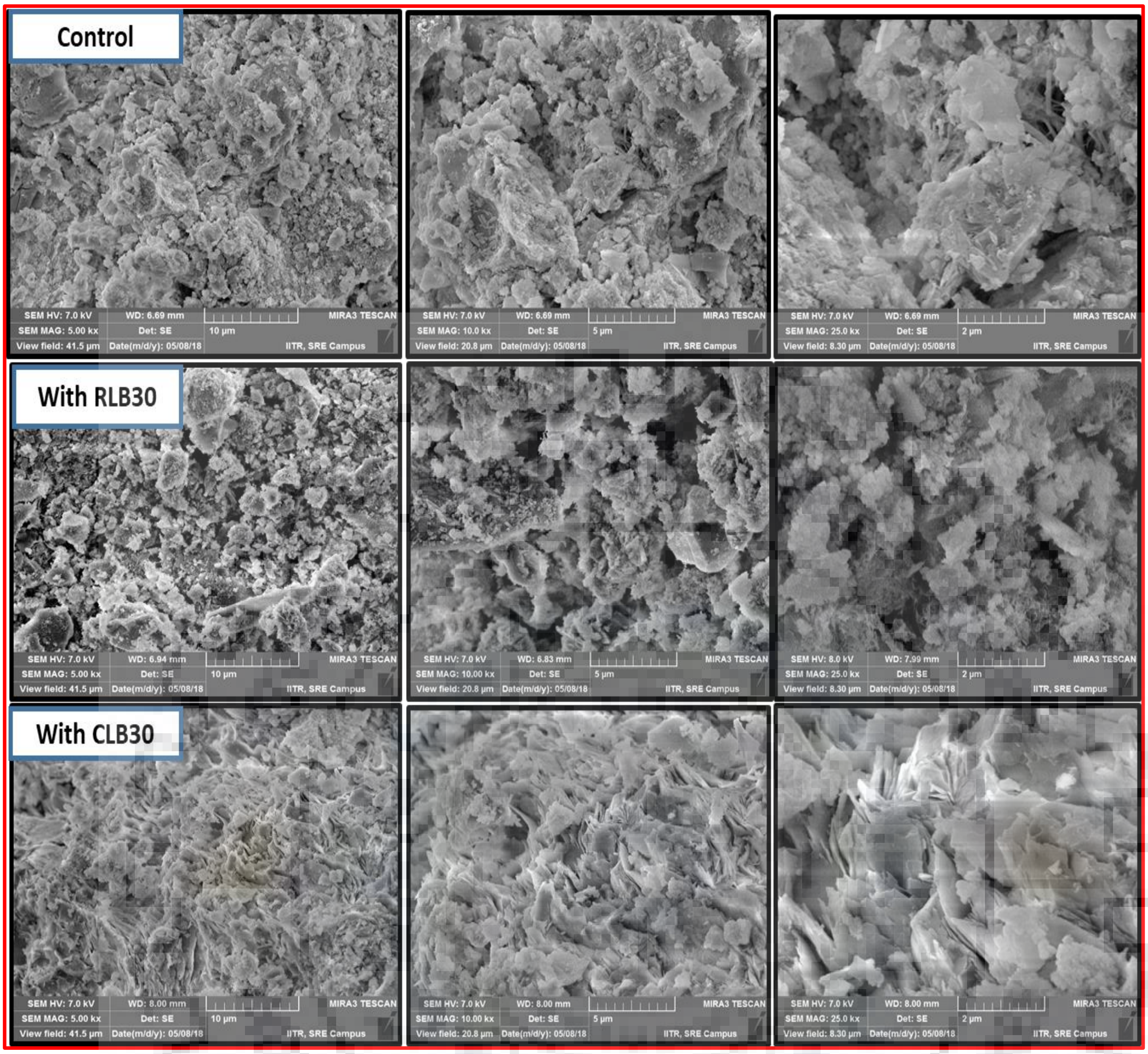


Fig. 4.7: SEM Micrographs of Concrete samples

4.3.5. Hydration study

The binder prepared with lime sludge and cement were evaluated for heat of hydration for 7 days. **Fig. 4.8** illustrates the normalized heat flow curve of the cement control, 30 % as received lime sludge blended with 70 % cement (RLB 30) and 30 % calcined lime sludge blended with 70 % cement (CLB 30). Two peaks, a rapid dissolution and an acceleration were illustrated by binders and control paste in their calorimetric response. The heat flow illustrates the rate of hydration, whereas normalized heat illustrates the degree of hydration. The early dissolution peak is caused by the wetting and dissolution of the binder particles [16]. An acceleration peak followed the dominance period, this acceleration represents the precipitation of the calcium hydroxide, calcium silicate hydrate (CSH), Calcium aluminate hydrate (CAH) and Calcium aluminum silicate hydrate (CASH) phases [17-19]**. Fig. 4.9** illustrates the normalized heat of cement control and prepared binders. Normalized heat flow and normalized heat of CLB 30 binder was more than control cement and RLB 30, this was due to the heat release on the hydration of Metakaolinite and calcium oxide of calcined lime sludge. It confirms the pozzolanic reactivity of the lime sludge calcined at 650 ^{0}C.

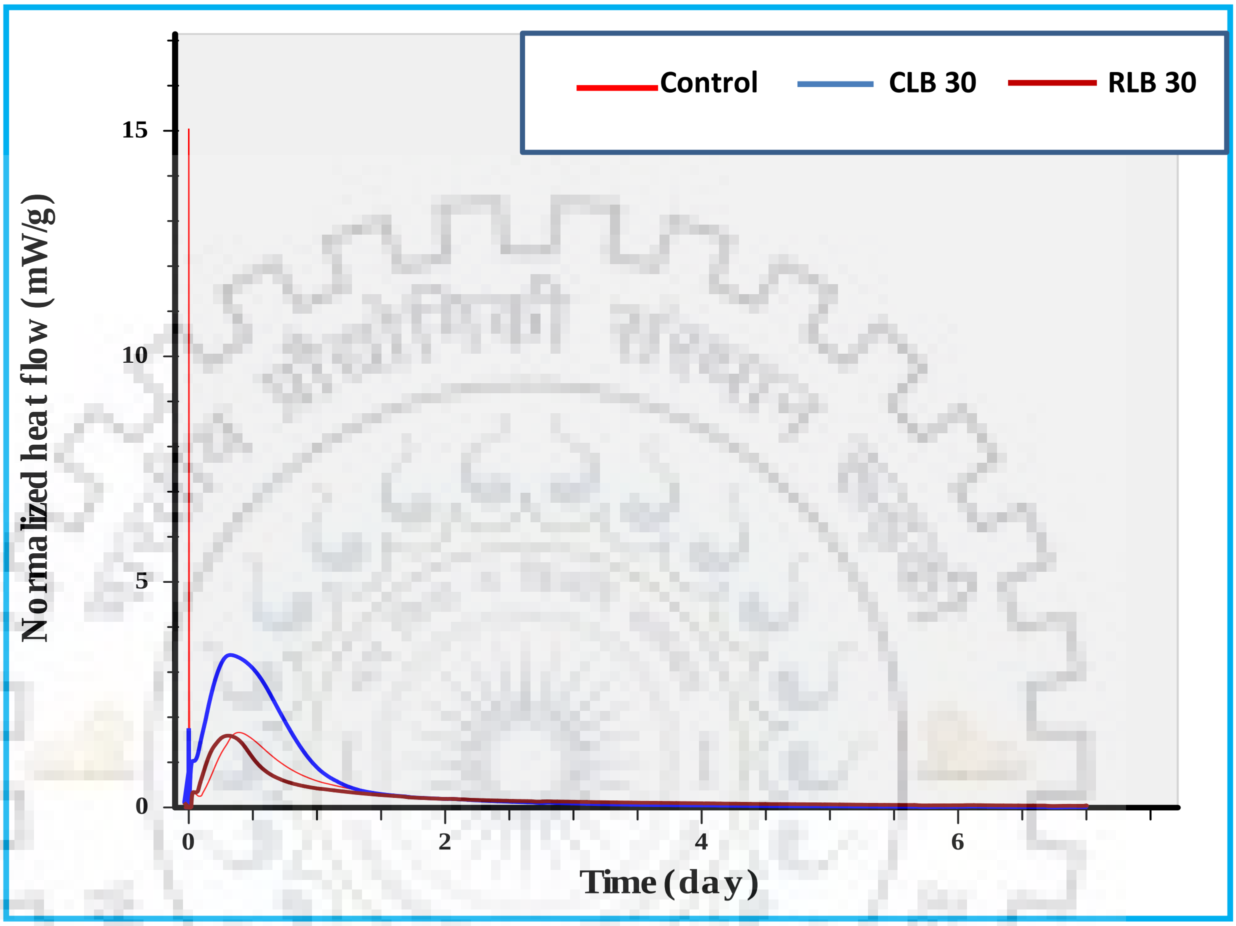


Fig. 4.8: Normalized heat flow of hydration of control and binders

Calcined lime sludge application can save the 300 g of cement on the preparation of 1 kg of binder. Reactive lime used for binder production was synthesized using only sludge from paper industry as raw material. Lime sludge reactivity was increased through calcination at very low temperature of 650 °C lime sludge, which is reasonably less than the temperature employed in Paper industries for the complete calcination of lime sludge (≈1000 °C). The cost of 1 kg developed binder is about Rs. 7.00 which is approximately Rs. 1.50 less than the commercially available OPC 43 grade of cement. The developed binder is economical and on site (Paper industries) production of binder can further decrease the cost. In addition to this binder is ecofriendly with less emission of greenhouse gases.

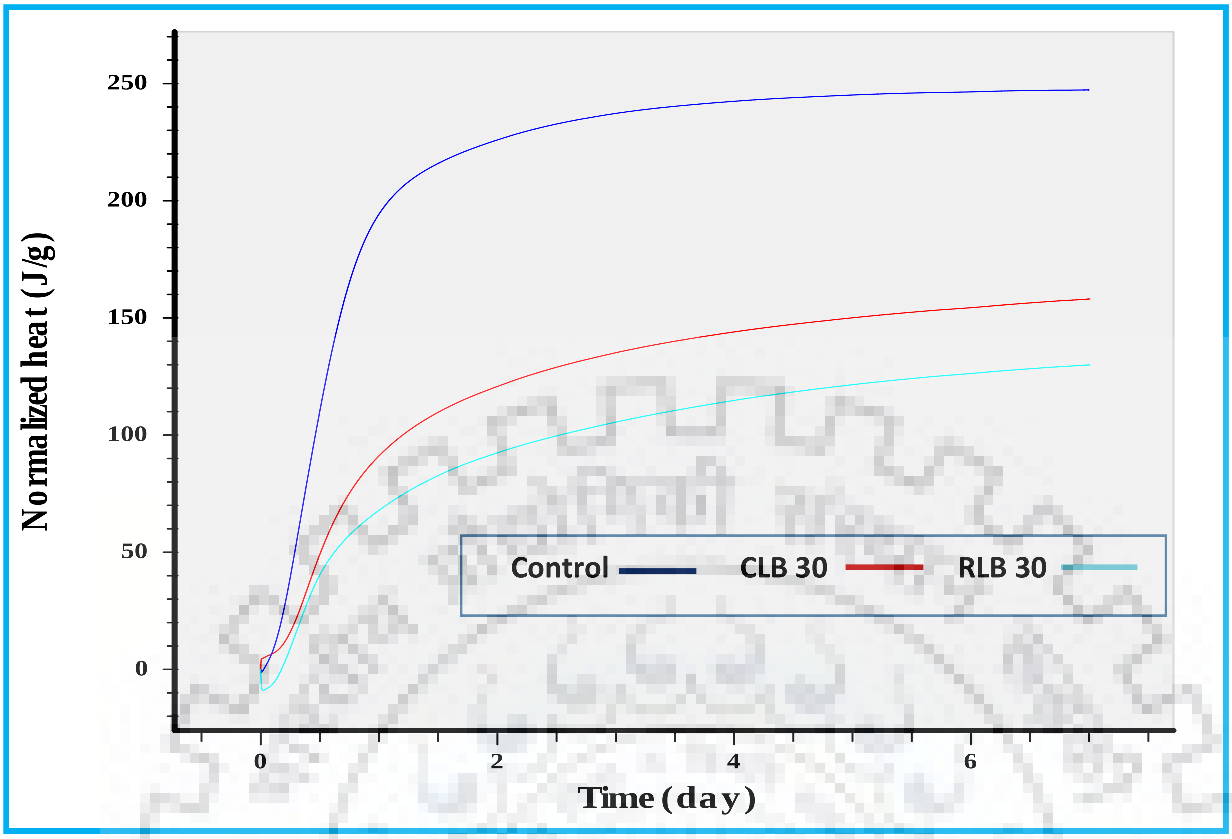


Fig. 4.9: Normalized heat of hydration of control and binders

4.4 CONCLUSION

Lime sludge calcined at low temperature of 650 ^{0}C can be applied productively as a pozzolana with cement. Compressive strength of produced concrete remains intact until 30 % application of calcined lime sludge in binder.

Based on the findings of this experimental study, the observations are as under regarding:

1) The pozzolanic behavior of lime sludge is due to the metakaolinite and calcium oxide produced after calcination of lime sludge at 650 ^{0}C. This is the sole reasons for increased lime sludge reactivity and accumulation of increased amount of calcium silicate hydrate (CSH) and hydrates of tetra calcium aluminates (TAH).

2) The. Morphological study of concrete and heat of hydration of prepared binder also confirms the increased reactivity of lime sludge.

3) The prepared binder is sustainable with 18 % less production cost and with 56 % less emission of greenhouse gases.

Therefore, Lime sludge makes a suitable material for the formation of reactive pozzolanic material. The utilization of lime sludge of paper industry is recommended as replacement material for cement in mortars and this will also beneficial for reducing environmental wallop.

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CHAPTER 5

CO-DIGESTION OF PAPER MILL ETP SLUDGE WITH COW MANURE

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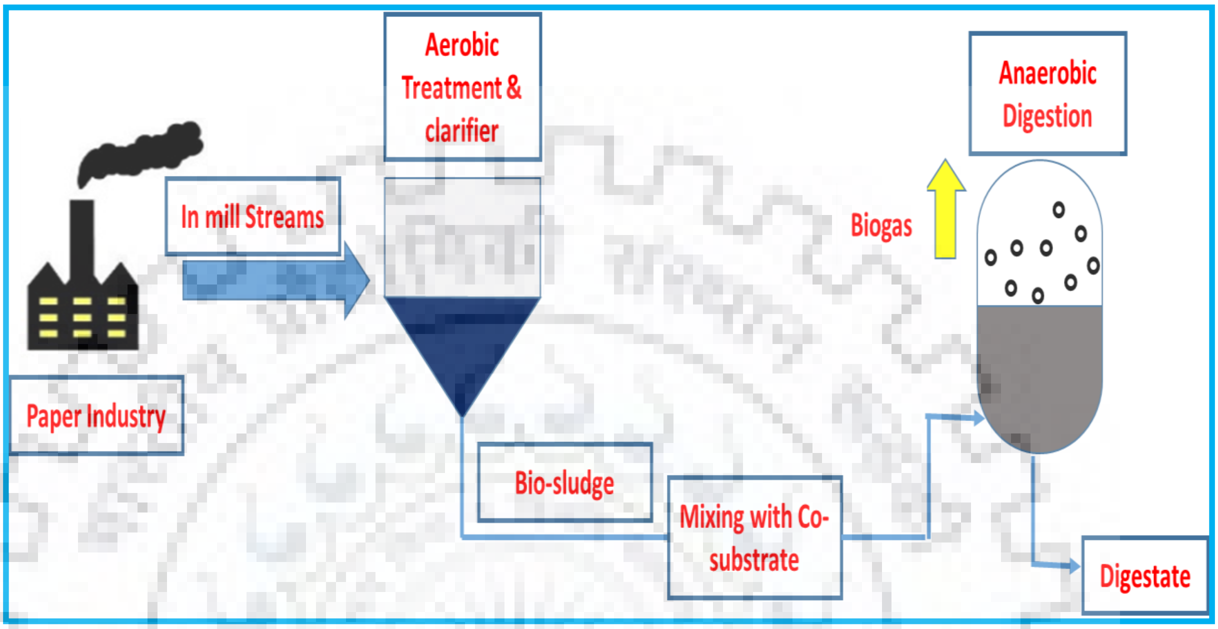
CO-DIGESTION OF PAPER MILL ETP SLUDGE WITH COW MANURE

GRAPHICAL ABSTRACT



5.1 INTRODUCTION

Ideal co-substrates would complement mill biosludge in a way that an appropriate chemical oxygen demand (COD) to nitrogen to phosphorus ratio (COD: N: P) can be achieved. Some studies have been published on the anaerobic digestion and co-digestion of paper industry secondary sludge. *Maat* (1990) [1] identified an optimum ratio of 350:5:1 in several full-scale operations. The volume ratio between the co-substrate and the bio sludge will likely be small, because the former will primarily be used to boost the digestion process.

In many studies, Biochemical methane potential (BMP) assays are applied for anaerobic digestion. BMP assays are based on mixing the inoculum (anaerobic biomass) and the substrate together in a batch reactor, and monitoring the cumulative methane production [2]. BMP assays are very useful in providing the anaerobic digestibility of substrates. Also, a relatively large number of different substrates can be tested at the same time. Moreover, methane produced from the anaerobic digestion can be a permanent solution as an alternative energy fuel and organic waste utilization. Anaerobic digestion (AD) has been applied successfully for different kinds of sludge like sewage sludge [3], Cow manure [4] and waste activated sludge [5]. However, studies on anaerobic digestion of Paper Sludge (PSS) are very few in number. *Lin et al.* [6] utilized paper sludge for anaerobic digestion with monosodium glutamate as supplement for the digestion reactions, this waste liquor produced 80% methane of total biogas composition with 200 mL methane/g of volatile solid (VS) added. But this method could be costly for small and medium scale industries because study was conducted on the controlled temperature. Another study by *Soetopo et al.* [7] conducted anaerobic digestion of paper sludge and concluded that 51.5% of methane was produced from biogas with digestibility of 140 mL/g VS in one month. This study was also conducted on controlled temperature which is less applicable in the industries. Thus, present study is aimed to investigate the co-digestion of paper industry secondary sludge with uncontrolled temperature, where both the conditions of co-digestion and uncontrolled temperature are found more applicable for small and medium scale industries.

5.2 MATERIALS AND METHODS

5.2.1 Materials

The Paper sludge (PSS) was procured from the effluent treatment plant (ETP) of typical integrated paper mill. The paper production process resulted with the co-production of waste water, which goes through the primary and secondary treatment in the ETP plant. The secondary treatment of waste water involves aerobic treatment which generates secondary sludge after the waste water treatment. The sludge was collected from the clarifier of secondary treatment. The samples were collected in cans and stored at 4 °C before feeding to the reactor for methane production. The cow dung manure used in this study was locally available and collected in the polybags.

5.2.2 Characterization of ETP sludge

The chemical characterization was conducted using X-ray fluorescence (XRF, Bruker S4 Pioneer spectrometer). It is a non-destructive analytical technique for chemical composition determination, which measures the sample generated fluorescent X-ray emission when a X- ray beam is used to excite the sample. The phases in the samples were determined by X-ray diffractometer, Bruker AXS D8 advance using a Co source (Kα = 1.79 À). The Bragg's law (2Θ) was used with the 1°/min scanning rate. The room temperature was maintained 25 °C at the time of instrument operation. The laser scattering diffraction particle size distribution analyzer (Partica LA-950) was used for particle size distribution analysis, which can determine particle size varies between 10 nano-meter to 3 millimeters. The PSS was also characterized for C,H, N, S values through CHNS analyzer.

5.2.3 Test setup and operation

One set of experiments were conducted in two different reactor bottles. Glass bottles of 1000 mL size were used for bio-methane test of the PSS and cow manure. The first bottle (B_1) consisted of the pure secondary sludge while reactor second (B_2) consisted of the cow manure with secondary sludge. In the second reactor, the C: N ratio was adjusted using cow manure to achieve the ideal range of 20-30 range. Water was used to dilute the total solid (TS) content of cow manure with 20 % of total solid content. After that it was combined with PSS in 60 % to 40 % volumetric composition in B_2. The digestate in the digesters were also diluted by adding the tap water to the 5 % of total solid content. The BMP test was conducted in the mesophilic conditions under the uncontrolled temperature between 28-34 °C. The initial pH of the B1 and B2 was recorded 6.7 and 6.8 respectively, which was slightly acidic. That is why, the small amount of sodium carbonate from 0.1g to 0.5 g, was also added for the prevention of critical pH drop. Each of the bottle was tightly packed with the silicon cork of 5 mm thickness. The bottle shaker was used to shake the packed bottles for 30 min at 80 rpm. Once in a day, every bottle of test was attached with an inverted alkaline solution containing bottle through a capillary tube. The capillary was equipped with the needles at both the sides to allow the gas transfer from bottle to the alkaline solution containing bottle.

5.2.4 Sampling

Chemical oxygen demand (COD) and Volatile fatty acid (VFA) were measured two times a week by taking 30 mL of sludge sample from each bottle. Digestion method and titration method were used for COD and VFA measurement, respectively [8]. Biogas production was measured through the water displacement method as illustrated in **Fig. 5.1**. The capillary connected with reaction bottle and alkaline solution bottle was opened once in a day to collect the generated biogas.

Fig. 5.1: Experimental set up of AD process

Meanwhile this gas displaced the NaOH solution from the bottle which was collected in a syringe connected with the NaOH solution bottle. Total amount of NaOH solution displaced from the bottle was collected in the syringe which represents the total amount of biogas produced [9]. Afterwards, gas composition was measured using the Shimadzu GC-8A. Argon was used as carrier gas at flow 40 mL/min.

5.3 RESULTS AND DISCUSSION

5.3.1 Characterization of ETP sludge

PSS and cow manure were characterized on the first day of experiment. **Table 5.1** represents the characteristics of ETP sludge (PSS) and cow manure.

Table 5.1: General characterization of substrates

	TS (g/L)	VS (% of TS)	C (Carbon) (wt%)	N (Nitrogen) (wt%)	P (Phosphorus) (wt%)	K(potassium) (ppm)
PPS (Bottle 1)	106.7	55.7	38.43	1.05	0.031	64
Cow manure	96.0	45.25	52.10	2.63	0.006	403
PPS + Cow manure (Bottle 2)	93.4	48.5	40.3	1.16	0.007	89

Table 5.2: XRF analysis of PSS

Raw Material	Oxide content (% weight)									
	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	MnO	Fe_2O_3	NiO
PSS	1.06	4.90	4.03	17.76	5.40	10.97	0.607	49.25	1.33	4.90	0.02

Table 5.2 represents the chemical composition of oven dried PSS. Calcium oxide and silicon dioxide are the major constituents of PSS, while elements like Ni, Mn and Fe are also present in minor amount. These three elements supplement the anaerobic digestion and can positively impact the digestion process of PSS. Ammonia generation in anaerobic digestion process works as inhibitor but the presence of Na and Mg can overcome the ammonia inhibition. XRF analysis shows the presence of both Na and Mg in PSS, which can also supplement the digestion process.

5.3.2 Analysis of AD process

Fig. 5.2 illustrates the variation in COD of bottle $B_1$and B_2. The first day COD of B_1containing only paper sludge was almost 5 times lower than the first day COD of the $B_2$with PSS and cow manure. However, COD of B_1 increased from 2800 mg/L to 6355 mg/L, whereas COD in B_2 increased only by 1.5 times from 9835 mg/L to 13335 mg/L in first 9 days of reaction. After 9 days of reaction, COD in B_1 almost remained constant with very less fluctuations and increased slightly in the last phase of the reaction at 28 days. Whereas, B_2 shows different trend of COD after 10 days and decreased drastically till 28th day of the anaerobic digestion reaction.

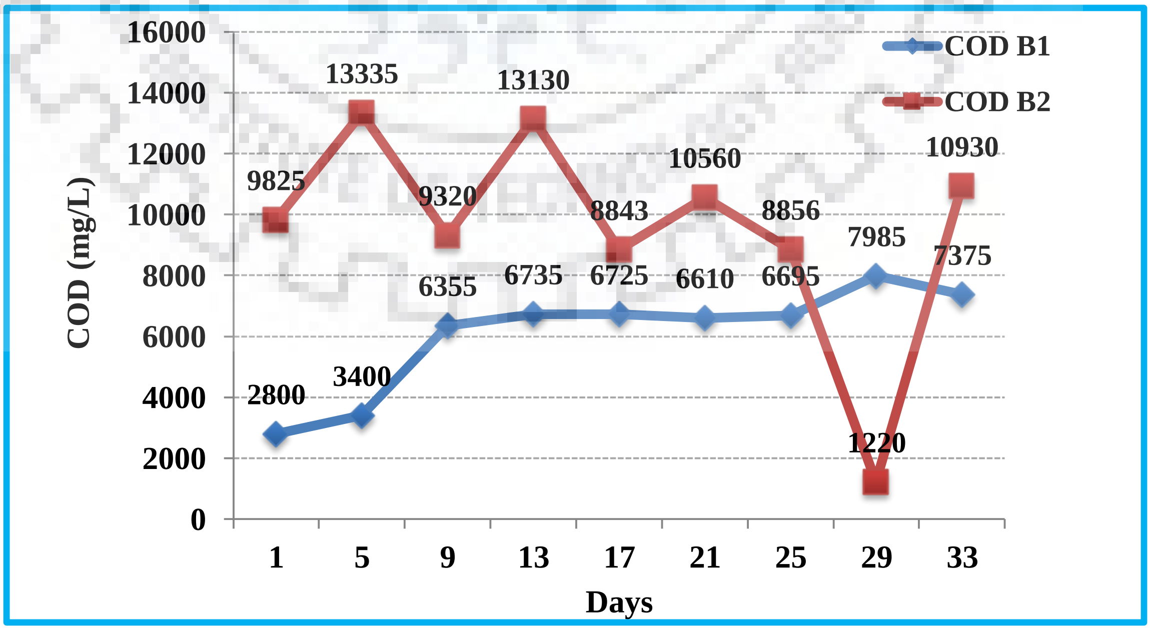


Fig. 5.2: Variation in COD of the bottles B_1 and B_2

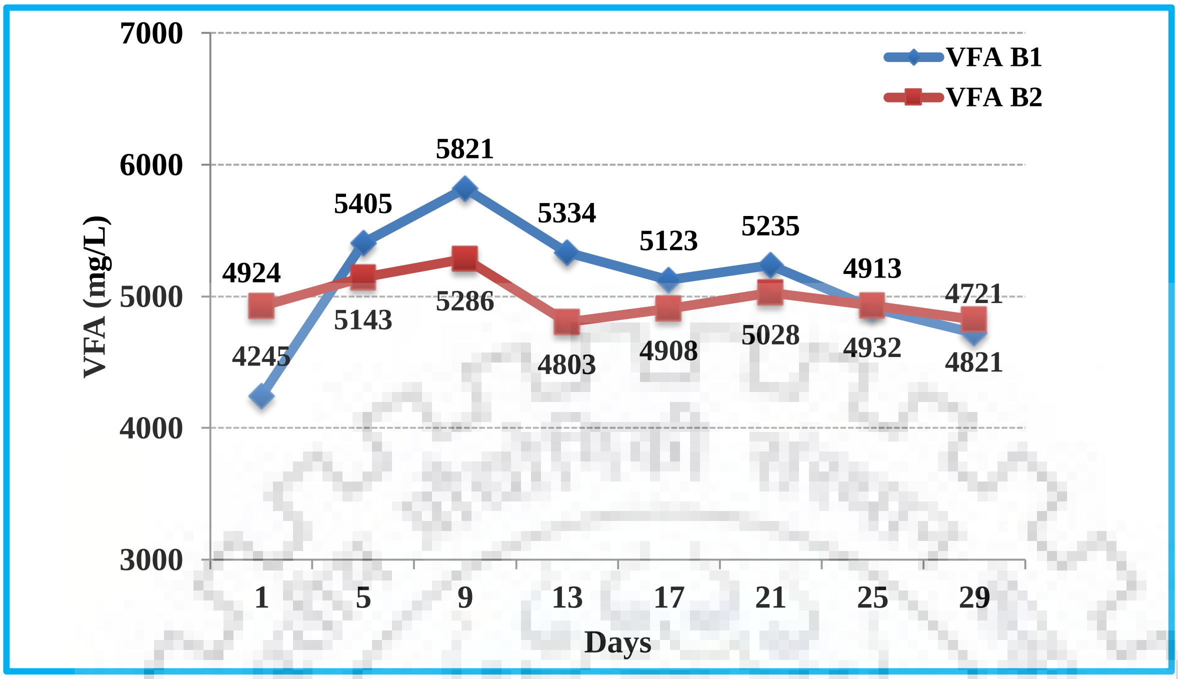


Fig. 5.3: Variation in VFA of the Bottles B_1 and B_2

The reactors were kept in uncontrolled temperature between 28-34 °C, which demonstrates the mesophilic range. The pH of B_1 ranged from 6.1- 7.1 showed less fluctuation in comparison to B_2 which fluctuate between the range of 6.0- 7.5. The fluctuation trend in COD for B_1 was nearly similar to the VFA trend of B_1. However, this kind of similarity was not evident in case of B_2. On considering the different trends in pH, COD and VFA of both bottles, results suggest that different process and reactions dominated each bottle. The results of biogas production for both the bottles (**Fig. 5.4 and 5.5**) confirmed this observation. Both substrates in the bottles did not start biogas production till 4^{th} day. For B_1, the biogas production was slow until day 8^{th}, while B_2 showed significant production of biogas from day 4^{th}. The peaks biogas production was observed at 11 and 17^{th} day for B_1 at 5.1 and 7.2 mL respectively, while in case of B_2, it demonstrates biogas production at 7, 11 and 17^{th} day at 25, 32 and 40 mL respectively. The cumulative biogas production for $B_1$was observed 105 mL till 30^{th} day of digestion and total methane production was 45 % of the total biogas. While B_2 demonstrated the production of 545 mL biogas with 55% of methane content till same period of time. The cumulative methane produced by B1 till day 30 was 13.5 mL/g of VS and in case of B_2 is almost 10 times higher than the B_1 with 134 mL/g of VS. This result is higher than the results published by *C. Priadi et al.* [10] and *Prameswaran et al.* [7]. The cumulative yield attained for B_2 is higher than results shown by *Lin et al.* [3] with AD of sludge paper mixing with monosodium glutamate liquor waste.

In the consideration of pH, COD and VFA both the bottles seemed to go through a different pathway for biogas production. Despite the fluctuation in COD, the VFA remained almost constant in B_2. This outcome suggested that biogas production in B_2 went to methanogenesis, directly from hydrolysis in first 7-9 days. Afterwards, Biogas production happened through the process of acetogenesis process, explained by the decrease of VFA in B_2 from day 11 to 15 and an increase in methane on day 14 The slow production of biogas and increasing amount of VFA from B_2 suggested that B_1 followed the pathway of typical anaerobic digestion which eventually ending with the methanogenesis.

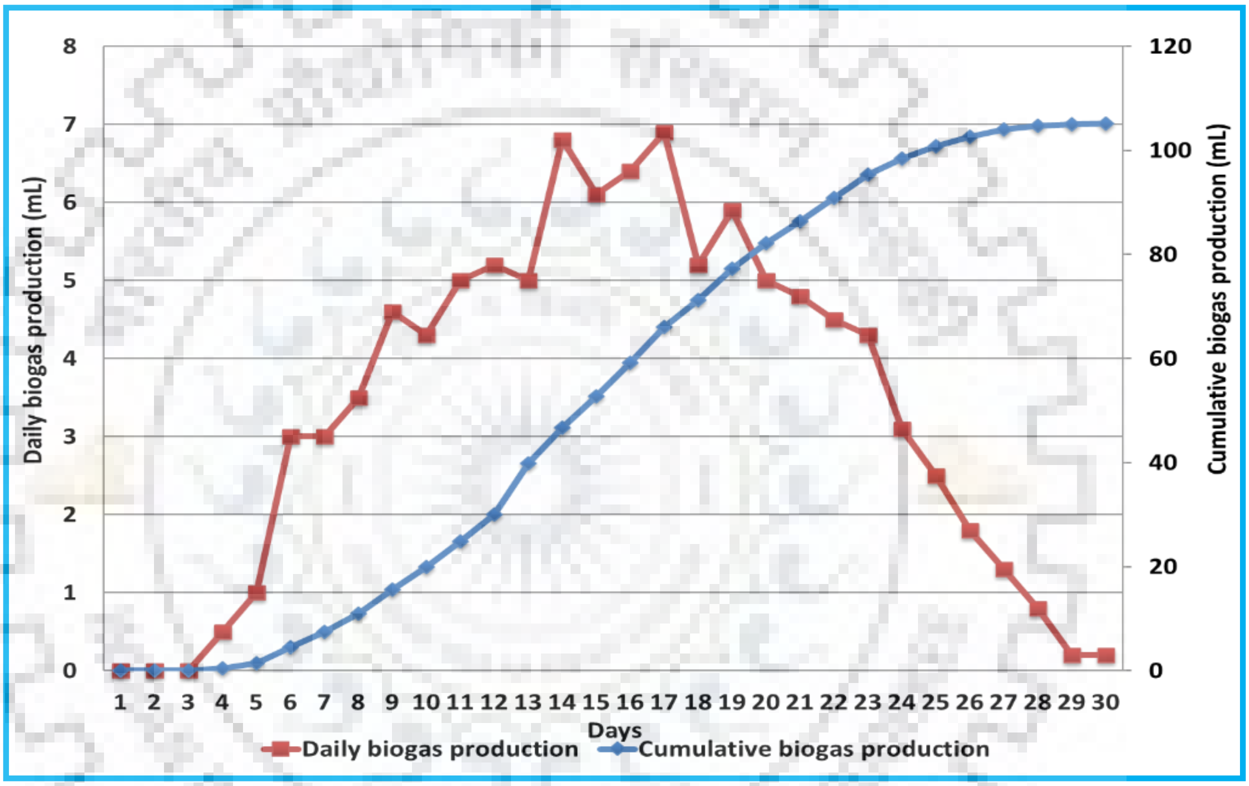


Fig. 5.4: Biogas generation from B_1

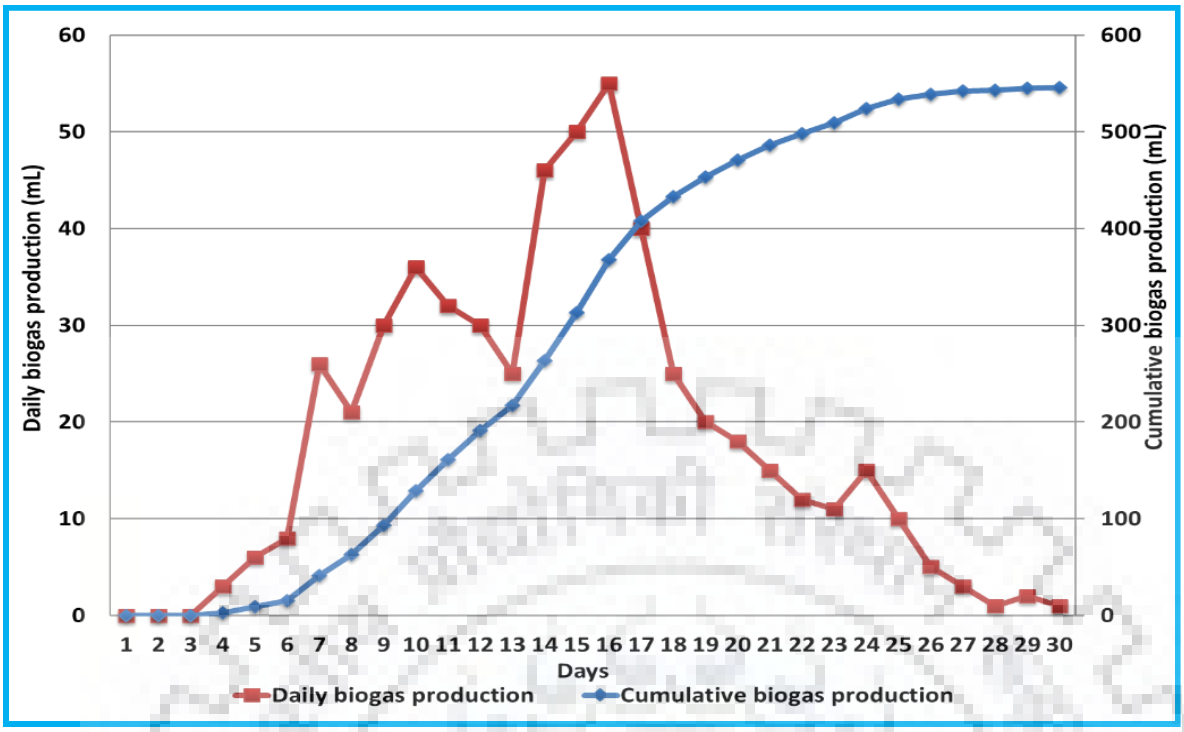


Fig. 5.5: Biogas generation from B_2

5.4 CONCLUSION

Pulp and Paper industry generated secondary sludge demonstrated the high potential for energy recovery from the process of anaerobic digestion. The co-digestion of sludge with cow manure resulted in more production of biogas and methane in comparison to the anaerobic digestion using sludge only. The methane recovered from co-digestion was 55 % of total biogas while digestion of sludge generate only 45 % methane of produced biogas. The co-digestion with easily available cow manure and uncontrolled temperature are two other advantageous factors with this process which can be easily adapted by small and medium scale of industries.

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CHAPTER- 6

CONCLUSION AND FUTURE PERSPETIVE

6. CHAPTER
CONCLUSION AND FUTURE PERSPETIVE

The objective of this research work was to utilize paper industry solid waste in different applications. All utilized waste materials were characterized and utilized according to their properties. This chapter represents a summary of prominent conclusions drawn from the investigations carried out in the present work.

6.1 CONCLUSIONS

Four different studies have been carried out in this research work and the important conclusions are listed point-wise as below:

1) Boiler ash has enough silica content (43.22 %) for the extraction and synthesis of nanosilica. The fine particle size, amorphous nature, and high surface area of synthesized nanosilica make it a valuable material for application in cementitious binder synthesis. Conventionally, belite is synthesized above 1,200 °C. But, Lime sludge application with nanosilica reduced the temperature of belite synthesis to 900°C without the addition of any chemical stabilizer and pre calcination of lime sludge. The heat of hydration of binder, compressive strength and density of the prepared mortars full filled the requirements of indoor and outdoor mortar applications. Lime sludge as cement manufacturing raw material has immense potential as lime sludge produced eco clinker with less carbon footprint at relatively less temperature and with bulk utilization of lime sludge. Lime sludge can be used directly (without calcination) in the synthesis of cement clinker, as calcium carbonate functions as the calcium phase during clinker synthesis. Its synthesis can be upgraded to large-scale production in cement industries. Therefore, lime sludge utilization in building materials can become an alternative solution for the tons of unmanaged waste produced by the pulp and paper industry every year. This practical and effective use of lime sludge can also slow down the exploitation of lime's natural resources

2) There is a possibility for partial substitution of fine aggregate. The compressive strength of concrete blocks found in accordance with M25 grade of concrete with the 10% substitution of cement and 20 % substitution of fine aggregate with lime sludge. Use of lime sludge with Plasticizer in concrete mixture enhanced the compressive strength and made it possible to replace cement & fine aggregates up to 20 and 30 % respectively. Nano silica application with lime sludge found suitable. Use of 1 % nanosilica in lime sludge-based concrete can enhance the lime sludge application up to 30 % without affecting the compressive strength comprehensively.

3) Lime sludge calcined at a low temperature of 650 ^{0}C can be applied productively as a pozzolan with cement. Compressive strength of produced concrete remains intact until 30 % application of calcined lime sludge in binder. The pozzolanic behavior of lime sludge is due to the metakaolinite and calcium oxide produced after calcination of lime sludge at 650 ^{0}C. The. Morphological study of concrete and heat of hydration of prepared binder also confirms the increased reactivity of lime sludge. The prepared binder is sustainable with 18 % less production cost and emission of greenhouse gases.

4) Pulp and paper industry generated secondary sludge demonstrated the high potential for energy recovery from the process of anaerobic digestion. The co-digestion of sludge with cow manure resulted in a better amount of biogas production in comparison to the anaerobic digestion using sludge only. The co-digestion with readily available cow manure and uncontrolled temperature are two other advantageous factors with this process, which can be easily adapted by the small and medium scale of industries.

6.2 FUTURE PERSPECTIVES

Considering the future research perspectives in the field waste materials valorization, a few recommendations have been made:

1) Utilization of waste generated from the process of nanosilica synthesis from boiler ash. The application of generated waste in mortar and concrete for the replacement of fine aggregates can be a future perspective in context this work. The application of this waste is possible due to the presence of residual silica, alumina in the waste material, which can function as pozzolana on application in concrete.
2) The work on chemical activation of lime sludge and then its application in different grades of concrete might produce more significant results of lime sludge application in concrete. At the same time, work on a better understanding of the mechanism of lime sludge in concrete might be the future prospects. The chemical activation of lime sludge with silicates, hydrates and peroxides can enhance the activity of the lime sludge.
3) Lime sludge application for the production of wall putty. In our future work, this study will be carried out by the addition of minerals and oil in as received and calcined lime sludge for the development of wall putty. The calcium carbonate and calcium oxide based wall putty can be produced from lime sludge. The challenges to attain better properties for wall putty are plasticity, consistency and

4) Application of pretreated (Thermal treatment, Sonication etc.) ETP secondary sludge for the anaerobic digestion.