INDUSTRIAL SCALE WASTE UTILISATION IN UNFIRED BRICKS

Ph.D. Thesis

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INDUSTRIAL SCALE WASTE UTILISATION IN UNFIRED BRICKS

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY

> by VIVEK GUPTA



DEPARTMENT OF CIVIL ENGINEERING INDIAN INSTITUTE OF TECHNOLOGY INDORE FEBRUARY 2021



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled INDUSTRIAL SCALE WASTE UTILISATION IN UNFIRED BRICKS in the partial fulfilment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the DEPARTMENT OF CIVIL ENGINEERING, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from July 2017 to January 2021 under the supervision of Prof. Sandeep Chaudhary, Professor, Department of Civil Engineering, IIT Indore.

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

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Dedicated to my family

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ABSTRACT

Lime stabilised fly ash bricks (a type of unfired bricks) are gaining popularity against fired clay bricks due to their green benefits. Several studies have shown the laboratory scale feasibility of waste incorporated unfired bricks. However, the waste utilisation at industrial scale is still limited. The detailed literature review and discussions with industries have been carried out to understand an up-to-date research status and reasons are identified behind the limited industrial-scale waste utilisation in unfired bricks. The key reasons have been identified as insufficient characterization data of locally available wastes, the poor economic viability of wastes available at distant sources and lack of clarity about optimized production parameters. In India, red colour is considered an auspicious colour, making the grey coloured fly ash bricks, difficult to compete against red coloured fired clay bricks in the consumer market. A large amount of coloured stone processing waste is available to use as a filler in unfired bricks, which has not been explored in detail till now. Ensuring the waste blended brick mix's homogeneity is vital for optimized production and needs an appropriate measurement tool for industrial scale implementation.

Looking at the various perspectives for improving the sustainability of unfired brick industries, the present thesis primarily focuses on exploring the potential of locally available industrial ash, establishing the suitable characterization protocol, investigating optimized production parameters such as mixing sequence and moulding moisture content, exploring stone waste for improved aesthetics of fly ash bricks and development of a simple non-destructive tool for measuring the homogeneity of the brick mix.

In the present thesis, an experimental program comprising micro-level characterization techniques (XRD patterns, FT-IR spectra, Raman spectra, and SEM images) and macro-level tests (loss on ignition, and lime reactivity values) has been used for comprehensive characterisation of industrial ashes and to evaluate the potential of utilizing industrial

ashes in unfired bricks. A total of six different ashes have been characterised, including two biomass ash and three coal-based ash from local industries, and one coal-based ash from a thermal power plant. To understand optimum mixing methodology and moisture content, the combined effect of two distinct mixing sequences (two-stage and threestage) at five different moisture contents (10% - 15%) has been experimentally examined on the mechanical properties, and microstructure of hydrated lime stabilised fly ash bricks. The coloured stone processing wastes have been explored to upgrade fly ash bricks' aesthetics for value addition and improved social acceptance. A total of four different stone processing wastes have been characterised using XRD patterns, FT-IR spectra, and Raman spectra. The stone processing wastes are blended with GGBS to produce coloured geopolymer mortars, and their potential is evaluated for producing coloured masonry bricks. To study the homogeneity of a dry binary blend, two stone processing wastes have been characterised adopting a three-stage procedure, and Raman spectromicroscopy has been established as a nondestructive tool to study the chemical homogeneity at the microscopic scale. To make the coloured bricks economically viable, the bi-layered bricks are conceptualised, and their manufacturability is demonstrated at the laboratory scale via a four-step process in an existing industrial set-up (used for conventional fly ash bricks).

It has been revealed in the thesis that a comprehensive characterization methodology comprising the macro-level tests (LOI and lime reactivity test) and micro-level characterization techniques (XRD, FT-IR, Raman spectroscopy and lime reactivity test) has been found suitable for characterization of industrial ashes. By and large, local coal-based industrial ashes can be suggested for potential utilization in lime-based fly ash bricks based on their comprehensive characterisation. Raman spectroscopy has been found to be instrumental in analysing the trio of amorphous, crystalline and carbon bands present in the industrial ashes. Bricks with 15% moisture content produced by a two-stage mixing sequence are found to have improved microstructure and enhanced physical characteristics. The incorporation of stone waste is found to decrease the compressive strength of geopolymer mortars. However, the stone waste blended coloured geopolymer mortars has still attained compressive strength greater than 10 MPa and corroborate the high potential for producing coloured masonry bricks equivalent to class designation 10 fly ash bricks as per IS 12894. Chemical imaging using Raman spectroscopy has been found a simple and effective tool to understand the homogeneity of the dry binary blend at the microscopic level, which was not possible by other simple techniques. The coloured bi-layered bricks have tremendous potential for cost-saving of up to 35% of the overall cost (accounting for the cost of a finished brick surface). These new bricks combine the desired features of aesthetics and durability, and therefore, show a great promise as a cost-effective alternative to conventional fly ash bricks.

LIST OF PUBLICATIONS

Peer reviewed journals (Thesis)

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ABBREVIATION

≈	No significant change;
1	Increase;
\downarrow	Decrease;
A _{MWC}	Approach to select moulding water content;
B/G	Ratio of binder: GGBS;
Cy	Cylindrical shaped;
C.D.E.	Center for Development of Enterprises;
CA	Coarse aggregates;
CIELAB	Colour space defined by the International Commission on Illumination;
CKD	Cement kiln dust;
CPWD	Central Public Works Department;
CS	Compressive strength;
CSH	Calcium silicate hydrate;
Di	Diameter;
EDX	Energy dispersive X-ray;
EPS	Expanded polystyrene;
F/S	Ratio of fly ash to sand;
F1	Type of binder;
F2	Amount of binder;

F3	Internal proportioning of blended binders;
F4	Internal proportioning of blended fines;
F5	Liquid content;
FA	Fine aggregates;
FE-SEM	Field emission scanning electron microscope;
FT-IR	Fourier transform infrared;
FWHM	Full width at half maximum;
G1	Type of binder;
G2	Concentration of binder;
G3	Internal proportioning in case of blended binders;
G4	Internal proportioning in case of blended fines;
G5	Liquid content;
GGBS	Ground granulated blast-furnace slag;
Ht	Height;
h	Hour;
H/S	Ratio of NaOH to Na ₂ SiO ₃ ;
H1	Type of binder;
H2	Amount of binder;
Н3	Internal proportioning in case of blended binders;
H4	Internal proportioning in case of blended fines;
H5	Liquid content;

HL	Hydrated lime;
HLF bricks	Hydrated lime-based fly ash bricks;
HPLC	High-performance liquid chromatography;
ICDD	The International Center for Diffraction Data;
ITZ	Interfacial transition zone;
LOI	Loss of ignition;
LR	Lime reactivity;
М	Molar;
Mc	Moisture content;
M-Sand	Manufactured sand;
MSWI-FA	Municipal solid waste incineration ash;
MT	Mine tailings;
NDC	Not disclosed, and constant water content;
NDV	Not disclosed and variable water content;
NHL	Natural hydraulic lime;
OMC	Optimum moisture content;
Op.	Optimum point;
OPC	Ordinary Portland cement;
PDF	Powder diffraction files;
Ref.	Reference;
RH	Relative humidity;

RHA	Rice husk ash;
RT	Room temperature;
S/N	Ratio of SiO ₂ to Na ₂ O;
SC	Standard compaction method;
SCT	Standard consistency test;
SEM	Scanning electron microscope;
SP	Steam pressure;
SPT	Standard proctor test;
Temp.	Temperature;
UC	Uniform consistency/ flow criteria;
UPV	Ultrasonic pulse velocity;
WCS	Water-cooled slag;
XRD	X-ray diffraction;
XRF	X-ray fluorescence;

Chapter 1

Introduction

1.1 Sustainable masonry products

The construction industry has been continuously evolving to incorporate various alternative materials as infrastructure making resources [1–3]. The masonry brick is an important component in the infrastructure development of societies since centuries [4, 5]. In ancient days, sundried mud blocks have been used for building construction, and are still in limited practice at some of the rural and desert areas in the developing countries [6, 7]. Ancient bricks were composed of soil, moulded by hand, and cured directly in sunlight without any additional compaction. These sundried bricks have much lower embodied energy and lower embodied carbon than the modern manufactured bricks available now a days [8]. A lot of modifications in raw materials and manufacturing processes have been made from time to time to improve the performance of the bricks, which results in the evolution of fired bricks.

The rapid development for improved performance somehow sacrificed the sustainability of the masonry bricks. In the modern world, the masonry bricks can be broadly classified into two categories: fired and unfired bricks [9]. Fired clay bricks are less eco-friendly than unfired bricks as their production emits a huge amount of greenhouse gases [1]. Besides, the use of topsoil for brick manufacturing is detrimental to the environment and leads to resource depletion. A recent study highlighted that famers are selling the agricultural soil to the clay brick manufacturers for short-term monetary gain [9]. It has been reported that farmers income gets reduced in long term due to reduced agricultural yield and has detrimental effect on the country`s food security. Therefore, a possible way to achieve a sustainable masonry product is to maintain the unfired manufacturing mechanism to limit greenhouse gas emissions and to utilise wastes to conserve natural resources.

Typically, unfired bricks are composed of soil or sand as base materials and are stabilized using suitable binders [10–13]. The stabilization of bricks improves the properties due to better bonding between the fine particles in the brick matrix. The unfired bricks are nowadays machine manufactured instead of hand moulding and compaction is done by vibration or compression of the fresh mix. Sometimes, the fresh mixes are prepared with self-compacting properties and are just poured in the moulds directly. Curing of unfired bricks in sunlight takes a longer time to achieve strength. Researchers [14–16] have attempted different curing techniques to accommodate the changes in raw materials and to achieve the required properties in a shorter time. However, the selection of suitable curing conditions depends on the raw materials and mainly on the binder used for the stabilization.

The growing need for sustainable binders has motivated researchers to investigate for viable alternatives of cementitious stabilizers. In general, cementitious binders (cement or lime) are used to stabilize the unfired bricks which adversely affects the environment due to their associated CO₂ emission. The high carbon footprint associated with these binders is considered as the major shortcoming [17, 18]. Therefore, cementitious binders along with pozzolana such as fly ash are undoubtedly better choices as stabilizers for achieving the low carbon footprint of the product [19–22]. Nowadays, laboratory scale attempts are being made for chemical based stabilization of bricks by adopting alkali activation or geopolymer mechanisms [23]. Alternatively, the use of additives to optimize the binder quantity can be a sustainable approach to decrease the overall carbon footprint of the unfired bricks.

binders [16, 24]. However, the use of costly resources as an additive to optimize the binder is not an ideal solution.

Disposal of waste materials is an ecological issue that can be partially resolved by incorporating them as an ingredient in unfired bricks [25]. While incorporating the wastes as partial replacement of binder, they give an added advantage to decrease the overall carbon footprint of the product. Researchers [26–29] have used various wastes (phosphogypsum, fly ash, and granulated blast furnace slag) to partially replace the cementitious binders (cement and lime) in unfired bricks. As binder is a minor component used for stabilization in the bricks, the utilization of wastes as a replacement of major component like clay seems to be more significant from a high volume recycling point of view [30].

Being abundantly available in nature, soil has been an obvious choice of manufacturers to use in unfired bricks by adopting a suitable binder. Mineral rich soil is important for agriculture production and continuous exploitation of soil from decades created a scarcity in near vicinity of industries. The use of waste materials in place of soil seems to be a viable option in conserving natural resources. Researchers have incorporated various waste materials in unfired bricks as a substitute to clay, such as fly ash [27], phosphogypsum [31], diatomaceous earth [24], ceramic mud [32], quarry dust [33], billet scale [33], stone mud [29], brick dust [29], recycled paper mill residue [34], crushed sand [12], and bottom ash [35]. In some studies, the sand was blended with fly ash [16], bio briquette ash [36], and phosphogypsum [37] and used as a fine aggregate. However, extreme sand mining showed the adverse environmental effects such as reduced carbon sequestration and nitrogen removal ability of soil in riparian areas of the river [38]. Although the studies have proven the laboratory scale feasibility for the incorporation of various wastes as a binder and as an aggregate in unfired bricks, however, the industrial scale waste utilisation is still limited in unfired bricks.

Based on the preliminary literature review and discussions with local brick manufacturing industries, the reasons behind the limited industrial scale waste utilisation are summarized below.

- Poor economic viability of wastes available at distant sources for incorporation in unfired bricks.
- Insufficient characterization data of locally available wastes
- Lack of clarity about optimized parameters for waste incorporated bricks

The understanding of waste characteristics is very important not only for optimum utilization of waste but also for the performance of waste incorporated bricks. The procurement of wastes from distant sources not only shows poor economic viability but also compromises sustainability due to transportation emissions. Therefore, local waste utilisation is a better way to achieve the sustainability in unfired bricks. However, insufficient characterization data of local wastes restricts manufacturers to incorporate the wastes at industrial scale in unfired bricks.

At global scientific platform, researchers have proven the feasibility of various wastes available to them in their demographic location. However, that always has certain limitations for generic industrial scale implementation of research outcomes in any other demographic location deferred from the study's location. Characteristics of wastes are highly dynamic, complex, and even difficult to control at source. Industries need to repeat the studies in their actual demographic conditions and with the actual waste available to them. It is not easy to propose a general range for characteristics of a particular waste. Besides, there is no generalized waste characterisation protocol available which can be applied to a random waste without knowing about its source and the targeted utilization.

Other than waste characterization, the lack of clarity about optimized production parameters for waste incorporated bricks is a major hurdle for industrial scale waste utilization in unfired bricks. The comprehensive knowledge on the feasibility aspects of waste incorporated bricks (Fig. 1.1) is not coherently available which restricts the industrial scale waste utilization in unfired bricks. Researchers have worked out extensively on the optimisation of mix proportions of waste incorporated bricks. However, limited attempts have been made to address the other production parameters such as mixing, compaction, and curing strategy for waste incorporated bricks. Manufacturing feasibility can only be assessed with the collective knowledge about characteristics and proportioning of wastes in the mix, mixing strategy, way of compaction and curing conditions suitable to incorporate the wastes in unfired bricks.



Fig. 1.1 Feasibility aspects for industrial scale waste utilization in unfired bricks

While commenting on the optimized production parameters, homogeneity of mix is an important aspect. The existing tools for

measuring the homogeneity of the mix have certain limitations for industrial scale implementation. Other than production-related parameters and technical checks (physical, mechanical, and durability properties), the sales checks like economic viability and social acceptance are important in the industry before adopting any waste for industrial scale utilisation In literature, an approach to utilising the waste for a product's value addition is not so explored. For industrial scale implementation of wastes in unfired bricks, all the feasibility and viability aspects (Fig. 1.1) are equally important and need to be evaluated before accepting these bricks for full-scale industrial production.

Nowadays, in India, lime stabilised fly ash bricks (a type of unfired bricks) are gaining popularity as a sustainable product against fired clay bricks. Manufacturers import the fly ash from distant thermal power plant. The locally available waste can be an alternate raw material for improved sustainability of unfired bricks. Other than this, fly ash bricks have an inherent grey colour. In India, red colour is considered as an auspicious colour which makes the fly ash bricks difficult to compete against red-coloured fired clay bricks, especially in rural areas' consumer market. Therefore, there is a need to upgrade the aesthetics of fly ash bricks for the improved social acceptance.

In the present work, a detailed literature review has been carried out to understand an up-to-date research status of waste incorporated bricks and to establish the research gap in line with the industry's needs for industrial scale waste utilization in unfired bricks. The following points are considered for the literature review.

- Utilization of locally available waste
- Optimum production parameters
- Suitable waste characterization protocol
- Ways for upgrading the aesthetics of existing masonry bricks
- Homogeneity measurement of the mix
1.2 Literature review on waste incorporated bricks

As established in the previous section, first, literature review has been presented on mix proportions attempted for various waste incorporated unfired bricks. After that other production parameters such as mixing strategy, way of compaction and curing strategy that were used by previous researchers for various waste incorporated bricks, are presented.

1.2.1 Mix proportions

Wastes are incorporated in both ways as partial replacement of binders and as fines in unfired bricks. The selection of a suitable binder, optimum quantity of waste in the mix, and liquid content for required plasticity are of considerable significance to stabilize the wastes in unfired bricks. In the present review, studies for various waste incorporated bricks are classified based on the binders used for stabilization: cementitious, chemical based and other binders and summarized below.

Bricks stabilized by cementitious binder

Different cementitious binders were used by researchers (Table 1.1) to stabilize the wastes in unfired bricks such as Portland cement, alumina cement, slag cement, natural hydraulic lime, calcareous lime, quick lime, slaked lime, and hydrated lime. Most cementitious binders, as shown in Table 1.1, were used in dry form (except for slaked lime). Fig. 1.2 classifies the stabilized wastes in unfired bricks (Table 1.1) in three categories such as ash wastes, industrial wastes, and other waste originated materials.

These wastes were incorporated fully or partially in addition to other materials such as clay, sand, crushed sand, crushed limestone aggregates, expanded polystyrene (EPS) beads, sand powder, calcium chloride and gypsum in unfired bricks as shown in Table 1.1.



Fig. 1.2 Different wastes stabilized by cementitious binders in unfired bricks

Further, it can be observed (Table 1.1) that the focus of researchers was to optimize the type of binder (denoted as F1), amount of the binder (F2), internal proportioning in case of blended binders (F3) and blended fines (F4), and the liquid content (F5) to get an optimized brick mix. In case of dry cementitious binders, researchers used different approaches to select the appropriate moulding water content as summarised in Table 1.2.

S. No.	Cementitious binder used	Waste and other raw materials stabilized	Focus of the optimization	A _{MWC}	Author/(s)	Ref.
1	Cement (15%), and lime (2%)	Clay (50%), pumice (15%), gypsum (3%), and plastic fiber (0.1%)/straw (2%)/polystyrene fabric (0.5%)	F1	NDC	Binici et al.	[7]
2	Lime (3.5%- 26.25%)	Fly ash (0.35:0.65 F/S), gypsum (0.5% - 10%), and sand (0.35: 0.65 F/S)	F2, F4, F5	NDV	Reddy and Gourav	[16]
3	HL (10%-50%)	Diatomaceous earth, and gypsum (0%-15%)	F2, F5	NDV	Pimraksa and Chindaprasirt	[24]
4	Cement (3%), NHL (3%), and calcareous lime (3%)	Fly ash (7%), alumina filler waste (20%, 40%, 60%), and clay (70%, 50%, 30%)	F1, F4	SC	Miqueleiz et al.	
5	Lime (10% - 60%)	Phosphogypsum (10%-40%), and fly ash (20%-80%)	F2, F4	SCT	Kumar	[27]
6	Lime (3%)	GGBS (11%), mud stone clay (52% -65%), and brick dust waste (0%-13%)	F4	SPT	Oti et al.	
7	HL (18%-20%), and Portland cement (0%-2%).	Calcined phosphogypsum (40%), and fly ash (40%)	F3	UC	Singh and Garg	[31]

Table 1.1 Cementitious binders used to stabilize waste in unfired bricks/blocks

8	OPC (15-30%)	Waste mud from ceramic tile industry	F2, F5	NDV	Wattanasiriwech et al.	[32]
9	Cement (10%-15%)	Quarry dust (50%-60%), fly ash (0%-40%), and billet scale (0%-40%)	F2, F4	UC	Shakir et al.	[33]
10	43 grade OPC (5- 20%)	Recycled paper mill residue (80% - 95%)	F2	UC	Raut et al.	[34]
11	Lime (6%-10%)	Fly ash (0% - 40% of lime percentage), soil, and crushed sand (0.7 :0.3)	F2, F4	SC	Izemmouren et al.	[12]
12	HL (10% - 30%) / cement (10% - 30%)	GGBS (30:70, 50:50, 70:30, B/G), fly ash (10%), and bottom ash (60%)	F1, F2, F4	NDC	Pahroraji et al.	[35]
13	53 grade OPC (10%)	Bio briquette ash (5%-55%), and sand (35%- 85%)	F4	NDC	Sakhare and Ralegaonkar	
14	Cement (4%), HL (1.3% - 1.7%)	Phosphogypsum (65% -85%), and sand (9.3%-29.7%)	F2, F3, F4	NDC	Zhou et al.	[37]
15	Cement (5%-15%)	Plastic fibers (carry bag fibers (0.1%-0.2%), PET bottle fibers (0.1%-0.2%) and soil	F1, F2	NDC	Subramaniaprasad et al.	
16	Cement (25%-50%)	Wood fiber waste (0%-25%), rice husk ash (0%-25%), limestone powder (0%-25%), and river sand (25%-50%)	F2, F4	NDC	Torkaman et al.	[39]

17	Lime (15%)	Glass powder (20%-35%) palm oil fuel ash (20%-35%), crusher dust (15%-45%), and oil palm fiber (0.25% - 1% by weight of binder)	F4, F2		Raut and Gomez	[40]
18	Hydrated lime (0%-15%)	Rice husk ash (0%-15%), sand (0%-30%), and clay (56%-100%)	F2, F4	SPT	Muntohar	[41]
19	Lime (5%-30%)	Calcined phosphogypsum (5%-30%), and fly ash (60%-90%)	F2, F4	SCT	Kumar	[42]
20	43 grade OPC (10%)	Recycled paper mill residue (70%-80%), and rice husk ash (10% - 20%)	F4	UC	Raut et al.	[43]
21	Cement (10%-23%)	Fly ash (26%-50%), and bottom ash (37%-57%)	F2, F4	UC	Naganathan et al.	[44]
22	Cement (10%)	Recycled paper mill residue (85%-89%), cotton waste (1%-5%)	f4	UC	Rajput et al.	[45]
23	Lime (8%,12%), cement (5%,8%), lime (3%,4%) + cement (5%,8%) and cement (5%,8%) + resin (50% of the compacting water weight)	Sand, and clay (30%:70%)	F2		Guettala et al.	[11]
24	GGBS, lime, and gypsum (81:15:4) (20%-50%)	Sand (50%-80%)	F2		Malhotra and Tehri	[46]

25	Lime (5%-15%)	Phosphogypsum (30%-50%), fly ash and sand (in internal ratio (1:2))	F1, F2		Yang et al.	[47]
26	Cement (11.36%-16.27%)	Cotton waste (0%-5.6%), and lime powder waste (88.64%-78.09%)	F4	NDC	Algin and Turgut	[48]
27	Lime (8%-14%)	Quartz sand (0%-40%), and fly ash (50%-90%)	F2, F4	NDC	Cicek and Tanriverdi	[49]
28	Cement (10%-30%), and lime (10%-35%)	Construction and demolition waste aggregate (65%-90%)	F2	NDC	Contreras et al.	[50]
29	Lime (6.7%-13.3%)	River sand (0%-83%), sand powder (0%- 13.3%), and copper tailings (0%-88%)	F2, F4	NDV	Fang et al.	
30	Cement (20%-25% by volume)	By volume: rice husk ash (0%-5%), sand (37.5%), and EPS beads (37.5%)	F2	NDC	Ling and Teo	[52]
31	Alumina cement/ slag cement/ Portland cement (32.5R and 42.5R)/ grounded cement clinker (B/F-1:0.5-1)	Wastewater sludge	F1, F2, F5	NDV	V Liu et al.	
32	Cement (1part by volume)	Oil palm kernel shell (1-3 part by volume), and sand (1 part by volume)	F4	NDC	Muntohar and Rahman	[54]

33	Cement (5.71%)	Natural river sand and crushed granite aggregates (0%-91.42%), and recycled aggregate (0%-91.42%)	F4	NDV	Poon et al.	[55]
34	Cement (3%) / lime (3%)	Class C fly ash (7%), stockpiled CFBC ash (ground (58.3% -100%) and unground (62.3% - 85.3%)), sand (13% - 30%), clay (10-30%), and CaCl ₂ (1.7%)	F1, F4	NDC	Shon et al.	[56]
35	Slaked lime (8% - 12%)	Fly ash (88% - 92%)	F2	NDC	Çiçek and Çinçin	[57]
36	Lime (6%-15%)	Hematite tailings (62%-89%), sand (5%-20%), and gypsum (0%-3%)	F2, F4	NDC	Zhao et al.	[58]
37	Cement (6.97%)	FA (73.64%), and CA (19.37%); by volume of cement: wood ash (0%-15%), and lime mud (0%-15%); by volume of FA: saw dust (0%-20%), and superplasticizer (1%)	F2, F4	NDC	Madrid et al.	[59]
38	Cement (11%-14.25%)	Crumb rubber (0%-40% by volume of crushed limestone), and crushed limestone (89%-85.75%)	F4	NDV	Sodupe-Ortega et al.	[60]
39	Cement (400 - 500 kg/m ³)	EPS beads (15-25% of total volume of concrete), sand (35%-41%), and crushed stone (59%-65%)	F2, F4, F5	NDV	Xu et al.	[61]

40	Cement (3%) / Lime (3%)	CFBC fly ash (77%-100%), and CFBC slag (0%-20%)	F1, F4, F5	NDV	Zhang et al.	[62]
41	Cement (10.73%)	Waste limestone (77.87%-85.92%), and waste glass powder (0%- 8.05%)	F4, F5	NDV	Turgut	[63]

Approach	Moulding water content	Ref.
Standard proctor test (SPT)	Determine the optimum moisture content (OMC) of the mix and taken as moulding water content	[29, 41]
Standard consistency test (SCT)	Determine the water content to achieve the required consistency, and 90% of that was selected as moulding water content	[27, 28, 42]
Uniform flow consistency (UC)	Water content was adjusted to achieve the required consistency parameter	[31, 33, 34, 43–45]
Standard compaction method (SC)	Determine the optimum moulding water content at constant static pressure.	[12, 26]

Table 1.2 Approaches used to select the appropriate moulding water content in previous studies

Moulding water content can be termed to the resultant water content at the time of brick moulding (including the free moisture present with raw materials and the added water before the moulding of the bricks). The static compaction method was proposed by the Center for Development of Enterprises (C.D.E.) [64]. As it can be seen in Table 1.1, many studies did not specify their approach to select the water content. Some of such studies kept the water to binder ratio or the water content in the mix constant, whereas some others considered it as a variable parameter. In some studies [11, 40, 46, 47], details related to moulding water content are not specified as such. However, the research outcomes of these studies regarding waste incorporation in unfired bricks are significant and are therefore incorporated in Table 1.1.

Mix proportions summarized here can give a reference to the industries for probable binders to be used to stabilize the locally available waste in unfired bricks. It is also noted that many studies did not specify the approach to select water content. Few studies which mentioned the approach are found to have a wide diversity between their approaches. However, no study is found to be commenting on the appropriate approach to select the water content. In view of this, it has been challenging to determine the trial range to incorporate the wastes at an industrial scale, since the same type of wastes could significantly differ in their characteristics because of their different origins.

Bricks stabilized by chemical-based binders

Different types of chemical binders, namely sodium hydroxide, sodium silicate and their blended forms, were used by researchers to stabilize the various wastes in unfired bricks as shown in Table 1.3. The wastes investigated in these studies are summarised in Fig. 1.3. These wastes were used alone or in combination with sand, manufactured sand (M-sand) and clay, as shown in Table 1.3.



Fig. 1.3 Different wastes stabilized by chemical binders in unfired bricks

S. No.	Chemical binders used	Wastes and other raw materials stabilized	Focus of the optimization	Author/(s)	Ref.
1	NaOH (10M), and Na ₂ SiO ₃	RHA (ground-11.55%, unground 0-28.45%), fly ash (17.32%), and sand (42.68%-71.13%)	G4	Hwang and Huynh	
2	NaOH(8M $-14M$), and Na ₂ SiO ₃ (H/S-1:3)	Crumb rubber with fly ash (ratio 1:1)	G2, G5	Mohammed et al.	
3	NaOH solution (10 M,15 M)	Copper MT	G2, G5	2, G5 Ahmari and Zhang	
4	NaOH solution (10-15M)	Copper MT (90-100%), and cement kiln dust (0-10%)	G2, G4, G5	Ahmari and Zhang	[68]
5	Na ₂ SiO ₃ (S/N: 1.2 – 2.0), NaOH (5 M, 10 M), KOH (5 M, 10 M), and LiOH (5M)	CFBC bottom ash	G1, G2	Chen et al.	[69]
6	NaOH solution (4 M- 12 M)	Alumino-silicate rich tuff, (Bafoundou Tuff)	G2	Diop and Grutzeck	[70]
7	NaOH	WCS (0% - 100%), and clay brick waste (0% - 100%)	G4	Ezzat et al.	[71]
8	Na ₂ SiO ₃ solution, NaOH in solid, and NaOH in solution form (10 M,14 M)	Weathered coal fly ash	G2, G3	Ferone et al.	[72]

Table 1.3 Chemical binders used to stabilize the wastes in unfired bricks

9	NaOH (8M - 12M), and Na ₂ SiO ₃ (H/S-1:2.5)	OH (8M - 12M), and Na ₂ SiO ₃ Fly ash (40%), GGBS (10%), recycled water in solution, and M-sand (50%) S-1:2.5) Solution, and M-sand (50%)		Radhakrishna et al.	[73]
10	Na ₂ SiO ₃ , NaOH (10M) (H/S- 0.4-2.3)	Fly ash (23%), and clay (77%)	G3, G5	Sukmak et al.	[74]
11	NaOH, and mix of NaOH and Na ₂ SiO ₃	nix of NaOH and Calcined clay		Mohsen and Mostafa	[75]
12	NaOH (10 M) Fly ash (25.27% - 11.15%), rice husk ash (0% and sand (74.72%)		G4	Huynh et al.	[76]
13	NaOH (10 M), and Na ₂ SiO ₃ Fly ash (16.66%-33%), and sand (66%-83.33%) (H/S- 1:2.5)		G4	Abdullah et al.	[77]
14	NaOH (12 M), and Na ₂ SiO ₃ (H/S- 1:2.5)	Bottom ash (20%-80%), and fly ash (20% - 80%)	G4	Deraman et al.	[78]
15	Sodium silicate	Fly ash and bottom ash	G4, G5	Freidin	[79]
16	NaOH, and sodium silicate solution (H/S- 2:1)	WCS (25%-100%), metakaolin (0%, 60%), CKD (25%-75%), and sand (15% - 50%)	G4	Khater et al.	[80]
17	NaOH (8M), and Na ₂ SiO ₃ (H/S- 1:1-1:9)	Recycled glass (77%), and fly ash (23%)	G3, G5	Arulrajah et al.	[81]

18	NaOH (0.31%-5.71%), and Na ₂ SiO ₃ (50.50%-53.29%)	Red mud (10%-18%), metakaolin (22%-30%), and aluminium powder (0.025%-0.1%)	G3, G4, G5	Ascensão et al.	[82]
19	NaOH (10M-17M), and Na ₂ SiO ₃ (S/N-1.15)	MSWI-FA (48%-60%), and coal fly ash (16%-20%),	G2, G4, G5	Ferone et al.	[83]
20	NaOH (5M-10M), and Na ₂ SiO ₃ (S/N-3.47)	GGBS (0%-30%), and clay (70%-100%)	G2, G3, G4, G5	Ferone et al.	[84]
21	NaOH, and Na ₂ SiO ₃ (S/N-1.6)	Fly ash (0%-100%), and brick powder (0%-100%)	G4, G5	Rovnanik et al.	[85]

In case of chemical binders, the binder content can be varied in two ways, i.e. (i) by varying the molar concentration and (ii) by varying total liquid content. It can be observed from Table 1.3 that the focus of researchers was to optimize the type of binder (denoted as G1), the concentration of binder (G2), internal proportioning in cases of blended binders (G3) and blended fines (G4), and the liquid content (G5) to get an optimized brick mix.

Bricks stabilized by other binders

Other than cementitious and chemical binders, some mixed/alternative binders were used to produce the unfired bricks, as shown in Table 1.4. In a study [86], a bio-based binder made from alginate was attempted to stabilize the soil. Some researchers [87–90] stabilized the clay bricks using waste materials without using conventional cementitious or chemical binders. In a recent study [91], a different approach was attempted, where a mixture of chemical and cementitious binders was used to produce solid bricks by stabilizing three different types of boiler ashes. In another study [92], CNF binder system (A mixture of hydrated lime, sodium carbonate, and fly ash with an internal ratio of 4.3:1:14.7) along with NaOH was used to stabilize red mud in unfired bricks. Mixed binders seem to be appropriate to overcome the cost considerations regarding the chemical binders. The potential of such mixed binders may be further explored to stabilize the other wastes.

S. No.	Binders used	Waste and other raw materials stabilised	Focus of the optimisation	Author/(s)	Ref.
1	Bio-based binder: Alginate (1-5:1000 by weight of soil)	Soil	H1	Dove et al.	[86]
2	Processed tea waste (0%-5%)	Soil	H2	Demir	[87]
3	MgO rich kiln dust (0%-18%)	Soil	H2	Espuelas et al.	[88]
4	Phosphogypsum (0%-25%), and natural gypsum (0%-25%)	Soil (75%-100%)	H2	Degirmenci	[89]
5	Fly ash, slag, clinker dust and some activator (15%)	Low silicon tailings (85%)	Н5	Zhao et al.	[90]
6	NaOH (0 M – 5M), and lime (10%)	Clay (0% - 30%), and boiler ash (60% - 90%)	H2	Poinot et al.	[91]
7	Ca(OH) ₂ , Na ₂ CO ₃ , and fly ash (internal ratio: 4.3:1:14.7) (70%-100%)	Red mud (0%-30%), and NaOH (0%-5%)	H2, H4, H5	Kim et al.	[92]

 Table 1.4 Mixed/alternative binders used to stabilize the wastes in unfired bricks

Overall, in this sub-section, following key observations can be made.

- Different binders have been used by researchers/industries to stabilize various wastes in unfired bricks.
- In recent studies, a shift towards the use of ash wastes as the base material (in place of the traditional practice to use soil or sand) has been observed to produce the unfired bricks.
- Cementitious binders have relatively lower cost as compared to chemical binders. However, by using a chemical binder, a high volume of wastes can be incorporated in unfired bricks.
- Researchers used different approaches to select the liquid content in case of unfired bricks stabilized by cementitious binders. Besides, chemical binders are generally used in liquid form and do not significantly contribute in terms of physical volume as compared to the cementitious binder.
- Locally available ash waste that has low transportation cost and low transportation emissions can significantly improve the economic viability and sustainability of unfired bricks.

After the mix proportions used by various researcher, next sub-section summarises the important production parameter i.e., mixing strategy used by previous researchers for various waste incorporated bricks.

1.2.2 Mixing strategy

Currently, at industrial scale, there is no agreed or standardized mixing strategy to prepare the fresh brick mix in India. The adopted mixing strategies at the laboratory scale vary considerably within the literature, and they are generally based upon the characteristics of raw materials used to prepare the mix. Researchers often adopted an improvised mixing strategy or previously cited strategy for the selected raw materials. However, limited discussions were made in the publications regarding the suitability of the adopted mixing strategy. In this section, mixing strategy adopted in previous studies to prepare the brick mix are summarized.

Mixing sequence

The mixing sequences used by various researchers to prepare the fresh brick mixes for unfired bricks are summarized in Table 1.5. Researchers adopted different mixing sequences, such as single-stage, two-stage, and three-stage mixing sequences to handle the heterogeneity in the physical state of the different raw materials. The selection of a suitable mixing sequence seems to be essential to manage the ingredients with varying physical states in the blended mix. Ahmari and Zhang [67] adopted a single-stage mixing sequence as only one ingredient is stabilized using the alkaline solution in the study. In another study, Zhao et al. [58] mixed all the dry ingredients along with water in a single-stage mixing sequence. However, the two-stage mixing sequence is the most common to handle dry binders and liquids.

S. No.	Author/(s)	Mixing sequence	Raw materials	Mixing time	Mixing equipment	Ref.
1	Reddy and Gourav	1. Dry mixing of the ingredients	Fly ash, lime, and gypsum	10 min.	Ball mill	[16]
		2. Addition of water	Water		Air sprayer for water, and mixing manually	
2	Miqueleiz et al.	1. Mixing of all dry ingredients thoroughly	Clay, alumina filler, and binder			[26]
		2. Addition of water in dry mix, and mixing	Water	5 min.	Industrial mixer	
3	Kumar	1. Mixing of dry ingredients	Calcined gypsum, and fly ash (screened from 4.75 mm sieve)			[27]
		2. Adding the wet slurry of ingredients, and mixing	Slaked lime slurry (sieved from 1.18 mm sieve)		Kneaded for uniform consistency	_
4	Oti et al.	1. Mixing of all dry ingredients	Lime, GGBS, mud stone clay, and brick dust waste	2 min.	Laboratory mixer	[29]

Table 1.5 Mixing strategy used to prepare the fresh mix in various studies related to unfired bricks

		2. Adding of water, and further mixed	Water	2 min.	hand-mixed	
5	Shakir et al.	1. Mixing of dry ingredients-I	Cement, and quarry dust	2 min.		[33]
		2. Adding dry ingredients-II, and mixed	Billet scale, and fly ash	2 min.		_
		3. Adding the water, and mixed again	Water	2 min.		_
6 Raut et al.		1. Mix the highly fibrous and lumpy wet waste with the dry binder.	OPC, and recycled paper mill residue	2 min.	Special mixer, and air pumps	[34]
		2. Spray the water, and mixed again		5 min.	to spray the water	
7	Pahroraji et al.	1. Mixing of all the dry ingredients	Hydrated lime/cement, GGBS, fly ash, and bottom ash	1 min.		[35]
		2. Adding the water, and further mixing	Water	10 min.	Pan mixer	
		3. Injecting foam into the mixed slurry, and mixing till the proper blending	Foam		-	
8	Zhou et al.	1. Mixing of dry ingredients-I	Hydrated lime, and phosphogypsum			[37]
		2. Adding dry ingredients-II and water, and mixing to get a homogeneous mixture	River sand, cement, and water			_

9 Algin and Turgut		1. Mixing of dry ingredients	Cement, lime powder waste, and cotton waste	1 min.	Concrete mixer, and air	[48]
		2. Added water during mixing	Water	3 min.	water	
10	Guettala et al.	1. Dry ingredients are mixed	Soil (pre-dried at 63 °C for 24 h), sand, and stabilizer (lime/ cement)	3 min. 51 malaxer (at 139 rev./min.)		[11]
		2. Added water, and mixed again	Water	2 min.		
11	Ling and Teo	1. Dry ingredients-I were mixed.	Sand, cement and RHA			[52]
		2. Liquid content was added, and mixed.	Water and superplasticizer	5 min.	Pan mixer	
		3. Dry ingredients were added and mixed again.	EPS beads	3 min.	-	
12	Muntohar and	1. Dry ingredients-I were mixed	Cement, and sand	10-15		[54]
	Kanman	2. Surface saturated coarse aggregates were added, and mixed again	Oil palm kernel shell (pre-soaked for 1 h)	mın.	Mechanical mixer	
		3. Water is added, and remixed	Water	-		
13	Naganathan et al.	1. Dry ingredients-I were mixed	Bottom ash and Cement	2 min.		[44]

		2. Dry ingredients-II was added, and again mixed.	Fly ash	2 min.		
		3. Water was added and mixed again.	Water	2 min.		
14	Raut and Gomez	ez 1. Dry ingredients including fibers were mixed in the first step Lime, glass powder ash, crusher dust, a fiber			Concrete mixer	[40]
		2. Water was added, and remixed	Water	2-3 min.		
15	Sodupe-Ortega et al.	1. Dry raw materials were mixed.	Cement, crumb rubber, and crushed limestone	3 min.	Concrete	[60]
		2. Stop the mixing, and keep the mix at rest		2 min.	mixer, and industrial	
		3. Added liquid solution progressively during the mixing	Water, and superplasticizer		mixer	
16	Xu et al.	1. EPS beads were wetted in partial water				[61]
		2. Dry ingredients-I, and remaining water were added, and mixed at low speed	Cement, and sand	3 min.		
		3. Dry ingredient-II was added and mixed again.	Crushed stone	3 - 5 min.		

17	Zhao et al.	All the ingredients were mixed with water in a single step.	Hematite tailings, sand, lime, and gypsum	5 min.		[58]
	Subramaniaprasad	1. Mixing of dry ingredients was done	Cement, and soil			[13]
18 et al.	et al.	2. Water was added in the second step(Fibers were added during the mixing by hand)	Water, and fibers (plastic fibers)			
19	Torkaman et al.	1. Mixing of dry ingredients in the first step	Cement, wood fiber waste, rice husk ash, limestone, and river sand	3 min.	Concrete	[39]
		2. Chemical admixtures in solution form, and water were added, and mixed again.	An aqueous solution of CaCl ₂ , and water	2 min.	mixer	
20	Turgut	1. Dry ingredients were mixed in the first step	Waste limestone, cement, and waste glass powder	1 min.	Concrete mixer for	[63]
		2. Water was added during the mixing in the second step	Water	3 min.	air sprayer for water addition	
21	Binici et al.	1. Dry ingredients are mixed	Cement, lime, clay, pumice, gypsum, and fibers			[7]

		2. Addition of water, and mixing till a uniform consistency	Water			
22	Ahmari and Zhang	Mix the dry ingredients with the alkaline solution	Alkaline solution, and dry mine tailings	10 min.		[67]
23	Abdullah et al.	1. Mixing of dry ingredients	Fly ash, and sand	5 min.		[77]
		2. Adding alkaline solution, and mixing	Alkaline solution	10 min.		
24	Khater et al.	1. Addition of dry ingredients with the alkaline activator, and mixing	Slag, metakaolin/ cement kiln dust (screened from 90-micron sieve), and alkaline activator	10 min.	Mixing by hand	[80]
		2. Addition of sand in the wet mix, and mixing	Sand (screened from 1 mm sieve)	5 min.	Electronic mixer	
25	Degirmenci	1. Dry ingredients are mixed	Phosphogypsum /natural gypsum, and soil	ypsum, 3 min. Mecl		[89]
		2. Added water, and mixed again	Water	2 min.	mixer	
26	Zhao et al.	1. Cementing materials were mixed, and ground.	Cementing material (fly ash, slag, clinker dust, and some activator)			[90]
		2. Fines, and water were added, and mixed	Low silicon tailings			

27	Kim et al.	1. Red mud slurry, and water was added	Red mud, and water	2 min.		[92]
		2. NaOH with water was added.	NaOH (with ref. to mix), and water		Mechanical mixer	
		3. Binder was added and mixed again.	Ca(OH) ₂ , Na ₂ CO ₃ , and fly ash	3 min.		

As shown in Table 1.5, majority of researchers adopted the two-stage mixing sequence in the case of blended mix. In these studies, dry ingredients were commonly mixed in the first stage, and liquid content was added separately in the second stage. However, in some studies [37, 61, 80, 90], dry ingredients were incorporated in two stages, and liquid content was added with them in any of the stages.

As can be seen in Table 1.5, some researchers adopted the three-stage mixing sequence. In some studies [33, 44, 54], the first two stages were dedicated to dry mixing of solids, and in the third stage, liquid content was added. However, in another study [35] with a three-stage mixing sequence, all the dry ingredients were mixed in the first stage of mixing. After that, water was added in the second stage and foam was injected into the mixed slurry in the third stage of mixing. In a few studies [52, 92], dry ingredients were added in two parts to handle the ingredients with different physical characteristics. In first stage, some of the dry ingredients were mixed. After that, liquid content was added and mixed in the second stage of mixing, the remaining dry ingredients were added and mixed to get the homogeneous mix.

Pre-screening of ingredients is another important aspect of ensuring the homogeneity of the mix. Algin and Turgut [48] reported the issues related to lump formation and accumulation at the one side of the mixer during mixing of unprocessed cotton waste and lime powder waste. To enable the mixing, pre-processing of cotton waste was done before incorporating in cement stabilized bricks. In a study [80], fine ingredients were pre-screened from 90-micron sieve, and coarse ingredient was pre-screened from 1 mm sieve before the mixing. In another study [37], a different approach was adopted to handle waste phosphogypsum. Hydrated lime was added into the phosphogypsum to neutralize residual acid impurities in the first stage of mixing. After that, in the second stage of mixing, other ingredients were added and mixed to get a homogeneous mixture. In another study [61], the EPS beads were pre-wetted before mixing in dry ingredients.

Different approaches have been adopted by researchers [27, 34] to handle the wet raw materials in the mix. Raut et al. [34] adopted the twostage mixing sequence to incorporate highly wet recycled paper mill residue in the bricks. In the first stage, cement and highly fibrous, wet, and lumpy paper mill residue were mixed using a specially designed mixer. In the second stage, additional water required was added and mixed again to get a homogenous mix. In the other study [27], the dry ingredients were pre-screened from 4.75 mm sieve and mixed in the dry state at the first stage of mixing. In the second stage of mixing, slaked lime slurry, pre-screened from 1.18 mm sieve was added to the dry mix and kneaded to get uniform consistency mix. Water content was calculated based on the standard consistency requirement, and 90% of that was maintained in the semi-dry mix based on measurements. However, in industrial set up, bulk slaking of quick lime is done in big slaking tanks. As per the author's manufacturing experience, it is difficult to provide controlled quantity of water just sufficient for slaking of quick lime in the practicing industrial setup for such bricks in India.

Mixing time

Mixing time used by various researchers has been stage-wise summarized in Table 1.5. It was observed that the total mixing time used for mixing was varied in the range of 4 min. – 15 min. In some studies, as shown in Table 1.5, mixing time was either partially specified or not specified. To understand the mixing strategies, mixing data related to these studies have been incorporated in Table 1.5, whereas for further analysis, these studies have been excluded. Further discussion has been made only for the studies which have mentioned the stage-wise mixing time details, as shown in Table 1.5. In a study [58] with one stage mixing sequence, mixing was done for 5 min. in a single stage. Studies [11, 29, 39, 48, 63, 89] incorporating the raw ingredients in two stages typically had the total mixing time varying between 4-5 min. The mixing time used for mixing of dry ingredients was varied between 1-3 min. Whereas the mixing time used for mixing of liquid in the second stage varied in the range 2-3 min.

In the studies [29, 48, 63], the mixing time used for dry blending of solids in the first stage was either equal or less than that used to mix the liquid in the second stage whereas the opposite trend was observed in the studies [11, 39, 89]. In the studies [33, 44], a three-stage mixing sequence was used, and the same duration (2 min.) was given for each stage of mixing. As noted above for the two-stage mixing studies, the mixing duration typically varied between 4-5 min., whereas, in some studies [77, 80], mixing was done for a long duration up to 15 min.

Mixing equipment

Mixing equipment used by various researchers are summarized in Table 1.5. It can be seen that the researchers used different mixing equipment, namely industrial mixer, pan mixer, concrete mixer, mechanical mixer or laboratory mixer to mix the raw materials. Raut et al. [34] adopted a unique mixing methodology to incorporate highly wet recycled paper mill residue in forced compacted bricks. A special mixer with multiple blades was designed and fabricated to shear the mix of cement and highly fibrous and lumpy paper mill residue with every rotation. The primary purpose was to scatter the mix to get a homogenous mix with cement. After mixing in the first stage, to maintain the homogeneity further, water was sprayed using air pumps over the mixture in the second stage and mixing was done again. A similar arrangement of air pump was used for spraying the homogeneous water in the mix in some other studies [16, 48, 63]. In a study [16], a ball mill was used for mixing dry ingredients, and water was added using a sprayer.

Focused studies are not available related to unfired brick mixes regarding the effect of variation in mixing sequence, mixing time and speed, and mixing equipment. Therefore, a brief review on the effect of mixing strategy for other construction materials has been presented in the next subsection to understand the importance of mixing strategy.

Effect of mixing strategy variation in other construction material

Variation in mixing strategy, such as mixing sequence, mixing time and mixing speed, and mixing equipment affects the performance of the prepared mixes. A detailed review [93] on the influence of mixing procedure and mixer type is available on fresh and hardened properties of concrete. In another study [94], it was observed that mixing time and mixing speed had a significant influence on the pore structure of the binder paste. With the increase in mixing time, the compressive strength of cement mortar was found to decrease. Regarding combined effect of mixing speed and mixing time, it was reported that high-speed mixing (1000 rpm) with 1 minute mixing time resulted in a ~20% increase in compressive strength as compared to normal speed mixing (140 rpm) for 10 minute mixing time. The rheological response of cement pastes was found to be significantly influenced by mixing sequence and superplasticiser dosage at different temperatures [95]. Similarly, Williams et al. [96] analysed the rheological parameters regarding the effect of different mixing equipment and varying mixing speed on cement paste. In another study, Hiremath and Yaragal [97] analysed the influence of the mixing method, speed, and duration on fresh and hardened properties of reactive powder concrete. In engineered cementitious composites [98], improved fiber distribution and mechanical properties were observed by adjusting the mixing sequence. Similarly, in high-performance concrete [99], properties were found to be significantly influenced by mixing techniques.

Overall, in this sub-section, following key observations can be made.

- It is noted that mixing strategies significantly influence the performance of fresh mixes. Therefore, more focused studies are required for brick mixes.
- Unprocessed waste materials may contain foreign elements in it. Pre-screening would be a better approach to ensure a uniform quality product.
- In case of lumpy raw material, pre-screening with a fine size sieve would break the lumps and ensure better distribution within the brick matrix. Especially in case of wet lumpy binder (slaked lime), a higher potential may be expected by adopting the pre-screening approach.

After the mix proportions and mixing strategy used by various researcher, next sub-section summarises the important production parameter i.e., moulding and compaction method used by previous researchers for various waste incorporated bricks.

1.2.3 Moulding and compaction methods

Different moulding and compaction methods, such as vibro-compaction, forced compaction, and self-compaction and manual tamping, were used to cast the unfired bricks, as shown in Table 1.6. Only in a few studies [39,60], more than one compaction method was used; however, a comparison between the adopted methods was not made.

Vibro-compacted

Many studies [7, 27, 28, 39, 40, 42, 53, 80] used vibro-compaction method to compact the bricks. However, the majority of studies did not mention the compaction parameters such as duration of vibration, frequency, and amplitude of vibrator except the studies [39, 53]. Liu et al. [53] mentioned the frequency 2800-3000 cm⁻¹ and amplitude 0.75 mm of vibrator used during the casting, whereas Torkaman et al. [39] mentioned the vibration duration as 1 minute. Majority of studies cast cubical or cuboidal shapes specimen whereas specimen size varied considerably. In a study [27], special-shaped hollow blocks were cast using vibration where the battens used to create hollow space were removed after 2 h of casting. This shows the limitation of vibration method which restricts the instant demoulding of bricks and blocks and multiple moulds are required to use this method.

S. No.	Author/(s)	Mode of compaction	Compaction parameter/(s)	Sample shape/ size (mm)	Ref.
1	Binci et al.	Vibro-compacted		150×150×150	[7]
2	Reddy and Gourav	Forced compacted	Screw jack arrangement	$38(D_i) \times 76(H_t)(C_y)$	[16]
3	Pimraksa and Chindaprasirt	Forced compacted	3.5 MPa	150×75×35	[24]
4	Miqueleiz et al.	Forced compacted	13 MPa	125×60×40	[26]
5	Kumar	Vibro-compacted		Special shaped	[27]
6	Kumar	Vibro-compacted	2-layer compaction	220×110× 75	[28]
7	Wattanasiriwech	Forced compacted	25 MPa – 75 MPa		[32]
8	Shakir et al.	Self-compacted		200×90×60	[33]
9	Raut et el.	Forced compacted		230×105×80	[34]
10	Izemmouren et al.	Forced compacted	5 MPa	100×100×200	[12]
11	Zhou et al.	Forced compacted	30 MPa	240×115×53	[37]

 Table 1.6 Moulding and compaction method used in various studies related to unfired bricks

12	Algin and Turgut	Forced compacted	1 min. and 2 -40 ton	105×90×75, 105×225×75	[48]
13	Cicek and Tanriverdi	Forced compacted		45 mm (D_i) with fix weight (100 gm)	[49]
14	Fang et al.	Forced compacted	20 MPa	100×100×50	[51]
15	Guettala et al.	Forced compacted	15 MPa	100×100×200	[11]
16	Kumar	Vibro-compacted		220×100×75	[42]
17	Ling and Teo	Self-compacted/ manual tamping		215×102.5×65	[52]
18	Liu et al.	Vibro-compacted	Frequency: 2800-3000 cm ⁻¹ , Amplitude: 0.75 mm	40×40×160	[53]
19	Muntohar	Forced compacted	15 MPa	230×110×55, 150×150×600	[41]
20	Muntohar and Rahman	Forced compacted	5 MPa	200×100×80	[54]
21	Naganathan et al.	Self-compacted		200×90×60	[44]
22	Raut and Gomez	Vibro-compacted		200×100×100	[40]
23	Shon et al.	Forced compacted	55.2 MPa	90×65×90	[56]

24	Sodupe-Ortega et al.	Manual tamping	In 3 layers	100×100×100	[60]
		Forced compacted	69 kPa, 5 sec.	100×115×250	_
25	Xu et al.	Self-compacted		100×100×100	[61]
26	Yang et al.	Forced compacted	20 MPa	240×115×53	[47]
27	Zhang et al.	Forced compacted	10-30 MPa	$50 (D_i) \times 50 (H_t) (C_y), 240 \times 115 \times 53$	[62]
28	Zhao et al.	Forced compacted	20 MPa	$50 (D_i) \times 23 (H_t) (C_y)$	[58]
29	Subramaniaprasad et al.	Forced compacted	1.25-7.50 MPa	101.5 (D _i) × 117 (H _t) (C _y)	[13]
30	Torkaman et al.	Vibro compacted	1 min.	150×150×150	[39]
		Forced compacted			_
31	Turgut	Forced compacted	160 MPa for 1 min.	225×105×150	[63]
32	Malhotra and Tehri	Forced compacted	~ 5 MPa	190×90×90	[46]
33	Çiçek and Çinçin	Forced compacted	4.6 MPa-12.26 MPa	$45(D_i) \times 100(H_t) (C_y)$	[57]
34	Hwang and Huynh	Forced compacted	35 MPa	220×105×60	[65]

35	Ahmari and Zhang	Forced compacted	10 min.	$33.4(D_i) \times 72.5(H_t) (C_y)$	[67]
36	Abdullah et al.	Forced compacted	10 MPa		[77]
37	Khater et al.	Vibro-compacted		25×25×25	[80]
38	Degirmenci	Self-compacted		50×50×50, 40×40×160	[89]
39	Zhao et al.	Forced compacted	~12.5 - 22.5 MPa	240× 115×53	[90]
40	Kim et al.	Self-compacted/ manual tamping		50×50×50	[92]

Forced-compacted

As shown in Table 1.6, majority of studies used compression method to cast the bricks, applying hydraulic press. Whereas, in a study [16], a screw jack arrangement was used to compact and extrude the cylindrical specimens of lime fly ash compacts. In general, compaction pressure was mentioned by researchers, whereas some of them [39, 48, 67] mentioned the compression duration. Few studies [13, 32, 48, 57, 62, 90] varied the compaction pressure and analysed the influence on performance parameters of the bricks. Majority of studies cast cubical and cuboidal shaped specimens except for the studies [13, 16, 49, 57, 58, 62, 67], which cast the cylindrical specimen of the brick mix.

In a study [34], a unique two-stage casting process was adopted to handle the high moisture-holding capacity of fibrous recycled paper mill residue to get smooth-surfaced bricks after drying. The two-stage casting procedure was found helpful to avoid uneven irregular shaped bricks produced with single-stage casting process. In another study [67], Ahmari and Zhang compacted the specimen in two stages and carried out investigations for optimum compaction parameters. In the first stage, minor compaction was used, whereas, in the second stage, the compacted specimen was further compressed for a longer forming duration of about 10 min. Specimens were compared at different loading rates and varying water content. The elastic deformation was observed to be less at high forming pressure and low water content (25 MPa and 12%), which was attributed to the effective volume decrease of voids within granular matrix [67] at the applied condition.

Self-compacted and manually compacted

As shown in Table 1.6, in many studies brick mixes were prepared with self-compacting properties or just manually tamped without a hydraulic press. Specimens were cast in cubical and cuboidal shape. Brick mixes with self-compacting properties may save the considerable cost of compression and vibration equipment.

Overall, in this subsection, following key observations can be made.

• Forced compaction method is the most adopted method for compaction of unfired bricks, in which instant demoulding has an additional advantage for industrial scale implementation.

After the mix proportions, mixing strategy and compaction method, next sub-section summarises the curing conditions used by previous researchers for various waste incorporated bricks.

1.2.4 Curing conditions

Selection of suitable curing conditions, i.e., the surrounding environment conditions (temperature, pressure, and humidity) and the curing medium (air, water, airtight or combination of them) for the specified period (curing duration) is crucial for a brick mix to achieve the targeted performance parameters cost-effectively. Curing duration of bricks is the period required to develop the targeted strength from the casting of fresh bricks to the dispatch of hardened bricks, which has a direct impact on the production cycle, as shown in Fig. 1.4. The optimum curing conditions majorly depend on raw material characteristics that indirectly govern the rate of chemical reactions involved to achieve the required performance.



Fig. 1.4 Typical production cycle of unfired bricks

Unfired bricks can be cured via several methods, such as air curing, water curing, and moist curing at atmospheric pressure and via autoclaved curing at elevated pressure. Air curing can be done at ambient temperature (ambient air curing) or elevated temperature (oven

curing). At ambient temperature, bricks can be wrapped with plastic sheets (airtight curing) or put under wet gunny beg (wet burlap curing) to conserve the moulding moisture in the bricks. In some studies, airtight samples were further put in moist conditions to ensure minimum moisture loss. Few researchers, however, varied the medium or the other curing parameters during the curing and adopted special multistaged curing strategies to produce unfired bricks. In this article, such curing techniques were referred to as hybrid curing techniques.

Air curing / air-tight / wet burlap curing at ambient or elevated temperature

Curing at ambient temperature in the air, with the relative humidity (RH) similar to natural environmental conditions can be termed as ambient air curing, whereas at elevated temperature, the air is relatively dry, and the curing techniques are termed as oven-dried curing. In some studies [39, 56, 89], ambient air curing was done at 23-25 °C whereas in studies [63, 65, 67, 77], oven-dried curing was done at 35-115 °C. In airtight curing [26, 29, 41], surrounding conditions may be similar to air curing/moist curing except for the interaction of the material with the surrounding air/moisture. In studies [12, 33], airtight curing was done for the whole curing duration whereas, in a study [11], samples were subjected to water curing for 1 day after 27 days of airtight curing. In some studies [7, 13, 16], samples were put under wet gunny bags at ambient temperature, to minimize the evaporation loss.

Moist curing at ambient and elevated temperature

Moist curing means curing of bricks at a high relative humidity (RH) (95%-100%) and ambient temperature. At elevated temperature, it can be termed as steam curing. In studies [44, 46, 61], moist curing of bricks was done for 28 days or until the testing at 95% or greater RH and a temperature between 20-27 °C. In some studies [12, 80, 92], steam curing was done for a particular duration ranging between 6 h to 90 days or until the testing at 95% or greater RH and a temperature between 40-75 °C. In some studies, bricks were kept in air for 1-2 days to achieve
sufficient green strength [12, 16, 44, 61, 80] whereas, in other studies [11, 31, 46, 92], bricks were directly subjected to moist/steam curing.

Water curing at ambient or elevated temperature

In water curing [48, 53, 60, 63], initial curing was done for 24 h either in the air or in the moist condition to achieve sufficient green strength, and after that, samples were put either in the water or in limewater for curing at 20-24 °C. In a separate study [42], long initial curing for a week was done under moist wet burlap bags before subjecting to water curing, whereas, in another study [52], water immersion duration was taken as variable between 0-28 days.

Autoclaved Curing

Many studies [24, 47, 49, 51, 57, 58, 62, 90] used autoclaved curing for unfired bricks, as shown in Table 1.7. In autoclaved curing, initially, bricks are kept for a pre-autoclaving duration to achieve sufficient green strength. After achieving green strength, bricks are put for autoclaving for a particular duration. Autoclaving duration includes the total time required for ramping up, holding and ramping down. In some studies [13, 49], pre-autoclaving duration was kept constant as 24 h, whereas some studies [24, 62] varied this duration in the range of 6 - 48 h and 1 - 11 days respectively. The majority of studies specified only the holding duration except [51], which specified the ramping up and ramping down durations as 2 h and 3 h, respectively. In some studies [24, 47] holding duration was kept constant as 4 h whereas, in other studies [49, 51, 57, 58, 62, 90], the holding duration was taken as a variable in a particular range between 2 - 14 h. In a study [24], the steam temperature was kept constant at 130 °C, whereas in another study [51], the steam temperature was varied between 170 °C and 190 °C. Constant steam pressure was considered in [24,47] as 0.14 MPa and 0.80 MPa respectively whereas, in other studies [49, 57, 58, 62, 90] the steam pressure was taken as a variable in a particular range between 0.5-2.0 MPa.

S. No.	Author/(s)	Curing strategy	Curing duration	Curing medium	Curing parameter (temp./pressure/RH)	Ref.
1	Binici et al.	Wet burlap air curing	7 days	Air		[7]
2	Pimraksa and	1.1 Initial curing	1 – 11 days	Moist	23 °C, and 90% RH	[24]
	Chindaprasiti	1.2 Autoclaved curing	4 h	Steam	130 °C, and SP- 0.14 MPa	
3	Reddy and Gourav	1.1/2.1 Initial curing	24 h	Air		[16]
		1.2 Steam curing	Till testing age	Moist	80 °C	
		2.2 Wet burlap curing	Till testing age			
4	Miqueleiz et al.	Airtight curing in a moisture chamber	Till the end of the curing	Airtight		[26]
5	Kumar	1.1 Ambient air curing	1-2 days	Air	27±3 °C, and RH > 80%.	[28]
		1.2 Wet burlap curing	Till the sufficient green strength	Air		
		1.3 Water curing	Till one day before testing	Water	23 ± 2 °C	

 Table 1.7 Curing strategies adopted by researchers in previous studies related to unfired bricks

		1.4 Air drying	For 1 day just before testing	Air	23 ± 2 °C	
6	Oti et al.	Airtight moist curing	Till the end of the curing	Airtight	At RT (20 °C).	[29]
7	Singh and Garg	Ambient to elevated temp. in moist conditions	Up to 90 days	Moist	27 °C – 50 °C, and 90% RH	[31]
8	Wattanasiriwech	1. Wet burlap curing without water immersion	Closed in a plastic box covered with damp cloth, and water sprayed every 24 h till testing			[32]
		2. Wet burlap curing with water immersion	Immersed for 5 min. in water every 24 h till testing			
9	Shakir et al.	Airtight wet burlap curing	Overnight cured in a plastic box	Airtight	22 °C, and RH>95%	[33]
10	Izemmouren et al.	1.1/2.1 Initial curing	First 24 h	Airtight		[12]
		1.2 Airtight curing	28 days – 18 months	Airtight		_
		2.2 Steam curing	6 – 30 h.	Steam	75 °C	_
11	Zhou et al.	1.1 Wet curing and sprinkled water thrice a day	1 day	Air		[37]
		1.2 Ambient air curing	2 days	Air		_

		1.3 Elevated temp. air curing	2 h	Air	180 °C	
		1.4 Ambient air cooling		Air	RT	
		1.5 Water curing	1 h	Water		
		1.6 Ambient air drying		Air		
12	Algin and Turgut	1.1 Initial curing	24 h	Air		[48]
		1.2 Lime saturated water curing	28 days	Water		
		1.3 Elevated temp. air curing	24 h	Air	105 °C	
13	Cicek and Tanriverdi	1.1 Initial curing	24 h	Air		[49]
		1.2 Autoclaved curing	3 h - 12 h	Steam	SP- 0.5 - 2 MPa	
14	Fang et al.	Autoclaved curing	Holding time (5h - 9h), ramping up (2 h), and ramping down (3 h)	Steam	170 °C - 190 °C	[51]
15	Guettala et al.	1. Humid curing	28 days	Airtight	70% RH	[11]
		2.1 Humid curing	27 days	Airtight		
		2.2 Water curing	1 day	Water	20 °C	

16	Kumar	1.1 Initial curing under wet gunny bag	7 days	Air		[42]
		1.2 Water curing	Until testing	Water	23±2 °C, and 50 °C	
17	Ling and Teo	1. Water curing	28 days	Water and	24±2 °C, and 100% RH	[52]
		2. Partial water curing-2 days		air	24±2 °C, and 100% RH in	
		3. Partial water curing-6 days			water; 26 ± 3 °C, and 73 $\pm5\%$ RH in air	
		4. Air dry curing		Air	26±3 °C, and 73±5% RH	
18	Liu et al.	1.1 Initial curing	24 h	Moist	20 °C, and 100% (RH)	[53]
		1.2 Water curing	Up to 28 days	Water	20 °C	
19	Muntohar	Airtight curing under moist condition	28 days	Airtight	30 °C	[41]
20	Naganathan et al.	1.1 Initial curing under wet cloth	2 days	Air		[44]
		1.2 Moist curing	Until testing	Moist	22 °C, and 95% (RH)	
21	Shon et al.	1.1 Initial curing	24 h	Moist	23 °C, and 100% (RH)	[56]

		1.2 Ambient air curing	Till the testing age	Air		
22	Sodupe-Ortega et al.	1.1 Initial curing	24 h	Air		[60]
		1.2 Water curing	Until testing	Water	$20 \pm 1 \ ^{\circ}\mathrm{C}$	-
		2. As per EN 12390-2			$23 \pm 4 \ ^{\circ}\mathrm{C}$	-
23	Xu et al.	1.1 Initial curing	24 h	Air	24 °C	[61]
		1.2 Moist curing	Until testing age	Moist	20 ±1 °C, and 95% (RH)	-
24	Yang et al.	Autoclaved curing	4 h	Steam	SP- 0.80 MPa	
25	Zhang et al.	1.1 Initial curing	6-48 h	Air	Air 25–30 °C, and 80%-90% (RH)	
		1.2 Autoclaved curing	Holding (3-8 h)	Steam	SP- 0.5 - 2.0 MPa,	-
26	Zhao et al.	1.1 Initial curing-I	2.5 h	Airtight		[58]
		1.2 Initial curing-II	Up to 24 h	Air		-
		1.3 Autoclaved curing	4-9 h	Steam	SP: 0.8-1.8 MPa	-

27	Subramaniaprasad et al.	Wet burlap air curing	28 days	Air		[13]
28	Torkaman et al.	1.1 Initial curing	24 h	Airtight		[39]
		1.2 Ambient air curing	Up to 28 days	Air	25±1 °C, and 60±5 % (RH)	
29	Turgut	1.1 Initial curing	24 h	Air	RT	[63]
		1.2 Lime water curing	Up to 28 days	Lime water	22 °C	_
		1.3 Elevated temp. air curing	24 h	Air	115 °C	_
30	Malhotra and Tehri	Ambient moist curing	28 days	Moist	27±1 °C, and 95% RH	[46]
31	Çiçek and Çinçin	Autoclaved curing	2 h - 8 h	Steam	6 – 12 Bar	[57]
32	Hwang and Huynh	Ambient air curing	Until testing age	Air	35 °C, and 50 % RH	[65]
33	Ahmari and Zhang	Elevated temp. air curing	7 days	Air	90 °C	[67]
34	Abdullah et al.	Elevated temp. air curing	1 h – 24 h	Air	40 °C - 95 °C	[77]
35	Khater et al.	1.1 Initial curing	For first 24 h	Air	RT	[80]

		1.2 Elevated temp. moist curing	Until the testing	Air	40 °C, and 100% RH	
36	Degirmenci	Ambient air curing	Until testing age	Air		[89]
37	Zhao et al.	1.1 Initial curing	6 h	Airtight		[90]
		1.2 Autoclaved curing	4 h - 14 h	Steam	SP: 0.75 - 1.75 MPa	
38	Kim et al.	Elevated temp. moist curing	3 days, 7 days and 28 days	Air	60 °C, and 99% RH	[92]

Note: 1,2,3...denotes a variety of curing methods adopted, whereas 1.1,1.2,1.3.... denotes the different stages of the curing method 1.

Overall, in this section, following key observations can be made.

- Ample studies are available related to optimizing the curing parameters of autoclaved curing. In limited studies, hybrid curing techniques have also been attempted.
- The use of low-cost hybrid curing conditions at ambient or low elevated temperature is expected to be future research trend to overcome the limitation of autoclaved curing regarding the high initial infrastructure cost to stabilize the waste incorporated unfired bricks.

Considering the observations made in the section 1.2.1, locally available ash waste that has potential to improve the economic viability and sustainability of unfired bricks, have been explored in the present study for utilization in unfired bricks. Therefore, in the present study, the literature on suitable waste characterization protocol has been kept limited to the industrial ash characterization. The literature review related to characteristics of industrial ash and suitability of characterization protocol is discussed in the next section.

1.3 Literature review on industrial ash characteristics and suitable characterization protocol

Thermal energy is one of the significant sources of energy which consumes coal as a major fuel. Stepping towards the sustainable energy sources, in India, Ministry of Power issued a separate policy for utilization of bio-briquettes (primarily of agriculture residue) for co-firing in pulverized coal-fired boilers which suggest incorporation of 5% - 10% blend of biomass pellets with coal in all coal-based thermal power plants for electricity production [100]. However, in industries, these bio-briquettes are frequently used as independent fuel like wood and coal in coal-fired boilers. Incineration of bio briquettes or wood commonly termed as biomass results in big amount of ash (further termed as biomass ash) that is disposed in landfills [101]. Biomass ash has large variations in chemical composition and morphology, depending on type of biomass, soil in biomass growing area, scale of the combustion

facility and other incineration parameters [101, 102]. Biomass ash has its application in development of various cementitious products [103– 105]. However, presence of unburnt carbon is a concern that affects the workability in cementitious materials and limits its utilization [106]. In case of concrete, higher doses of superplasticizers are required to encounter the high amount of unburnt carbon [107, 108].

Fuels (Coal, wood or agriculture residue-based briquettes, etc.) are selected and fired at different firing temperatures based on the required temperature profiles and economic feasibility in industries, which creates a significant variation in characteristics of ash generated among various industries. Considering the recent shift towards sustainable energy policies, and the considerable difference in the industrial ashes depending on the source, understanding of industrial ash characteristics originated in different manufacturing setups is highly required to use them in masonry construction products. Currently, fly ash generated in thermal power plants is being utilized in many construction materials such as cement, concrete, fly ash bricks, and building blocks [44, 109–111]. It has become an important raw material for various industrial ash in India is still limited due to lack of required technical data and non-fulfilment of technical standards.

As per Indian technical standards, firstly, fly ash generated only in coalfired boilers is allowed to use as pulverized fuel ash in lime based fly ash bricks. Pulverized fuel ash shall conform to the physical and chemical requirements specified in IS 15648 [113] for use in limepozzolana mixture applications. In chemical requirement terms, it must contain minimum overall 70% of SiO₂ + Al₂O₃ + Fe₂O₃ out of which SiO₂ must be 35% (with at least 20% reactive silica) and maximum 5% MgO, 5% SO₃, 2.5% Na₂O, 0.05% total chlorides and 5% loss on ignition (LOI) value [113].

Loss of Ignition (LOI) value is generally considered as a primary parameter and a low-cost tool to get an idea about carbonaceous matter present in the fly ash. However, LOI value may include the loss due to oxidation of carbonaceous matter, the loss due to decomposition of carbonate mineral, and the gain due to the oxidation of any ferrous present. Therefore, LOI value may not confirm the presence of unburnt carbon, and a more precise characterization tool is required to confirm the same. As per Indian standards [113], fly ash must have a minimum of 250 m²/kg specific surface area, a minimum of 3.5 N/mm² lime reactivity, and maximum 40% particle retention on 45-micron sieve on wet sieve analysis. However, industrial ash generated with poor combustion efficiency has improper particle size and high amount of unburnt carbon [114].

Deviation in properties of fly ash from the limits specified in IS 15648 [113] confines its utilization and is considered as a potential environmental hazard if not disposed safely. However, they may be processed, beneficiated, and segregated to modify their physical or chemical characteristics. Suitable technologies such as removal of unburnt carbon, sieving /grading for fineness, grinding for reducing particle size, thermal treatment, and blending of fly ash of different qualities may be applied to improve the quality of fly ash. Selection of suitable technology for the necessary improvement require a comprehensive detailing of physical, chemical and mineralogical properties of fly ash. Foner et al. [115] suggested a suitable beneficiation process, to produce a high-quality, reproducible material based on characteristics of coal fly ash collected from Israeli power plants.

Although in cases where fly ash confirms to specifications, Indian standard [116] does not provide any guidelines for mix design or percentage utilization of fly ash in lime based products. The standard [116] only specifies the physical characteristic requirements for different classes of manufactured fly ash bricks. Therefore, to utilize the industrial ash in lime-based bricks only with this criteria, large number of trial mixes are to be checked to determine the optimum quantity of ash incorporated which is not economically feasible. Since physical characteristics of fly ash bricks depend on mix composition and quality of raw materials, a utilization strategy can be suggested after thorough characterization of fly ash, including its mineralogical characteristics.

Characteristics of fly ashes generated in coal-fired thermal power plants have been studied [112, 114, 115, 117–124] extensively in various parts of the world to suggest potential utilization. Sarkar et al. [114] carried out a comprehensive characterization study on fly ash collected from a thermal power plant in eastern India. They fractioned the fly ash in five groups (+104 μ , -104 μ - +66 μ , -66 μ - +53 μ , -53 μ - +45 μ and -45 μ) based on size and further separated in two subgroups (magnetic and nonmagnetic component) using magnetic separator. They presented the potential utilization of various fractions of fly ash based on their morphological, mineralogical features, and physicochemical properties.

Studies are also available on the characterization of biomass ash. Rajamma et al. [125] investigated the two biomass fly ash samples collected from electrostatic precipitator of a biomass thermal power plant and of a co-generation plant situated in Portugal. They also characterized cement pastes and cement mortars by replacing ordinary Portland cement (OPC) with varying amounts of biomass fly ashes (10%, 20%, and 30%) along with dry biomass fly ashes. They concluded that up to 20% of biomass ash could be incorporated as cement replacement in cement-based mortars. The above studies [114, 125] clearly imply that evaluation of potential utilization of fly ashes (coal based thermal power plant ashes or biomass ashes) based on a comprehensive characterization is a well-established approach adopted by the researchers. Most of the studies discussed above are focused on the utilization of ashes as cement replacement. However, the use of fly ash in lime-based water/air cured and steam cured products has been relatively less studied.

Fly ashes may differ significantly in their chemical composition. Levandowski and Kalkreuth [117] determined the mineralogical and chemical composition of bottom ash and fly ash collected from Figueira Power Plant in Brazil. The ash collected at the same time with the same coal feed from cyclone separator, mechanical hoppers, conveyors, and bottom ash tank was found to have significantly differed in quantitative chemical composition. It implies that to incorporate such a variable compositional compound in construction material, it requires rigorous characterization before use.

Traditional destructive chemical characterization using the titration method requires enormous time and high-cost consumable chemicals. Owing to the variable characteristics of fly ash, quick and non-destructive characterization methodology are highly necessary for the easy incorporation of such ashes. In a study, Malik et al. [17] determined the chemical composition of fly ash collected from nine different plants of NTPC, India. They used energy dispersive X-ray Fluorescence (XRF) spectrometry and found it to be a useful tool for analysis of fly ash. It may be noted that the particle size of the samples significantly influences the results of XRF analysis for heterogeneous powdered samples such as fly ash. However, they followed a controlled procedure (cleaning, fine grinding, and sieving the fly ash through 45 μ mesh) to preserve the homogeneity among samples.

Determination of the mineralogical composition of fly ash using XRD is not new. XRD is a powerful technique to identify crystalline phases, though it only detects the phases when they are present in sufficient quantity [126]. Since the reactivity of fly ash depends on the amorphous part as well as reactive crystals of the fly ash, assessment of reactivity of fly ash using only XRD merely implies the true reactivity of fly ash. Crystal such as mullite are not so reactive, and their presence significantly hinders the reactivity of fly ash, whereas the presence of reactive crystals such as anhydrite, hematite increases the reactivity of fly ash. Additionally, FT-IR is useful for conformance of mineral phase identified using XRD and to identify the additional bonds present due to amorphous phase present in the fly ash. Therefore, collective use of nondestructive characterization techniques such as Energy Dispersive X-ray (EDX) spectroscopy, Powder X-ray diffraction (XRD), and Fourier transform infrared (FT-IR) spectroscopy may give some useful insights about the materials [127]. However, this will still have certain limitations when it comes to the conformance of unburnt carbon present in industrial ashes.

Raman spectroscopy is a quick, non-destructive characterization tool that does not require any specific sample preparation and widely used by researchers [118, 119, 128–130] for conformance of amorphous carbon present in the fly ash. In a study, Garg and Wang [128] characterized three fly ashes with different CaO content, OPC, and their blended pastes to follow the hydration mechanism up to 56 days. They assessed the pozzolanic reactivity of fly ash using advanced characterization techniques of Raman spectroscopy and compared with the results obtained from the strength activity index test. It is interesting to note that fly ash-I (SiO₂-29.2%) with LOI (0.4%) and OPC (SiO₂-20.2%) with LOI (1.1%) do not show any peaks of D band and G band of carbon whereas in fly ash-II (SiO₂-55.9%) with LOI (0.58%), and in fly ash-III (SiO₂-47.6%) with LOI (3.82), broad dominating peaks of D band and G band of carbon were clearly visible. The broad peaks are solely attributed to the presence of carbon neglecting the significant variation in percentage silica in materials. It may be noted that the majority of studies [118, 119, 128–130] related to the characterization of fly ash using Raman spectroscopy have considered only low LOI fly ashes. However, the presence of amorphous carbon in high amount hinders the reactivity of fly ash significantly. Therefore, the study of Raman spectra can give further insights by confirming the presence of amorphous carbon in characterization of high LOI industrial ashes.

The strength activity index is an essential parameter as per ASTM C618 [131], which allows coal fly ash to use in concrete. In a study carried out by Foner et al. [115], two different fly ashes (South African and Columbian) collected from Israeli power plants were examined for their mineralogical, chemical, physical and other technical properties. They

compared the fly ashes based on the strength activity index to use in concrete. In another study, Fernandez-Jimenez and Palomo [120] characterized five different Spanish fly ashes to determine their potential for alkali activation. They found that all investigated fly ashes are suitable to be alkali activated. They also demonstrated that reactive silica and vitreous phase content are the critical factors for their potential reactivity. The above studies [115, 120] were carried out to evaluate the direct reactivity parameters of fly ash for use in concrete and in alkali activated materials. Lime reactivity was not evaluated in above studies [115, 120] as it was not required to be evaluated to use fly ash in cement based and alkali activated materials. However, to use industrial ash in lime based fly ash bricks, lime reactivity potential of industrial ashes is an important parameter as per IS 15648 [113] and needs to be evaluated accurately.

Overall, in this section, following observations have been made.

- Majority of characterization studies available in literature are for ash generated in thermal power plants, whereas characterization of industrial ash originated in different manufacturing setups has been studied less.
- Industrial ashes are supposed to be more complex than thermal power plant ash for which a robust characterization based experimental programme is required to suggest their utilization in lime-based masonry construction products.
- The utilization of thermal power plant ashes has been suggested based on just the mineralogical characteristics, whereas, to suggest utilization of ash in lime-based masonry products, evaluation of lime reactivity potential is also required.
- Utilization of industrial ash in lime-based products has not picked up due to the unavailability of the required technical data.
- It is to be noted that the conventional LOI test does not truly confirm the presence of carbonaceous matter or specifically the unburnt carbon in fly ash for which Raman spectroscopy can be

used that has been widely used by researchers for conformance of amorphous carbon in the fly ash.

 Considering the limitations and advantages of individual characterization techniques, combined use of different characterization tools such as XRD, FT-IR and Raman analysis is expected to be useful to characterize the industrial ash.

After presenting the review related to complexity of industrial ash and suitable characterization protocol, the literature on stone processing waste and their suitability for upgrading the aesthetics of bricks has been reviewed.

1.4 Literature review on stone processing waste and their suitability for upgrading the aesthetics of bricks

Heavyweight stones feature as masonry materials in old buildings due to their high load-bearing capacity and durability [132–137], and therefore, stay intact after centuries [138–141]. In modern age buildings, there is a shift in the construction technology from load-bearing structures to frame structures. Depending on the local availability of the stones, stone masonry is still used in load-bearing structures [132]. However, in frame structures, lightweight composite bricks such as the fly ash bricks are preferred over stones [142, 143].

Fly ash bricks have an inherent grey colour, which makes it difficult to compete in the consumer market, especially in rural areas. While fly ash bricks can be imparted colour using synthetic pigments, the significantly high cost of such pigments cannot fit into the budget of the low-cost composite materials used for fly-ash bricks (generally not more than INR 1.0 per kg; 1 USD \approx INR 70.0). An attractive method is to develop coloured bricks using some natural or synthetic pigment-laden waste along with cost optimization. Adopting this method, Chandrasekaran and Malathy [144] developed the coloured bricks using colour absorbed fly ash obtained via after-treatment of dye effluent, which resulted in slightly decreased compressive strength. As an alternative method, if coloured stone wastes are used instead of pigment-laden waste, coloured

bricks can be realized that will offer a collective advantage in terms of durability (due to inherent high-durability of source stones), satisfyingly high compressive strength, and the flexibility to customize the brick colour by varying the colour of the stone waste.

Stone wastes are generated as a by-product in dimensional stone processing industries. Dimensional stones are processed and polished for various applications, such as the wall cladding material for the building façade [145]. The western part of India has a vast reserve of estimated ~900 million tons of dimensional stones, which caters to many industries associated with the extraction, processing, and supply of processed stones and stone-based products [146-151]. In these industries, several types of stone wastes are produced, such as boulders, chips, fine aggregates, and sludge [152–155]. While the boulders, chips, and even the fine aggregates (> 1mm size) are recycled and used in the mosaic flooring [156], the sludge wastes are a burden for the stone processing industry [157]. In general, around 20-30% of the total stone wastes generated by the processing plants are in the form of sludge wastes [158], which are simply dumped into the designated dumping yards, where they lie unutilized. With time, the sludge waste loses moisture and turns into the powdered form. This powdered sludge waste is freely available in huge amounts (dump yards) and can be utilized as a filler for brick manufacturing [159].

The viability of powdered stone waste as a filler has been under continuous evaluation in the past decade [160–169]. For instance, Bilgin et al. [168] used the powdered marble waste (ground to less than 40 μ m) with the brick mortar to produce fired bricks, and reported that increasing the marble powder concentration decreases the flexural strength of the bricks. He et al. [169] used the sandstone powder as a mineral additive to study its effect on the compressive strength of concrete reduced by at most 35 % on replacing 50 wt. % of the cement with sandstone powder. However, this reduction in the compressive strength

could be compensated by the adding 5 wt.% of silica fume. Recently, Tressmann et al. [170] proposed the use of marble powder as an alternative filler for building paints. Some studies [171–174] have used stone wastes for developing different composites, while some other studies [175–177] have developed coloured mortars using different industrial wastes. However, none of these studies has assessed the viability of stone wastes for producing coloured bricks. However, to realize coloured bricks with the desired properties, the binder matrix must be selected carefully to achieve the required compressive strength and to maintain the product aesthetics, the factors which may increase the cost of the bricks.

Silica and alumina rich materials like fly ash and ground granulated blast-furnace slag (GGBS) are stabilized using chemical-based binders (strong alkali solution) such as a mixture of alkali hydroxide and alkali silicate solutions (in most cases) [178, 179]. The synthesized materials are known as geopolymers and alkali-activated materials. Recent studies [180–186] have shown huge potential to utilize high waste volume using chemical based binders. In case of chemical binder, the colour of the binder matrix depends on the colour of the solid precursor. For instance, GGBS is an industrial waste of light grey colour, and blending of high volume of coloured stone waste with GGBS can be an attractive option to prepare a coloured solid precursor for geopolymer bricks.

On the way to effectively utilize stone waste for producing coloured bricks, the first step is to characterize stone waste. This will help in selecting a suitable binder matrix to achieve the optimum colour properties and compressive strength of bricks. The characteristics of stone waste depend strongly on the composition of the parent stone rock and the machines used in the processing plant [152, 187, 188]. The simultaneous presence of both amorphous and crystalline materials makes the characterization process difficult. The X-ray patterns are used conventionally to determine the mineralogical composition of crystalline materials; however, the FT-IR spectra are more useful to

identify the amorphous elements present in the material. As observed in section 1.3, Raman spectroscopy-based characterization was found suitable for comprehensive and robust in identifying mineral phases in such complex waste materials. Raman spectra are beneficial in obtaining additional information about the presence of amorphous carbon, FT-IR inactive phases (which are Raman active), and corroborating the minerals estimated using the X-ray and the FT-IR spectra of the material [189].

Overall, in this section, following observations have been made.

- It is apparent that stone processing wastes are an attractive option for upgrading the fly ash bricks into coloured bricks as they syndicate the desired properties of durability (typical of stone masonry) and aesthetics (inherently coloured).
- Despite the known potential of stone wastes, the existing open literature lacks comprehensive characterization studies of stone wastes. XRD, FT-IR, and Raman-spectroscopy can be utilized to allow a comprehensive and robust characterization of the complex stone wastes.
- Blending of high volume of coloured stone waste with light grey coloured GGBS can be an attractive option to prepare a coloured solid precursor for geopolymer bricks.

After presenting the review on stone processing waste and their suitability for upgrading the aesthetics of bricks, the literature on existing tools for homogeneity measurement and complexity with reference to unfired bricks has been reviewed.

1.5 Literature review on homogeneity and its measurement with reference to unfired bricks

Any experimental technique is chosen for a specific purpose based on its ability to deliver the desired information with accuracy. The best among all techniques tends to keep evolving so that its applicability can be expanded as per the expansion of other fields. It becomes more important for technological applications where due to advancements therein, the characterization and diagnosis are needed, which are dynamic processes. Characterization tools that can cope up the above challenge can be said a versatile one. Raman spectroscopy, developed based on a light scattering phenomenon [190, 191], is one such technique that has potential applications in the areas across the fields spreading from physics, chemistry, and engineering [192–195]. Developing an analytical tool based on such scientific technique, to resolve the engineering challenges, will be a significant contribution to both the fields of analytical sciences and engineering.

In construction engineering, measuring the homogeneity of construction materials is a key industrial challenge for quality control engineers [196]. The homogeneity can be measured by confirming the presence of its constituent elements uniformly throughout the matrix at any discussed scale. The homogeneity, in such materials, can be considered at two different scales (Fig. 1.5): (i) macroscopic scale and (ii) microscopic scale. Additionally, the homogeneity measuring tools can be classified in terms of physical homogeneity and chemical homogeneity based on the property of the material used to identify its constituent elements in the matrix.





Physical homogeneity is measured based on the distinct physical characteristics of constituents such as particle size, optical reflection, colour, and other hardened properties of a resulting matrix such as

density and pore distribution. Whereas the chemical homogeneity is measured based on the distinct chemical characteristics of constituents such as elemental composition and vibrational characteristics of bonds. At the macroscopic scale, usually physical homogeneity is examined. In construction materials, uniform distribution of aggregates throughout the matrix is considered as a measure of physical homogeneity [197], which is considered essential to achieve optimum mechanical and durability properties in the cementitious mixes [198, 199]⁻ However, in some cases, where the ingredients are having similar physical characteristics, measuring the macroscopic homogeneity is not so easy.

The physical homogeneity, at the macroscopic scale, is often evaluated through the optical image analysis [200], electric resistivity measurements [198], rheological performances [201], and sometimes, can be quantified as the degree of segregation in an easy manner. Researchers have also used some high-end methods based on the gamma-ray attenuation (GRA) [202] and the ultrasonic pulse velocity (UPV) [203] tester to determine the homogeneity of cementitious mixes which only indicate the physical homogeneity at a macroscopic level based on the variation in density and compaction of the material. Besides this, López and Sarli [204] used a different methodology to determine the homogeneity of coloured mortars based on CIELAB (colour space defined by the International Commission on Illumination) and the colour difference formulae. However, CIELAB has certain limitations when it comes to a blended mix having similar coloured materials. In another study, Liu et al. [205] used an imaging method based on X-ray computed tomography and fractal theory to assess the homogeneity of asphalt concrete. Even these methods (CIELAB and tomography) require highend scientific knowledge and sophisticated setup and still has access only to the physical homogeneity at the macroscopic level. There is a scarcity of simple tools measuring the chemical homogeneity at the microscopic level in the literature.

At the microscopic level, scanning electron microscope along with energy-dispersive X-ray (EDX) spectroscopy are generally used to identify the presence of constituents and the chemical composition based on the morphology of particles and the obtained EDX spectra respectively [206, 207]. These tools can measure the homogeneity of the complex hydrated phases (calcium hydroxide and calcium silicate hydrate phases) present in the materials. However, it requires certain sample preparation and measurements need to be carried out in vacuum conditions. Practically, in porous samples, it takes hours to achieve the required vacuum conditions. Therefore, an easy technique is required that can test the chemical homogeneity at the microscopic level in blended building materials to establish the optimized mixing of different compositions, and thus help to ensure the quality of the blended recipe.

On the other hand, the binder phase in the hardened cementitious matrix not only contains the cementitious binding material (cement or lime) but may also contain the silt [208, 209] and other solid additives [210] (e.g., gypsum) with similar particle size. As an example, in the cement industry, cement is dry blended with fly ash, stone wastes, and other pozzolanic materials to reduce the overall carbon footprint of cement [152, 211, 212]. Similarly, in paint industries, stone waste generated from dimensional stone processing industries is used as filler based on the mineralogical characteristics. Such stone wastes may have similar morphology and particle size distribution therein, and it may be difficult to evaluate their homogenous mixing in the presence of pigments through the existing physical imaging technique. The stone waste can be used in a blended mix in a more efficient way if the homogeneity can be ensured chemically.

Raman spectroscopy is a powerful technique for identifying the chemical bonds and their localization in the mix. Therefore, Raman chemical mapping can be a better solution to handle this challenge as materials may be distinguished by spectroscopy based on their mineralogical or chemical characteristics, and the same can be mapped

for being used as readily available in image form for technologists or engineers. This technique is being extensively explored in the field of pharmaceutics and food industry for quality control related applications in the manufacturing of medicinal tablets and instant food mixes [213– 215]. This technique has been evaluated as a process analytical tool to determine the end point of the mixing for pharmaceutical blends [216]. Riolo et al. [216] compared the Raman spectroscopic data with the data obtained by conventional high-performance liquid chromatography (HPLC) method based on the standard deviation analysis and found that the Raman data are more substantial than HPLC ones. Besides this, the analysis of homogeneity based on the high-end technical spectra is difficult to understand by the semi- or non-technical user involved in the construction and allied building product manufacturing industries. Alternatively, the coloured images are easy to understand.

Overall, in this section, following key observations can be made.

- Raman imaging can be evaluated to establish as a simpler and reliable tool to check the chemical homogeneity of the dry blended mix at a microscopic scale, for building construction materials.
- The Raman area maps developed based on chemical characteristics of ingredients may represent the true homogeneity of the mix more accurately up to micro-level and seems easy to understand even for semi-technical and nontechnical people involved in the construction and allied building product manufacturing industries.

In above sections 1.2, 1.3, 1.4 and 1.5, thorough literature review on following focus areas has been carried out.

- Mix proportions and other production parameters related to waste incorporated unfired bricks
- Characteristics of industrial ash and suitability of characterization protocol for complex industrial ashes

- Stone processing waste and their suitability for upgrading the aesthetics of bricks
- Existing tools for homogeneity measurement and complexity with reference to unfired bricks

To maintain the industrial significance of research outcomes, sustainability challenges of unfired brick manufacturing industries has been reviewed.

1.6 Sustainability challenges of unfired brick manufacturing industries

In India, around twenty thousand brick manufacturers are involved in the production of unfired brick manufacturing in different industries. Economic viability is a deciding factor to incorporate any waste as an ingredient in the industry. Most research studies so far have considered waste as a cost-free material, but it is not true from the manufacturer's point of view. Procurement of waste incurs logistic costs to brick manufacturers. In a country like India, most vehicles use diesel as fuel. Since per litre diesel costs INR 70.0 – 80.0 (1 INR \approx 0.014 USD) in India, the average procurement cost is not less than INR 3.0 - 4.0 per ton per km. Importing a raw material from a 200.0 – 300.0 km. distant source, the procurement of even unprocessed waste costs not less than INR 0.6 - 1.2 per kg. In the Indian scenario, the weight and selling price of a typical brick (90 mm \times 90 mm \times 190 mm) range between 2.5 – 3.2 kg and INR 4.0 – INR 6.0 (~INR 1.5- 1.8 per kg) respectively. The average procurement cost for waste (INR 0.6 - 1.2 per kg) is very significant compared to the selling price of brick (INR 1.5 -1.8 per kg).

As the procurement cost of waste mainly depends on the distance between the source of waste and the industry, locally sourced wastes may have better economic feasibility. For local utilization of wastes in unfired brick industries, waste maps should be prepared like the other geographical maps. As shown in section 1.2, unfired bricks have high potential to incorporate different types of wastes. Thus, mapping of the wastes is considered helpful not only for effective waste management but also to resolve for a cost-effective way of sourcing suitable raw materials to be used for producing unfired bricks.

In India, the use of slaked lime for industrial scale manufacturing of fly ash based unfired bricks is a common practice. The slaked lime putty is generally prepared onsite using the tank slaking method as per recommendations of IS 1635 [217]. Tank slaking of quick lime is carried out in big open-to-air tanks with a sufficient quantity of water for 3-4 days [218]. It is difficult to provide a controlled quantity of water for onsite slaking of quick lime to obtain a low moisture content / dry hydrated lime through the tank slaking method. Adding less water results volume expansion of unslaked particles during the curing phase, which may give cracks in finished products [218]. On the other hand, excess water results in bleeding [32] and may imbalance the binder quantity in the finished product. In the rainy season, raw materials like fly ash and stone dust stored in the open area consist of a high amount of moisture. The use of wet slaked lime with other moistened materials may result in excess moisture content, which adversely affects the production of compressed bricks [32] and leads to downtime for days. Additionally, during procurement from distant sources and slaking in open-to-air tanks, partial carbonation of quick lime may occur.

In the Indian technical standard IS 1635 [217], platform slaking method is suggested for slaking of quick lime which provides a dry form of hydrated lime. The lime putty can be prepared by adding a controlled quantity of water to the dry hydrated lime for the required consistency. In India, fly ash brick manufacturing industries come under micro to small scale enterprises and have a low-cost infrastructure set up with a typical investment less than ten million Indian rupees (1 INR \approx 0.014 USD) [219, 220]. Since platform slaking requires a specific manufacturing set up, onsite slaking through this method seems to be uneconomical compared to simply procuring the pre-manufactured dry hydrated lime. Another aspect is related to the cost comparison of different wastes for incorporation in unfired bricks. In India, standard size bricks are sold or purchased in bulk, measured by a certain brick number or volume. So, volumetric cost should normally be considered. However, wastes are procured and incorporated by weight in the bricks. Since the wastes differ in their specific volume and loose bulk density, the wastes procured from a similar distance may have different volumetric cost. Therefore, in a country like India, the wastes should be compared based on their volumetric cost to determine the economic feasibility.

Based on the review of unfired brick manufacturing industries in section 1.6, following key observations can be made.

- Procurement cost of waste has significance in case of low-cost unfired bricks. Therefore, locally sourced wastes have better economic feasibility in unfired bricks.
- The lime putty produced onsite in the tank slaking method has certain industrial challenges that needs a solution.
- Wastes procured from similar distance may cost differently to the manufacturers, for that the wastes should be compared based on their volumetric cost to determine the economic feasibility.

Summary of literature and research significance of the thesis

The literature discussed above in sections 1.2 to 1.6, and discussions held with brick manufacturing industries, the following can be summarized to highlight the research significance of the thesis.

• From the literature reported and industrial challenges discussed in section 1.3, the industrial ashes originated in different manufacturing set up can have more complex characteristics than the thermal power plant ash. The existing technical standards specified for thermal power plant ash have certain limitations for suggesting the potential of industrial ash originated in different manufacturing set up. Based on the literature review, the limitations and advantages of macro-level tests (LOI test and lime reactivity test) and micro-level high-end non-destructive techniques (SEM, EDS spectra, XRD patterns, FT-IR spectra, and Raman spectra) have been understood with reference to characterization of industrial ash. The combined use of these macro-level tests and micro-level characterization tools is expected to be useful to characterize the industrial ash.

Therefore, a suitable experimental programme is proposed in the present thesis for the characterization of industrial ashes accommodating a wide range of LOI values. The suitability of the proposed comprehensive methodology comprising the macro-level and micro-level techniques is accessed for characterization of complex industrial ashes.

- From the literature reported and industrial challenges discussed in section 1.2, the influence of liquid content on the compressive strength of bricks was found inconsistent. Specific studies regarding the mixing methodologies are not available for unfired bricks, though the studies focused on concrete and mortar have shown that optimum moisture content and correct mixing techniques can improve the characteristics of finished products. Therefore, in the present thesis, the optimum mixing sequence and moisture content are investigated to help in selecting the appropriate production methodology for unfired bricks. Based on the literature, two most common mixing sequences reported for unfired bricks are considered to identify the optimum one. The range of workable moisture content (10%-15%) was selected based on the laboratory trials for the studied mix, maintaining the other manufacturing parameters similar to present practice in the industry.
- From the literature reported in section 1.5, measuring the microlevel chemical homogeneity of construction materials is a key industrial challenge for quality control engineers. The existing techniques either access the physical homogeneity at the macro level or require controlled sample preparation and high vacuum

conditions for measuring the micro level chemical homogeneity. Practically, in porous samples, it takes hours to achieve the required vacuum conditions. It is noted that Raman spectroscopy can handle this challenge of identifying and locating the different ingredients of the mix in the non-vacuum conditions.

Therefore, in the present thesis, Raman imaging has been explored to establish a simpler and reliable tool to check the chemical homogeneity of the dry blended mix at a microscopic scale, first time for building construction materials. Such an easy technique can help to evaluate the optimized mixing of different ingredients, and thus help to ensure the quality of the blended recipe.

It is apparent from the literature discussed in section 1.4 that stone processing wastes are an attractive option for upgrading the fly ash bricks into colored bricks as they syndicate the desired properties of durability (typical of stone masonry) and aesthetics (inherently colored). The potential of utilizing the high-volume stone waste to develop the colored mortar is neglected due to deteriorated performance of mortar while utilizing the high-volume stone waste. A possible way is to select the sufficiently high-grade mortar so that the reduced mortar could still satisfy the required performance parameters with the improved aesthetics. However, it may increase the cost. The existing literature lacks in this approach where the high-volume stone waste is utilized to improve the product's aesthetics for getting the economically viable colored bricks of desired performance. A detailed characterization is expected to access the suitability of stone waste and to suggest the possible way for utilizing the stone waste for improving the aesthetics of the unfired bricks.

Therefore, in the present thesis, a comprehensive characterization of different stone wastes is explored. While improving the aesthetics of the unfired bricks using the colored stone waste, the focus has been kept on finding an economically viable and easy-to-adaptable way, considering the existing manufacturing set up of the industries.

The key objectives of the thesis thus decided are mentioned in the next section.

1.7 Objectives

The scope of present study is kept limited to the characterization of locally available industrial ash and stone processing wastes and accessing their potential for utilization in unfired bricks. Regarding production parameters, the present study is kept limited to optimizing mixing sequence and moisture content for waste incorporated unfired bricks. Further, Raman spectroscopy has been established as a tool for measuring the homogeneity of dry blended mix. In the end, economic viability of stone waste incorporated bricks with improved aesthetics have been evaluated. Following are the key objectives addressed in the present thesis work.

- To establish a comprehensive methodology for characterization of industrial ashes (biomass and coal ashes) for potential utilization in unfired bricks.
- To optimise the mixing sequence and moisture content for unfired bricks.
- 3. Characterisation of stone processing waste and their utilisation for value addition in unfired bricks.
- 4. Development of a non-destructive tool for measuring the homogeneity of dry blended mix.
- 5. To evaluate manufacturability and economic feasibility of stone waste incorporated value-added bricks.

1.8 Organization of the Thesis

The research work carried out in Ph.D. thesis has been reported chapter wise as follows.

• Chapter 1 (the current chapter) gives the introduction of sustainable masonry products, relevant literature review for

industrial scale waste utilization in unfired bricks and defines the objectives of the thesis work.

- Chapter 2 presents a comprehensive methodology to characterize the locally available industrial ashes and to evaluate their potential to use them as raw material in masonry construction products.
- Chapter 3 deals with the investigations related to optimum mixing sequence and moisture content for hydrated lime based fly ash bricks
- Chapter 4 presents a comprehensive methodology to characterize the stone processing wastes and to evaluate their potential to use them as raw material in masonry construction products.
- Chapter 5 presents the work related to homogeneity measurement of blended powders using Raman spectroscopy.
- Chapter 6 presents the conceptualization and economic viability of coloured bi-layered bricks. The manufacturability of coloured bi-layered bricks at lab-scale is also demonstrated.
- Chapter 7 presents the conclusion and future scope.

Chapter 2

Characterization of Biomass ash and Coal ash for Utilization in Unfired Bricks

Background and chapter organization

The productive utilization of the vast amount of industrial ash generated is of economic and environmental importance. The use of locally available industrial ash in brick manufacturing gives the two-fold advantage of the reduced cost of fly ash bricks as well as efficient disposal of industrial ash. However, industrial ashes differ in the mineralogical characteristics due to variation in fuel, firing temperatures and ash collection facility among different industries. Highly varying mineralogical characteristics and unavailability of suitable characterization protocol often leads to restricted use in lime based fly ash bricks. To overcome this, a comprehensive characterization methodology and characterization data of locally available industrial ashes are necessary to suggest their utilization in the lime based fly ash bricks.

In this chapter, XRD patterns, FT-IR spectra, Raman spectra, SEM images, and chemical reactivity method have been collectively used for comprehensive characterization of industrial ashes, including their mineralogy, particle morphology, and lime reactivity. A total of six different ashes have been characterized, including two biomass ash and three coal-based ash from local industries, and one coal-based ash from thermal power plant. The primary aim of the study is to assess the suitability of the proposed experimental programme to characterize local industrial ashes and to evaluate their potential to use them as raw material in masonry construction products. The characterization results

of industrial ash presented here are expected to provide helpful insights to evaluate their potential to manufacture masonry construction products.

2.1. Experimental details

Although fly ashes from coal-based thermal power plants are being utilized since decades as an ingredient in lime-based bricks, understanding of the mineralogical composition of different industrial ashes can extend their utilization in brick manufacturing industries. Six different industrial ashes from various sources have been examined for their physical, chemical, mineralogical, morphological, and technical properties and analysed primarily to use them in lime based fly ash bricks.

2.1.1 Materials

Fuels (Coal, wood, or agriculture residue-based briquettes, etc.) are selected and fired at different firing temperatures, based on the required temperature profiles and economic feasibility in industries, which creates a significant variation in characteristics of fly ash generated among various industries. The concern related to quality control of fuels, firing conditions, and ash collection facilities vary from industry to industry based on their production scale, amount of ash produced, infrastructure set up, which indirectly creates a variation in the quality of fly ash.

A total of six representative samples of fly ash from different industries are collected, as shown in Table 2.1. Five ashes from local industries (two biomass ashes and three coal-based ashes) and one coal-based ash from thermal power plant have been characterized. Biomass ash A-I is collected from Bag filter installed at a snack manufacturing industry, which uses agriculture residue-based bio-briquettes in the boiler for heating of eatable oil used for manufacturing of different snacks. The typical furnace temperature in these industries is around ~800 °C. Biomass ash A-II is collected from dust collector installed at a local potato chips manufacturing industry, which uses forest residues such as wood in the boiler for heating of eatable oil used for manufacturing of potato chips. The typical furnace temperature in these industries is around ~800 °C. Coal ash A-III is collected from bag filter installed at a beverage manufacturing industry, which uses coal as a fuel in boiler for the generation of steam required for various operational purposes in the beverage industry. The typical furnace temperature in these industries is around ~750 °C - 880 °C. Coal ash A-IV is collected from an electrostatic precipitator installed at a textile industry, which uses coal as a fuel in boiler for steam generation for various manufacturing processes in the industry. The typical temperature in the furnace is ~850 °C - 900 °C. Coal ash A-V is collected from an electrostatic precipitator installed at graphite electrode manufacturing industry, which uses coal as a fuel in boiler. The typical temperature in the furnace is ~ 1000 °C. Coal ash A-VI is collected from an electrostatic precipitator installed at thermal power plant dedicated to electricity production, which uses pulverized coal as a fuel in coal-fired boiler. The typical furnace temperature is ~1000 °C.

Chemical composition of fly ashes collected from different industries obtained using the energy-dispersive X-ray Spectroscopy (EDX) are as shown in Table 2.2. Variation in fuels (Agriculture residue-based bio briquettes, wood, and coal), firing conditions, and ash collection facilities (dust collector, bag filter, and electrostatic precipitator) created a significant variation in characteristics of fly ash.

Fly och	Bioma	ss ash	Coal ash				
Fly ash	A-I	A-II	A-III	A-IV	A-V	A-VI	
Type of industry	Snacks industry	Potato chips industry	Beverage industry	Textile industry	Graphite electrode industry	Thermal power plant	
Fuel used	Bio briquette	Wood	Coal	Coal	Coal	Coal	
Scale of industry	Small scale	Small scale	Small scale	Medium scale	Medium scale	Large scale	

Table 2.1 Different types of fly ash used in the present study which are collected from Central India

 Table 2.2 Chemical composition (%) of different types of fly ash

Chemical	Fly ash						
compound	A-I	A-II	A-III	A-IV	A-V	A-VI	
Al ₂ O ₃	7.68	0.00	2.82	12.44	21.44	2.55	
CaO	30.68	31.15	16.20	6.00	12.60	13.09	
FeO	13.81	0.00	2.01	6.58	3.18	0.76	
K ₂ O	0.27	0.44	0.00	0.91	0.00	0.42	
MgO	1.18	1.68	0.65	0.00	0.00	2.02	
Na ₂ O	0.64	0.00	0.00	0.00	0.00	0.00	
SiO ₂	34.80	66.74	77.28	73.38	62.42	81.17	
SO_3	10.55	0.00	0.87	0.00	0.00	0.00	
TiO ₂	0.39	0.00	0.00	0.67	0.00	0.00	
ZnO	0.01	0.00	0.19	0.04	0.37	0.00	
Al ₂ O ₃ +FeO + SiO ₂	56.28	66.74	82.11	92.39	87.03	84.48	

The physical and chemical properties of fly ash are presented in Table 2.3. The values of loss on ignition (LOI) and specific gravity have been determined by test methods specified as per IS 1727 [221]. The pH of

different types of ash has been measured after 1-hour agitation using digital pH meter. Suspension of each ash sample has been prepared using distilled water in a 2.5:1 liquid to solid ratio. Electrical conductivity has also been measured using conductivity meter in a similar way. The hydrated lime (Ca(OH)₂) used in the lime reactivity test is classified as "Class C" as per the guidelines of IS 712 [222]. The specific gravity of hydrated lime has been found 2.24. Standard sand used in the experiment is confirmed to IS 650 [223].

Duon outru	Fly ash						
Property	A-I	A-II	A-III	A-IV	A-V	A-VI	
Specific Gravity	2.12	2.27	2.31	2.27	2.26	1.97	
рН	10.94	12.76	4.57	8.05	12.29	6.46	
Electrical Conductivity (µS)	45300	18468	1514	1203	3000	339	
LOI (%)	60.38	23.16	12.18	7.83	10.80	2.22	

Table 2.3 Physical and chemical properties of different types of fly ash

2.1.2 Methodology

For mineralogical characterization, powdered samples of raw fly ash have been oven-dried at 100 °C for 24 hours, to avoid the inference of moisture, before putting to scan. XRD patterns of powdered samples of raw fly ash have been collected in continuous scanning mode at a scan rate of 0.2 s/step & step size of 0.01°, using "smartlab" (make: Rigaku) automated multipurpose x-ray diffractometer. A half gram-powdered sample of each fly ash has been subjected to scan. The mineral phase identification and semi quant analysis have been carried out using X`Pert high score plus software and standard powder diffraction files (PDF) as per ICDD 2003 database [224]. Semi quant composition gives an idea of the quantitative composition of minerals within the fly ash. To identify the bonds, present in fly ash, FT-IR spectra of powdered samples have been collected using "spectrum two" (make: Perkin Elmer) FT-IR spectrometer in absorbance mode. The scans have been recorded over the range of 400-4000 cm⁻¹. Baseline correction has been done automatically. Peaks identified in FT-IR spectra are analysed based on the previous reported literature. Raman Spectra of powdered samples of fly ashes in its raw form as well as after ignition at 1000 °C have been collected using "Labram HR" (make: JY- Horiba) Raman spectrometer in backscattering geometry with 633 nm laser source. For post ignition characterization of fly ash, samples obtained after LOI test have been used. Peaks identified in Raman spectra are analysed based on previously reported literature. Morphology of ash particles has been studied using "Supra 55" (make: Zeiss) Field-Emission Scanning Electron Microscope (FE-SEM). Samples have been pre-coated with copper before analysing them under electron beam.

Further, the lime reactivity of fly ashes is measured in terms of compressive strength as per the procedure specified in the IS 1727 [221]. Lime reactivity denotes the direct reactivity of pozzolanic material with hydrated lime to use pozzolana in hydrated lime-based masonry product application. Class C hydrated lime and standard sand are used in the test. To determine the lime reactivity of fly ash, 50 mm mortar cubes have been cast. The mix designs for six different types of fly ashes are shown in Table 2.4. The mix proportioning are determined as per the guidelines specified in the IS 1727 [221] for the lime reactivity test of fly ash. The mix proportions calculated here differs for individual ash based on the specific gravity and the surface characteristics affecting the water requirement to get a desired flow.

The following procedure has been adopted.

- 1. Determine the value of "M" which is the ratio of specific gravity of pozzolana to the specific gravity of lime used in the study.
- Calculate the proportions of dry materials (lime: pozzolana: standard sand) of the standard test mortar in the ratio 1: 2M: 9 by weight.
- 3. Calculate the amount of gauging water for different mixes, equal to that required to give a flow of 70 ± 5 percent with 10
drops in 6 seconds as determined following the procedure mentioned in clause 9.5.3 of IS 1727 [221].

Note: The quantities of materials are selected for preparing six test specimens as suggested in IS 1727: (i) Hydrated lime: 150 g; (ii) Pozzolana: 300 x "M" g; (iii) Standard sand: 1350 g; (iv) Water: As determined to get the required flow.

Type of ash	Μ	Hydrated lime (g)	Fly ash (g)	Standard sand (g)	Water	Flow (%)
A-I	0.95	150	284	1350	385	71.00
A-II	1.01	150	304	1350	375	69.75
A-III	1.03	150	309	1350	421	74.00
A-IV	1.01	150	304	1350	360	73.50
A-V	1.01	150	303	1350	330	72.00
A-VI	0.88	150	264	1350	260	70.00

Table 2.4 Mix design for lime reactivity of different types of fly ash

The prepared fresh mortar has been adjusted for water content to achieve the required flow $(70 \pm 5\%)$ as per IS 1727 [221]. Cubes have been filled and compacted in three layers with the flowable mortar and put for initial 48 hours under wet gunny bags after covering with cover plates. Demoulding of cubes has been done after 48 hours of casting, and cubes are then put at 50 °C and 90-100% relative humidity for a period of eight days. Samples are bought to room temperature before testing for compressive strength. Average compressive strength of three cubes have been presented as representative lime reactivity of fly ash.

2.2. Results and discussion

2.2.1 XRD Analysis

XRD patterns of different types of fly ash are presented in Fig. 2.1. PDF (ref. no. mentioned in Table 2.5) as per ICDD 2003 database with X`Pert high score plus software have been used to analyse the peaks obtained in diffraction patterns. Various mineral phases identified from these XRD patterns are summarized in Table 2.5 along with their semi quant

composition, highest peak intensity, full width at half maximum (FWHM) value, and respective $2\theta^{\circ}$ angle. It is observed from Table 2.5 that quartz (SiO₂) mineral phase is present as a major constituent in all coal-based fly ash. Similar observations have been reported in previous studies conducted on Indian coal-based ashes [124, 127]. From Fig. 2.1, it is also observed that the intensity of SiO₂ peak is maximum in coalbased ash A-VI (1667.45), which is collected from the thermal power plant, as compared to other coal ashes. The intensity of SiO₂ peak in fly ash A-III (529.12) and A-V (529.24) are almost equal but lower than fly ash A-IV (726.85) and A-VI (1667.45). Crystalline nature can be estimated with the help of full width at half maximum (FWHM) value of respective peak [225]. From Table 2.5, it can be noted that the largest FWHM value (0.2160) of quartz is observed for fly ash A-VI. Highest peak intensity and largest FWHM value point towards the smallest crystallinity of silica in fly ash A-VI. However, it does not guarantee the highest reactivity as other minerals present with quartz also play a significant role in the reactivity. Other than quartz, calcium aluminium oxide (Ca₉(Al₆O₁₈)), anhydrite (CaSO₄) and mullite (Al_{4 54}Si_{1 46}O_{9 73}) are identified in fly ash A-III, A-V, and A-VI, respectively. Partial replacement of fly ash in Portland cement decreases the amount of available reactive aluminates for the reaction [226]. Increase in the reactive aluminates available for the reaction may lead to higher reactivity with lime. Inherent presence of calcium aluminium oxide in fly ash A-III significantly improves the early age strength in lime based fly ash bricks. Anhydrite exhibits hydraulic properties similar to lime [122]. It has been observed by Poon et al. [259] that anhydrite is a better activator for early age strength than gypsum and can be used as an activator for fly ash. The presence of anhydrite in fly ash A-V may enhance the reactivity of fly ash, as well. Mullite hinders the reactivity since it has been classified as a less reactive crystal in a previous study [227]. Semi quant analysis of fly ash A-VI (Table 2.5) shows the comparable presence of mullite (47%) with quartz (53%), which may create a hindrance in the reactivity of fly ash.

Minerals identified in coal based ashes such as quartz, anhydrite, and mullite have been previously reported in many studies [72, 127, 228, 229]. The presence of calcium aluminium oxide is not reported in this form, whereas other mineral phases of calcium oxides and aluminium hydroxides have been reported previously [117, 229]. It is clear from Table 2.5, in wood-based fly ash A-II, calcite (CaCO₃) is identified as a major mineral present along with portlandite (Ca(OH)₂ and sylvite (KCl). On the other hand, in bio briquette based fly ash A-I, sylvite is identified as a major mineral phase along with a comparable amount of aphthitalite ($K_3Na(SO_4)_2$). Inherent presence of calcite and portlandite may reduce the requirement of lime, or it may increase the demand for silica for completion of the reaction. Minerals identified in biomass ashes such as calcite and portlandite were previously reported in wood based biomass ashes [125, 230, 231] whereas sylvite was reported in agriculture residue based biomass ashes [232]. Other sulfate minerals were reported to be in biomass ashes previously [230], however, aphthitalite was not reported as such.

Mineral phases present along with their semi quant composition, and their respective FWHM give useful inferences to evaluate the utilization potential of industrial ash for masonry construction products. It can be understood from the mineralogical analysis that high electrical conductivity of biomass ashes (A-I and A-II) (Table 2.3) is due to the presence of sulfate and chloride minerals. Similarly, in fly ash A-V, due to the presence of sulfate mineral anhydrite, electrical conductivity is more as compared to the other coal-based fly ash samples. It may also be noted that high LOI value of fly ash A-V (Table 2.3) indicates the presence of carbon, while no crystalline carbon in the form of carbonate mineral is identified as such in the mineralogical analysis. In general, absence of carbon in crystalline phase (except fly ash A-II) and high LOI values indicate the likely presence of carbon in amorphous form for which further analysis was carried out using FT-IR and Raman spectroscopy.

Fly ash	Mineral identified	Semi quant (%)	2θ (degrees)	Peak intensity	FWHM (degrees)	PDF Reference no.
A T	Sylvite	52	28.4594	178.32	0.2880	01-072-1540
A-1 —	Aphthitalite	48	30.5829	51.35	0.3360	01-074-1742
A-II	Calcite	69	29.3457	1125.71	0.1800	01-072-1937
-	Portlandite	22	34.0187	390.26	0.2520	01-084-1265
_	Sylvite	9	28.3132	181.03	0.1440	00-004-0587
A-III	Quartz	95	26.6206	529.12	0.0720	01-078-1252
_	Calcium aluminium oxide	5	33.1623	22.59	0.2880	01-070-0839
A-IV	Quartz	100	26.6299	726.85	0.0600	01-086-1560
A-V	Quartz	83	26.6444	529.24	0.0840	01-079-1906
	Anhydrite	17	25.4500	32.01	0.2880	01-072-0503
A-VI	Quartz	57	26.6863	1667.45	0.2160	01-086-1628
-	Mullite	43	26.2935	381.45	0.1080	01-079-1456

 Table 2.5 Mineral phase identified in different types of fly ash



Fig. 2.1 XRD patterns of different types of fly ash

Possible impact of identified mineral phases on the performance of unfired bricks

In biomass ashes (A-I and A-II), sylvite (KCl), Aphthitalite (K₃Na(SO₄)₂), Calcite (CaCO₃), and Portlandite (Ca(OH)₂) are identified. The presence of chloride minerals may affect the durability of cementitious mixes by solubilizing calcium. At high concentrations, chloride may destabilize the portlandite by forming the calcium chlorohydroxy hydrates [233] which may lead to the poor performance of unfired bricks. The influence of aphthitalite on cement hydration has been investigated in a previous study [234]. Inducing the high Na₂O_e content (>1.42%) by aphthitalite restricts the formation of ettringite. The lack of ettringite will influence the strength development and shrinkage compensation of the hardened cement pastes. It has been emphasized that high content of aphthitalite may negatively impact hydration and physical properties of cement. The presence of calcite in pozzolana affects the early age strength of pozzolanic mortars [235].

In coal-based ashes (A-III, A-IV, A-V and A-VI), Calcium aluminium oxide (Ca₉(Al₆O₁₈)), Anhydrite (CaSO₄), Quartz (SiO₂), and Mullite (Al_{4.54}Si_{1.46}O_{9.73}) are identified. Partial replacement of fly ash in Portland cement decreases the amount of available reactive aluminates for the reaction [226]. Increase in the reactive aluminates available for the reaction may lead to higher reactivity with lime. The inherent presence of calcium aluminium oxide is expected to enhance the early age strength in lime-based fly ash bricks. The role of CaSO₄ has been explored by Giergiczny [236] and found the accelerating pozzolanic reactions while using the CaSO₄ in the Ca(OH)₂- fly ash system. Quartz mineral phase are inert in nature as such. However, the amorphousness present in mineral phase makes it reactive which can directly enhance the pozzolanic reactivity of fly ash.

Overall, the use of the XRD technique is beneficial to provide information about the various crystalline mineral phases (reactive and unreactive) in the different samples of industrial ash. However, the inability of XRD to detect amorphous phases is usually the biggest limitation due to which several amorphous minerals can go un-detected.

2.2.2 FT-IR Analysis

The FT-IR spectra of different types of fly ash are presented in Fig. 2.2. Peaks identified in the FT-IR spectra of fly ash have been analysed based on previously reported literature [228, 237-252]. Based on the characteristic vibrational frequencies of bond, minerals identified in section 2.2.1 are confirmed, as shown in Table 2.6. Along with functional bonds of crystalline minerals, additional peaks (Table 2.7) are also observed in FT-IR spectra, which helps in investigation of noncrystalline functional bonds. In fly ash A-I, characteristic peaks of aphthitalite are observed at 446 cm⁻¹, 618 cm⁻¹, 1102 cm⁻¹, and 1194 cm⁻¹ ¹ (Fig. 2.2). Lane [237] reported aphthitalite as the only anhydrous sulfate phase which gives a single, sharp and very strong vibrational component (asymmetric bending of SO_4^{2-}) at 626 cm⁻¹. However, in the present study a sharp shifted peak for asymmetric bending of SO_4^{2-} was observed at 618 cm⁻¹. It may be noted that firstly, in case of aphthitalite v_4 band is likely to be doubly degenerate due to C_{3v} symmetry of sulphate ion [237] but, contrary to it, only single sharp band was noted in a previous [237] as well as in the present study. Secondly, a small peak at 990 cm⁻¹ is also observed in the present study, which was assigned previously to symmetric stretching vibrations of S-O bond in case of C_{2v} symmetry [238]. Combining both the observations together, it might be possible that aphthitalite has partially bidentate SO_4^{2-} ion (bonded by two oxygen atoms) in the form of chelate or bridge structures showing C_{2v} symmetry [238].



Fig. 2.2 FT-IR spectrum of different types of fly ash

Mineral phase	Peaks observed in the present study (cm ⁻¹)	Peaks observed in previous studies (cm ⁻¹)	Reference
Quartz	456-462, 692-694, 776-778, 792-798, 1058, 1086 -1102	458, 778, 796, 1104	Mozgawa et al. [228]
Aphthitalite	446, 618, 990, 1102, 1194	446, 626, 1047, 1105, 1222	Lane [237]
Sylvite	-	-	-
Calcite	712, 876, 1414, 1794	725, 874, 1090, 1409, 1805	Rodriguez -Blanco et al. [241]
Portlandite	3642	3642	Khachani et al. [240]
Calcium aluminium oxide	-	-	-
Anhydrite	594, 678, 1098	510, 596, 619, 687, 882, 1098, 1158, 1200, 1230, 1628	Lane [237]
Mullite	596, 736, 826, 886	456, 567, 751, 882, 1137, 1152	Gören et al. [242]

 Table 2.6 Mineral phases confirmed using FT-IR spectra for different types of fly ash

Table 2.7 Additional peaks observed in FT-IR spectra for different types of fly ash

Fly ash	A-I	A-II	A-III	A-IV	A-V	A-VI
Peaks	772	564, 620,		564	564,612	414, 486,
(cm ⁻¹)		772, 1044,				506, 524,
		1110				562, 584

Sylvite could not be confirmed in fly ash A-I using FT-IR spectroscopy as it is transparent in mid IR region. Other than this, broad peak at 1412 cm⁻¹ and a weak absorption band at 874 cm⁻¹ are also observed, which may be attributed to the presence of carbonate minerals likely in amorphous form.

In fly ash A-II, characteristic peaks at 712 cm⁻¹, 876 cm⁻¹, 1414 cm⁻¹, and 1794 cm⁻¹ of carbonate mineral i.e., calcite are observed. The absorption band at 712 cm⁻¹, 876 cm⁻¹, and 1414 cm⁻¹ can be associated with doubly degenerate planar bending, normal mode out-of-plane bending $(A_2^{"}$ symmetry) [239] and C-O stretching bond vibration for CO_3^{2-} ion respectively. The weak absorption band at 1794 cm⁻¹ is due to $v_1 + v_4$ vibrations of CO_3^{2-} ion. In a previous study [241], vibration bands of crystalline carbonate (calcite) were observed at 725 cm⁻¹, 874 cm⁻¹, 1090 cm⁻¹, 1409 cm⁻¹ and 1805 cm⁻¹ and by comparing this with the vibration bands of amorphous calcium carbonate, it has been concluded that the 725 cm⁻¹ is a characteristic absorption band of crystalline calcium carbonate. Strong peak at 712 cm⁻¹ confirms the presence of calcium carbonate in crystalline form as determined using XRD analysis. In addition to this, the characteristic peak for the O-H bond is also observed at 3642 cm⁻¹ which confirms the presence of portlandite [240]. However, characteristic peaks for sylvite (identified in XRD analysis) could not be assigned in the FT-IR spectrum of fly ash A-II for similar reasons as explained above in the case of fly ash A-I.

In all coal-based fly ash (A-III, A-IV, A-V, and A-VI) samples, quartz is identified as a common mineral phase in the previous section 2.2.1. Absorption band due to asymmetric stretching of bridging oxygen (Si-O-Si) is observed between 1086 cm⁻¹ and 1102 cm⁻¹ in all coal-based fly ash, whereas an additional peak is also observed at 1058 cm⁻¹ in some fly ashes (A-III, A-IV, and A-V). In a previous study [239], this additional peak was also assigned to the same asymmetric stretching vibration of bridging oxygen, however, it might be due to the multiphase presence of silica or intrinsic impurity of other cation in the tetrahedral arrangement of SiO₂. Double peak band is also observed in 776-778 cm⁻¹ and 794-798 cm⁻¹ range in all coal-based fly ash, which represent the symmetric stretching vibration of Si-O-Si (Quartz). Symmetric vibrations of Si-O bond are observed between 692-694 cm⁻ ¹, whereas asymmetric bending vibrations of Si-O bond are observed between 456-462 cm⁻¹ in all coal-based fly ash (except A-VI). In A-VI, a higher intensity peak is observed at 434 cm⁻¹ along with shoulder peaks at 450 cm⁻¹ and 470 cm⁻¹, which may either correspond to shifted peak of Si-O or due to the presence of any other metal oxide bond present in amorphous phase. In a previous study [243], band at 434 cm⁻¹ was assigned to ZnO bond stretching vibration. The presence of characteristic bands (456-462 cm⁻¹, 692-694 cm⁻¹, 776-778 cm⁻¹, 1058 cm⁻¹, and 1086-1102 cm⁻¹) confirms the presence of quartz in all coalbased fly ash samples. However, the shift in peaks and additional peaks indicate the multiphase presence or presence of amorphous phase of silica.

Other than quartz, calcium aluminium oxide, anhydrite, and mullite are identified in coal-based fly ash in the previous section 2.2.1. For calcium aluminium oxide (Ca₉(Al₆O₁₈)), no additional peaks could be assigned in the observed spectra. It may be due to its presence in very low quantity (5% as shown in Table 2.5) or due to overlapping of characteristic peak of Al-O bond with that of Si-O peak in sample A-III. For anhydrite, major characteristic peaks were observed previously at 596 cm⁻¹, 687 cm⁻¹, 1098 cm⁻¹, 1158 cm⁻¹, and 1200 cm⁻¹ [237]. In present study, peaks are observed at 594 cm⁻¹, 678 cm⁻¹, and 1098 cm⁻¹ while the degeneration of other peaks might be due to overlapping in the broad peak between 800 cm⁻¹ and 1200 cm⁻¹ in FT-IR spectrum of fly ash A-V. For mullite, the band at 730 cm⁻¹ and 860 cm⁻¹ are assigned to AlO₄ vibrations and the band at 600 cm⁻¹ and 814 cm⁻¹ to AlO₆ vibrations [244]. In present study, very weak bands at 596 cm⁻¹, 736 cm⁻¹, 826 cm⁻¹ ¹ and 886 cm⁻¹ are observed which confirms the presence of mullite in fly ash A-VI. In previous research, peak at 886 cm⁻¹ was attributed to OH deformation band between 886-888 cm⁻¹ [245]. However, absence

of main peak in the range $3500-3700 \text{ cm}^{-1}$ indicates the absence of hydroxide or presence in too low quantity.

Some additional peaks are also identified, as shown in Table 2.7 which may correspond to either some organic compounds or non-crystalline inorganic materials. In fly ash A-II, peaks at 564 cm⁻¹, 620 cm⁻¹, 772 cm⁻¹ ¹, 1044 cm⁻¹ and 1110 cm⁻¹ are observed. The characteristic peak at 564 cm⁻¹ (previously reported at 560 cm⁻¹) and 620 cm⁻¹ can be assigned to Fe-O bond [246, 247]. Similar peaks in the range 562-564 cm⁻¹ are also observed in fly ash A-IV, A-V, and A-VI. A small peak at 772 cm⁻¹ can be associated with the presence of rocking CH₂ [248]. A similar peak at 772 cm⁻¹ is observed in fly ash A-I too. Presence of 1044 cm⁻¹ and 1110 cm⁻¹ peaks can be associated with stretching vibration of C-O and C-O functional groups (ketones, aldehyde) [249], which are in agreement with high LOI value of fly ash A-II (Table 2.3). In fly ash A-V, a small peak of 612 cm⁻¹ is observed which can be associated with Fe-O bond [250]. In fly ash A-VI, strong peaks of 414 cm⁻¹, 584 cm⁻¹, some shoulder peaks at 450 cm⁻¹, 470 cm⁻¹, and discrete peaks at 486 cm⁻¹, 506 cm⁻¹ and 524 cm⁻¹ are observed. Characteristic peaks at 414 cm⁻¹ and 486 cm⁻¹ can be assigned to In₂O₃ [251]. However, EDX results did not confirm the presence of 'In' which may be due to its presence in trace amount. The band at 506 cm⁻¹ can be assigned to oxygen-deficient Zn-O (previously reported at 505 cm⁻¹) [243], which strengthens the possibility of Zn-O peak at 434 cm⁻¹ or overlapped peak of SiO₂ and ZnO. On calcination of prepared Fe₂O₃, peaks vary between 430-460 cm⁻¹ and between 540-590 cm⁻¹ due to change in phase at different temperatures [252]. In present study, peaks are observed at 450 cm⁻¹ and 584 cm⁻¹ in fly ash A-VI, which might be due to the presence of intermediate phase or complex Fe oxide in amorphous phase.

In brief, minerals identified in XRD analysis such as aphthitalite, calcite, portlandite, quartz, anhydrite, and mullite could be confirmed, whereas sylvite and calcium aluminium oxide could not be confirmed using FT-IR spectra of fly ashes. However, presence of additional peaks has given

further insights about other organic and inorganic bonds present in fly ash, which may play significant role in reactivity of fly ash. It may be noted that similar to present study, an earlier study [228] has also attributed additional peaks in IR spectra to organic and non-crystalline inorganic bonds.

The FT-IR technique was instrumental in detecting the amorphous mineral bond bands and even bond bands of minerals present in traces. The FT-IR spectra further identified the mineral such as quartz, mullite, and anhydrite. The bond band-based classification of these mineral phases as crystalline and amorphous form is generally useful as it defines the mutual exclusivity between the two. Furthermore, the bond band delineation using FT-IR gives insight into the chemical formation of industrial ash and their characteristics. However, it should be noted that although FT-IR was beneficial in detecting the amorphous mineral phases, the carbon-based phases were still not clearly identified in the spectra.

2.2.3 Raman Analysis

Raman spectra of different types of fly ash samples (without thermal treatment) are presented in Fig. 2.3. Peaks identified in Raman spectra of fly ash have been analysed based on previously reported literature [118, 128–130, 253–257]. A broad feature between 77 cm⁻¹ and 100 cm⁻¹ has been observed in all the spectra, which is often assigned as Boson peak. Boson peak is associated with the intermediate-range order in glass and generally present in the frequency range 20 cm⁻¹ and 110 cm⁻¹ [256]. Secondly, broad intense peaks between 1300 cm⁻¹ and 1600 cm⁻¹ have been observed in all the spectra, which can be assigned to G band and D band of amorphous carbon [128]. High Boson peak and broad band due to carbon, diminishes the intensity between 200 cm⁻¹ and 1000 cm⁻¹, due to which identification of glassy minerals in the observed Raman spectra was difficult. In the Raman spectra observed by Garg and Wang [128], amorphous carbon phases were clearly seen in ashes (LOI: 0.58% and 3.82 %), and in spectra of latter fly ash (LOI: 3.82%),

intensity of other mineral peaks was difficult to distinguish. Here, in the present study (Fig. 2.3), similar difficulties have been faced while analysing the Raman spectra of untreated ashes having high LOI values (2.22% - 60.38%). To avoid the Boson peak and to validate the presence of carbon, Raman spectra of post ignited (at 1000 °C) fly ash samples have been collected and analysed in spectral range between 200 cm⁻¹ and 2000 cm⁻¹. Raman spectra of thermally treated samples are presented in Fig. 2.4. In thermally treated samples, peaks for D- & G-band of carbon disappeared, which confirms the presence of amorphous carbon in the original samples. Based on previous studies, Raman peaks of minerals (identified in XRD analysis) are summarized as shown in Table 2.8.

In fly ash A-I, without thermal treatment (Fig. 2.3), very small peaks have been observed at 455 cm⁻¹, 621 cm⁻¹, 1081 cm⁻¹, and 1190 cm⁻¹, whereas in thermally treated sample (Fig. 2.4), clear peaks have been observed at 453, 622 cm⁻¹, 992 cm⁻¹, 1083 cm⁻¹ and 1202 cm⁻¹ which are in good agreement with the Raman spectra of aphthitalite, observed in previous study (452 cm⁻¹, 621 cm⁻¹, 992 cm⁻¹, 1083 cm⁻¹ and 1204 cm⁻¹ ¹) [254]. In fly ash A-II, in thermally treated samples (Fig. 2.4), peaks for portlandite (353 cm⁻¹) and amorphous calcium carbonate/ vaterite / calcite (1076 cm⁻¹, 1091 cm⁻¹, and 1775 cm⁻¹) have been observed, which are in good agreement with literature reported in previous studies [129]. Although vaterite is thermodynamically least stable product [129], however formation of vaterite (during ignition) may be possible due to the partial decomposition of calcite in calcium oxide, and further absorbance of ambient CO_2 which might have resulted in surface carbonation and the formation of transformed phase. Besides, small peaks (1076 cm⁻¹, 1091 cm⁻¹) at a broad stretch indicated the presence of amorphous CaCO₃.

In fly ash A-V, in thermally treated samples (Fig. 2.4), peaks for quartz (203 cm⁻¹, 263 cm⁻¹, 355 cm⁻¹, and 463 cm⁻¹) have been observed, which are in good agreement with previous studies for quartz (202-206 cm⁻¹,

265 cm⁻¹, 355 cm⁻¹, and 463-465 cm⁻¹) [118, 257]. Other than quartz, peaks for anhydrite (401 cm⁻¹, 660 cm⁻¹, and 1008 cm⁻¹) have also been observed. Peaks of anhydrite were observed at 415 cm⁻¹, 497 cm⁻¹, 626 cm⁻¹, 674 cm⁻¹ and 1016 cm⁻¹, whereas peak for gypsum was observed at 1007 cm⁻¹ [128]. The shifted peaks of anhydrite here indicate the possible transformation of anhydrite into gypsum after ignition due to the absorbance of atmospheric moisture.

In thermally treated samples of fly ash A-III, A-IV, and A-VI, the mineral phases present could not be identified due to the strong luminescence observed (Fig. 2.4). It may be noted from EDX results (Table 2.2) that silica percentage is more in these coal ashes. The presence of luminescence only in these coal ashes may be attributed to the presence of amorphous silica in ignited samples.



Fig. 2.3 Raman spectra of different types of fly ash prior to ignition



Fig. 2.4 Raman spectra of different types of fly ash after ignition at 1000 $^{\circ}\mathrm{C}$

Mineral phase	Raman peak (cm ⁻¹)	Reference
Quartz	460	Garg et al. [130]
Aphthitalite	452, 621, 992, 1083 and 1204	Prieto-Taboada et al. [254]
Sylvite	No peaks*	
Calcite	1085	Garg [129]
Portlandite	260, 359, 684	Padanyi [255]
Calcium aluminium oxide	No standard Data	
Anhydrite	~1018	Garg et al. [130]
Mullite	305, 340, 415, 600, 720, 870, 960, 1035 and 1130	Bost et al. [253]

 Table 2.8 Raman Peaks observed in previous studies for minerals identified in fly ash

* Sylvite is transparent in Mid IR region

From the present study, it can be revealed that the presence of high carbon content in biomass ash and coal ash makes it difficult to analyse the samples in the pre ignited stage. Comparison between Raman spectra of without thermally treated samples and thermally treated samples confirmed the presence of carbon in the fly ashes. Besides, Raman spectroscopy was observed to be an efficient method for the identification of minerals in thermally treated samples in case of biomass ash rather than coal based fly ash. Since luminescence was observed in all coal-based fly ash except A-V (less silica percentage as compared to other coal-based fly ash), mineral identification using Raman spectroscopy in post ignited samples was found not so suitable in case of silica-rich coal-based fly ashes. Raman analysis presented advantage of high spatial resolution. The identification of two prominent carbon bands, i.e., D and G highlighted the difference between the different types of ashes used in the study. Furthermore, the identification

of various crystalline and amorphous phases of minerals was also in good agreement with that of XRD and FT-IR spectra.

2.2.4 Lime reactivity and particle morphology

Lime reactivity (LR) of fly ash is an essential parameter that majorly governs the use of fly ash in hydrated lime-based fly ash (HLF) bricks. The LR of fly ash is presented in Fig. 2.5. A total of eighteen Nos. samples, three Nos. for each mix have been tested. LR of A-V was found to be maximum (8.17 N/mm^2) , and that of A-I was found to be minimum (0.082 N/mm²). Not many studies are available for LR of industrial ashes. Only LR of coal based ash collected from the thermal power plant has been reported previously [16, 258] in the range 1.21-4.53 MPa, which are in good agreement with the LR results reported for fly ash (A-VI) obtained from thermal power plant in the present study. The high LR value of A-V will directly contribute to the properties of HLF bricks. Apart from A-V, A-III also qualify as Grade-I fly ash based on LR of fly ash as per IS 15648 [113]. As per IS 15648 [113], the minimum LR requirement to use pulverized fuel ash for lime-pozzolana mixture for air/water cured and steam cured products (at atmospheric pressure) is 3.5 N/mm^2 . However, for lime based autoclaved products, minimum LR requirement is 3.0 N/mm². Hence A-IV qualifies as Grade-II fly ash and can only be used in lime based autoclaved products.



Fig. 2.5 Lime reactivity of different types of fly ash

Biomass ash A-I and A-II have very low LR. The reduced LR might be due to high LOI contents of ash (Table 2.3). In biomass ash, high LOI content is due to the presence of the high amount of amorphous carbon, as shown by Raman analysis of samples. As per the Indian technical standard, IS 15648 [113], maximum LOI allowed is 5%, which restricts all other fly ashes except A-VI to qualify for utilizing in lime based fly ash bricks. Suitable thermal treatment techniques are required to improve the LOI value of biomass fly ashes. The inherent presence of portlandite and calcite in treated fly ash A-II may result in high LR when it is used in combination with other silica-rich ash.



Fig. 2.6 Scanning Electron Microscopic images of different types of fly ash

Similarly, the inherent presence of calcium aluminum oxide (cyclic reaction product of tricalcium aluminate) can be associated with high LR of fly ash A-III. High LR of A-V can be related to the presence of anhydrite. Inherent presence of anhydrite may result in increased

hydration products, which are reflected in terms of high compressive strength in the LR test. Anhydrite worked as an internal activator for the chemical reaction between fly ash with lime. A previous study [259] has already shown that anhydrite is a better activator for early age strength in the cementitious material. However, extended studies are required to understand the exact mechanism and role of anhydrite in increased LR by characterizing LR cubes at different ages.

Fly ash A-VI qualifies in LOI criteria but slightly lags from the required standards of LR, which might be enhanced after selecting the appropriate processing technique based on their physical, chemical, and mineralogical composition. In fly ash A-VI, low LR may be attributed to the presence of mullite; however, to understand the exact role, extended studies are required.

Particle morphology is also known to play a vital role in deciding appropriate utilization strategies of fly ash. Morphology of fly ash particles is studied using scanning electron microscopic images from the utilization point of view. It can be seen from Fig. 2.6 that fly ash particles (except A-IV and A-VI) are irregular in shape. Among these, fly ash particles of A-I, and A-II ash (Fig. 2.6) are observed to be highly porous, which point towards the unburnt fuel particles with fused deposition due to improper burning of fuel. Similar to biomass ash A-I and A-II studied in present study, irregular shaped particles with highly porous nature of woody fly ash have also been reported previously [231, 260]. From Fig. 2.6, it is also observed that fly ash A-III has plate-shaped particles with few deposits, whereas fly ash A-V has abundant fused deposits on irregularly shaped particles. Similar plate shaped particles have been observed by researchers in fluidized bed combustion fly ash with very few spherical glass particles [69, 261]. As compared to these ashes (A-III and A-V), fly ash A-IV has a mixture of spherical and angular particles [245], whereas fly ash A-VI has abundant of spherical particles (Fig. 2.6). Similar spherical shaped particles in coal based ashes have been reported previously [262, 263]

In a previous study [264], in zero slump concrete, higher green strength was reported in the mixes with angular shaped particles as compared to spherical particles. Spherical shape particles are preferred where flow properties are required [265], whereas irregularly shaped particles can be successfully utilized in forced compacted or zero slump masonry products. However, the utilization of irregularly shaped fly ash particles with the required flow properties can be achieved with the help of suitable admixtures. Fly ash is generated during the combustion of fuel and collected through bag filters and dust collectors. The irregular shapes of the particle show improper melting.

In lime-based bricks, low moist mortar is compacted through forced compaction using a compression machine, which does not require any flow properties as such. As spherical particles have less surface area in comparison to irregularly shaped particles, high surface area, and high frictional characteristics may have contributed to high LR of fly ash A-III and A-V (Fig. 2.5). However, the irregular shape of particles may limit its cost-effective utilization in materials having workability requirement.

Fly ash A-III and A-V seem to be more efficient for utilization in lime based fly ash bricks due to their irregular shape, LR, and inherent presence of calcium aluminium oxide and anhydrite minerals, respectively. However, further LR test on treated fly ash (A-I and A-II) is required to comment on their utilization in lime based fly ash bricks. In the case of A-IV and A-VI fly ash, a suitable methodology is required to enhance the LR to utilize in lime based fly ash bricks.

Based on the results obtained, it can be stated that LR is an efficient technique to classify the different types of ashes into different grades and suggest potential utilization capacity of each. Additionally, the particle morphology also provides insight into the particle shape and provides complementary support to the results obtained in LR.

Discussion

The present study characterized the unprocessed biomass ash (A-I & A-II) which have shown low lime reactivity (0.08 -0.39). In a recent study carried out by Eliche-Quesada et al. [266], quartz and calcium carbonate were observed as major mineral phases with small diffraction peaks of calcium oxide in processed biomass ash. In the present study, similar Ca-rich phases have been observed in biomass ash (A-II). They have additionally observed the high amount of Al_2O_3 (9.3%) in chemical composition analysis whereas the peaks corresponding to Al-rich compounds were reported to be absent in the XRD pattern of that biomass ash. The biomass ash was processed (size reduced to 100% passing from 150 µ) to use as fines along with a Ca-rich waste in unfired bricks. Although, the lime reactivity has not been done, the processed biomass ash has shown the potential to utilize in unfired bricks due to the presence of Ca, Al and Si-rich phases.

In another study carried out by Pavlíková et al.[267], similar mineral phases (quartz and calcium carbonate) were observed along with minor peaks of Anorthite (aluminosilicate) in XRD pattern of biomass ash, whereas, iron containing phases could not be detected. In the present study, additional Fe-O phases were detected in FT-IR spectra which are absent in the XRD patterns of the respective ashes.

In a previous study [268] on Indian biomass ash, high LOI (28.4%) was reported and attributed to the poor combustion efficiency of the boiler. Additionally, sylvite was also detected as a minor phase in the XRD pattern of the ash. In the present study, A-II ash has a similar LOI (23.16%) and sylvite mineral was detected in both the biomass ashes.

In a previous study [269], anhydrite containing boiler ash has shown good pozzolanic properties when used with lime. Up to 30% lime/slaked lime have been used in the binary blend to activate the boiler ash. In another study [270], anhydrite has been categorized as active mineral, whereas mullite and quartz are categorized as inert mineral phase. They have categorized Ca-containing glass such as calcium aluminum oxide as semi-active and Glass as pozzolanic based on the individual's or synergetic behavior of mineral phase during hydration- dehydration and hydroxylation- dihydroxylation process of fly ash.

To summarize the discussion, the macro-level characterization revealed the high lime reactivity of industrial ashes (A-III and A-V) having more LOI (10.80% -12.18) as compared to other coal-based industrial ashes (A-IV and A-VI) which are having low LOI (2.22% - 7.83%). This suggests that the macro-level tests are unable to explain the behavior in isolation. Further, the detailed mineralogical characterization carried out using the micro-level characterization techniques revealed the inherent presence of Ca-rich reactive mineral phases such as calcium aluminum oxide and anhydrite in industrial ashes (A-III & A-V) which explained the reason behind the high pozzolanic property of these industrial ashes.

The mineralogical characterization of biomass ashes (A-I and A-II) revealed the presence of both reactive minerals such as portlandite and aphthitalite as well as rocking CH_2 bonds which restricts the pozzolanic property of these industrial ashes. This revealed the confined capability of micro-level characterization techniques to be conclusive in isolation for commenting the pozzolanic reactivity of such industrial ashes. However, the results of macro-level tests such as high LOI (23.16% - 60.38%) and low lime reactivity (0.08 -0.39) brought the clarity about the governing factor (i.e. presence of rocking CH_2 bonds) behind the low reactivity of such biomass ashes.

Overall, a comprehensive characterization methodology comprising the macro-level tests (LOI and lime reactivity test) and micro-level characterization techniques (XRD, FT-IR, Raman spectroscopy and lime reactivity test) has been found suitable for characterization of industrial ashes and instrumental to provide a qualitative potential to use in lime-based masonry products.

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2.3. Summary

In the present study, a comprehensive experimental programme have been suggested for the characterization of industrial ashes accommodating a wide range of LOI values. The experimental programme includes the study of mineralogical characteristics using XRD patterns, FT-IR spectra, and Raman spectra along with study of particle morphology using SEM images and chemical reactivity using lime reactivity test. The qualitative potential of six different industrial ashes (procured from different industries in India) for utilizing in lime based unfired bricks has been evaluated.

The following key observations are made.

- The macro-level characterization revealed the high lime reactivity of industrial ashes (A-III and A-V) having high LOI (10.80% -12.18) as compared to other coal-based industrial ashes (A-IV and A-VI) which are having low LOI (2.22% -7.83%). This behavior required the micro-level characterization for the necessary explanation.
- 2. Different crystalline minerals such as sylvite, aphthitalite, calcite, and portlandite are identified in biomass ashes (A-I & A-II) whereas, in coal-based fly ashes, quartz, mullite, anhydrite, and calcium aluminium oxide are identified as major crystalline phases. The inherent presence of Ca-rich reactive mineral phases such as calcium aluminum oxide and anhydrite in industrial ashes (A-III & A-V) explained the reason behind the high pozzolanic property of these industrial ashes.
- 3. FT-IR analysis of fly ashes has revealed the presence of amorphous inorganic bonds such as FeO, ZnO, and In₂O₃, and organic bonds such as C-O and rocking CH₂ bonds in fly ashes, which could not get identified in the XRD analysis.
- 4. The micro-level characterization of biomass ashes (A-I and A-II) revealed the simultaneous presence of both reactive minerals such as portlandite and aphthitalite, as well as rocking CH₂ bonds that restricts the pozzolanic reactivity of ashes. The macro-level

tests are essential for such industrial ashes to be conclusive about their pozzolanic reactivity and the governing factor. The results of macro-level tests such as high LOI (23.16% - 60.38%) and low lime reactivity (0.08 - 0.39) brought the clarity about the governing factor (i.e., presence of rocking CH₂ bonds) behind the low reactivity of these biomass ashes.

- 5. Mineral phase identification in silica deficient biomass ashes has been carried out successfully using Raman spectroscopy by analyzing Raman spectra of ash in its raw form and after thermal treatment, whereas luminescence has been observed in post ignited samples in silica-rich coal-based fly ashes. The presence of carbon could be confirmed successfully in all samples of industrial ash using Raman spectroscopy.
- Morphological analysis of coal-based fly ashes has revealed that fly ashes containing irregularly shaped particles have more lime reactivity than fly ash consisting of spherical particles irrespective of LOI values (in the low range between 2.22 % -12.18%).

Overall, a comprehensive characterization methodology comprising the macro-level tests (LOI and lime reactivity test) and micro-level characterization techniques (XRD, FT-IR, Raman spectroscopy and lime reactivity test) has been found suitable for characterization of industrial ashes and instrumental to provide a qualitative potential to use in lime-based masonry products.

The evaluation based on the adopted comprehensive methodology suggested the possible utilization of irregular shaped coal-based industrial ashes (A-III & A-V) locally in limebased fly ash bricks without any treatment rather than transporting the low LOI ashes from a distant thermal power plant. Industrial ash utilization in unfired brick manufacturing industries can resolve the ash disposal issue and provide a lowcost resource to the brick manufacturing industries.

Chapter 3

Optimum Mixing Sequence and Moisture Content for Unfired Bricks

Background and chapter organization

In India, lime stabilised fly ash bricks (a type of unfired brick) are gaining popularity against fired clay bricks due to their green benefits. However, the lack of technical guidelines on mixing methodology, and disproportionate moisture content in raw materials adversely affect the performance and production of fly ash bricks.

In this chapter, the investigations related to optimum mixing sequence and moisture content have been carried out for lime stabilised fly ash bricks. In this study, a total of ten brick mixes comprising two distinct mixing sequences at five different moisture contents have been experimentally examined and compared for their physical characteristics. The compressive strength, dry bulk density, water absorption, percentage voids, dynamic modulus of elasticity, impact energy, and drying shrinkage have been taken as parameters for comparison.

3.1. Experimental details

Although lime stabilised fly ash bricks are not new construction materials, there is a general need for literature suggesting a proper mixing sequence and moisture content based on their technical merits. In order to bridge the knowledge gap, an experimental investigation has been designed to compare the mechanical performance of bricks manufactured using two different mixing sequences at five different moisture contents.

3.1.1 Materials

Industrial ash from a graphite electrode manufacturing industry (A-V, showed potential in previous Chapter 2) and commercially available powdered form of hydrated lime are used in the study. Wet sieve analysis, specific gravity, and lime reactivity of industrial ash (further, termed as fly ash) have been observed according to the guidelines of IS 1727 [221], as shown in Table 3.1. Particle size distribution and D₅₀ of fly ash have been measured (Model: Mastersizer 3000; Make: Malvern Panalytical, U.K.) in the range $0.01 - 3500 \,\mu\text{m}$ in dry dispersion mode and are presented in Fig. 3.1. The hydrated lime is classified as "Class C" as per the guidelines of IS 712 [222]. Waste stone dust is used as fine aggregates. The water absorption, specific gravity, and fineness modulus of stone dust have been found 4.3%, 2.93 and 2.52, respectively. Fig. 3.1 also shows the gradation curve of stone dust by which it is classified as Zone-II crushed stone dust as per IS 383 [271].

Characteristics	Unit	Observed value	Requirement *
Particles retained on 45-micron sieve	Percentage	39.88	≤40
Lime reactivity	N/mm ²	8.17	≥3.5
Specific Gravity		2.26	
D ₅₀	μm	17.5	

Table 3.1 Physical properties of fly ash

*As per IS 15648 [113]



Fig. 3.1. Gradation curve of fly ash and stone dust

3.1.2 Methodology

An automated brick manufacturing unit is used to prepare compressed hydrated lime stabilized fly ash (HLF) bricks of standard size 190 mm \times 90 mm \times 90 mm as per Indian standard IS 12894 [116]. Fig. 3.2 shows the flat pan mixer attached to the brick production unit. It can be noted that two rollers are attached to grind the raw materials. Such type of arrangement is more beneficial in removing the lumps in case of wet slaked lime; however, in the present study, dry hydrated lime is used to provide a controlled moisture in the production of bricks.



Fig. 3.2. Flat pan mixer used to produce HLF bricks

Two different mixing sequences of raw materials have been adopted, along with five different moisture contents (M_c). The mixing sequence I is designed to thoroughly mix the binders and bring them to wet conditions before adding the stone dust, whereas the mixing sequence II is designed with the focus on dry mixing of solids for their homogenous distribution in the matrix and the liquid is added after the stone dust. Mixing sequences are named as Three-stage (mixing sequence I) and Two-stage (mixing sequence II) based on the number of stages involved in introducing the raw materials during mixing. In both mixing sequences, a rest time of 15 seconds has been introduced in the last stage of mixing, and final mixing has been done for 45 seconds after the rest time to ensure the homogeneity of the mixes. As shown in Fig. 3.3, a total duration of 240 seconds consists of 180 seconds as mixing time and 60 seconds as resting time equally maintained for both the mixing sequences. Table 3.2 highlights the different stages of the mixing sequences, and Table 3.3 presents the mix composition details.

There are no specific guidelines for the mix design of low-moist mortar used for fly ash based unfired bricks. Based on the past industrial experience and the feedback taken from industries, trial-mix approach has been adopted to select the mix proportions. The mix composition has been decided based on the trials so as to obtain a desired compressive strength of 10 N/mm² as per the CPWD norms for building bricks. For initial laboratory trials, the dry proportions of ingredients are selected considering a nominal ratio of binder (a mix of lime and fly ash) to fine aggregate as 1:3. Further, considering the economic viability of the mix, the lime is kept at a lower side (7.5% by weight of the total mix) and an internal blending ratio of lime and fly ash has been chosen as 0.3:0.7 to achieve the desired targeted compressive strength of the bricks.

	Mixing sequence-	I		Mixing sequence-I	I
Stages	Description	Duration	Stages	Description	Duration
Stage-1	Addition of fly ash and lime	15 s	Stage-1	Addition of fly ash, lime, and stone dust	30 s
	Mixing	45 s	-	Mixing	90 s
Stage-2	Addition of liquid component	15 s	Stage-2	Addition of liquid component	15 s
	Mixing	45 s	-	Mixing	45 s
Stage-3	Addition of stone 15 dust		-	Rest	15 s
	Mixing	45 s	-	Final mixing	45 s
	Rest	15 s			
	Final mixing	45 s	-		
Total mixing time		180 s	Total mixing time		180 s
Total duration		240 s	Total duration 2		240 s

 Table 3.2 Different mixing sequences considered in the present study

Referring to the current industrial practices, the bricks were compressed under a hydraulic pressure of 17 N/mm². Based on the past industrial experience, for the initial trials, the moisture content was varied by weight of the total mix with an interval of 1.25%. After several trials, the operating range of moisture content was selected as 10% -15% for the material proportions used in the study. Below 10%, the mix obtained was so dry, that can not be bound, whereas, above 15%, the mix shows the visual bleeding during the compaction of the bricks. After production, the bricks have been covered with wet gunny sacks, kept in the laboratory environment for 24 hours and then moist cured up to 28 days by water sprinkling method (twice a day).

Sample	Binder		Stone	M _C	Mixing	Liquid to
coue	Fly ash (kg)	Hydrated lime (kg)	(kg)	(%)	sequence	ratio
M1	0.70	0.30	3.00	10.00	Ι	0.40
M2	0.70	0.30	3.00	10.00	Π	0.40
N1	0.70	0.30	3.00	11.25	Ι	0.45
N2	0.70	0.30	3.00	11.25	Π	0.45
01	0.70	0.30	3.00	12.50	Ι	0.50
O2	0.70	0.30	3.00	12.50	Π	0.50
P1	0.70	0.30	3.00	13.75	Ι	0.55
P2	0.70	0.30	3.00	13.75	П	0.55
Q1	0.70	0.30	3.00	15.00	Ι	0.60
Q2	0.70	0.30	3.00	15.00	Π	0.60

 Table 3.3 Mix proportions of hydrated lime stabilised fly ash bricks



Fig. 3.3 Mixing procedure flow chart for different mixing sequences

Sampling, sample preparation and quality control measures

Regarding controlling the mixes in wet conditions, measured quantity of water (by weight of total dry mix) has been added. The mixing has been done for a large batch size between 60-70 kg to minimize the error in moisture content. The wet mix has been additionally checked for uniform distribution of moisture content by evaluating the moulding moisture by oven drying method as per IS 2720 (part II) [272] for three random samples for each mix. Only the mixes within ±5% tolerance limit for the moulding moisture have been considered while selecting the testing specimen. The brick specimens have been manufactured in single size (90 mm x 90 mm x 190 mm) using automated brick manufacturing plant to maintain the uniformity. Specimens with the required sizes have been later produced for different tests using the high precision cutting machine. Every specimen is measured for dimensional accuracy and only the specimens under the tolerance limit, as mentioned in IS 12894 [116] are considered for the testing. Before every test, specimens are again checked for any physical damage for accuracy of the results. No additional surface finishing procedure has been applied before carrying out any test.

Testing Methods

The test for 28 days compressive strength has been carried out on a half brick cubic specimen of 90 mm size as per the recommendations of ASTM C67 [273]. Three specimens have been tested to represent the average compressive strength of bricks. The dry bulk density, water absorption, and percentage voids of 90 mm cubic half brick specimens have been evaluated as per the guidelines of ASTM C642 [274]. The average of three specimens is presented as a representative value for the respective mix. For observing the efflorescence, three nos. full-size bricks have been used as per the recommendations of IS 3495 (part 3) [275]. The SEM images have been taken at two different resolutions (2500X and 5000X) using a scanning electron microscope (Model: Nova NanoSEM 450; Make: FEI, Oregon, USA) to study the homogeneity and interfacial transition zone between stone dust and hydrated paste at a microstructural level for the different mixes.

A non-destructive test has been conducted on full-size bricks (190 mm \times 90 mm \times 90 mm) as per IS 13311 (part 1) [276] to measure ultrasonic pulse velocity (UPV) of hardened bricks. The dynamic modulus of elasticity is calculated from the measured UPV on 28 days cured samples. The following equation is used to calculate the dynamic modulus of elasticity which is used previously by other researchers on similar cementitious materials [277,278].

$$E_d = \frac{\rho V^2}{g} * 10^{-2} \ (1)$$

Where E_d = dynamic modulus of elasticity in GPa

 ρ = density in kg/m³

g = standard acceleration of gravity (9.81 m/s²)

V = ultrasonic pulse velocity in km/s

The impact energy of bricks has been measured by drop test on full-size bricks of 190 mm \times 90 mm \times 90 mm. A steel ball of 1000 grams has been dropped from a fixed height of 1000 mm (Fig. 3.4) on 28 days cured samples. A modified test setup suitable for hardened bricks has been used which is similar to the set up used in previous studies to

determine the impact resistance of concrete specimens [279]. The number of blows for the formation of first visible crack (N_i) and the final failure of the specimen (N_f) has been recorded. The following equation is used to calculate the impact energy of HLF brick [279].

Impact Energy =
$$N_i mgh$$
 (2)

Where N_i = number of drops for first visible crack

m = mass of drop ball in gram

 $g = \text{gravity in m/s}^2$

h = drop height in mm

Test specimens for drying shrinkage have been prepared as per IS 4139 [280]. Twenty-eight days cured bricks of size 190 mm \times 90 mm \times 90 mm have been embedded with 5 mm non-corrosive spherical balls at each end (Fig. 3.5). Wet and dry length of bricks have been measured using the drying shrinkage apparatus with a dial gauge of 0.001 mm accuracy. For observing the wet length of bricks, the specimens have been immersed in water under constant temperature conditions at 27 °C for four days. The wet length has been measured immediately after the removal of the specimen from the water bath in saturated conditions. Specimen have been then dried at 50 °C for 44 hours. Before observing the dry length of bricks, all the specimens have been put in a desiccator for four hours to allow them to reach a uniform temperature of 27 °C. The drying shrinkage is then reported as the difference between the wet and dry length expressed as a percentage of the wet length.



Fig. 3.4 Apparatus used to conduct the drop test



Fig. 3.5 Drying shrinkage brick specimens and length comparator

3.2. Results and discussion

3.2.1 Compressive strength

Fig. 3.6 presents the compressive strength values of different brick mixes. A total of thirty Nos. samples, three Nos. for each mix have been
tested. It can be observed that the moisture content and mixing sequence plays an important role in the mechanical performance of HLF bricks. For mixing sequence I, the lowest compressive strength (9.94 N/mm²) was observed for mix O1 (12.5% M_C), whereas, for mixing sequence II, the lowest compressive strength (11.25 N/mm²) was observed for mix P2 (13.75% M_C). By comparing most of results at certain moisture content, it can be stated that mixing sequence II is more suitable (except for P series) in producing HLF bricks. It can be seen that all brick mixes (except O1) passed the minimum strength values (10 N/mm²) specified for Class 10 laid down by IS 12894 [116].



Fig. 3.6 Compressive strength of HLF bricks

The development of strength in compressed fly ash bricks is governed by the proper mixing of binders and the homogenous distribution of raw materials. In mixing sequence I, the liquid content is introduced to the binder materials only, and stone dust is incorporated after the formation of a moisten binder mix. The addition of water only to the binder materials (without stone dust) results in a high liquid content in the binder, which can create localized pockets of liquid to binder imbalance in finished bricks lowering the compressive strength. For mixing sequence II, the liquid content is introduced to the entire mixed raw material (binder and stone dust), which results in a much more homogenized brick matrix (Fig. 3.7(c,d)), resulting in increased compressive strength. Another possibility is that part of the mixing water might be absorbed immediately by the stone dust in the case of mixing sequence-II, resulting into a drop of the effective water/binder ratio, which usually translates to greater strength. However, it can be commented accurately only after studying about the priority absorption of water by binder and stone dust.

The second aspect of the strength development of brick is the moisture content in the mix. The lower values of effective moisture content might be insufficient to complete the hydration reaction in the binder. On the other hand, higher values of effective moisture content might result in an excessive amount of liquid content, causing bleeding, segregation, or both. The stone dust also slightly governs the effective liquid content of brick mixes. The effect is more visible at 15% moisture content. In mixing sequence II, the stone dust absorbed some of the liquid content and lowered the effective moisture content to an optimum content to complete the hydration reaction. It may be noted that no such notable influence was reported by Prasad et al. [281], in a similar study, where the fine aggregate to binder ratio was 1:3, and there was only 25% of rock dust in fine aggregate. In the present study, the fine aggregate to binder ratio is 3:1, and fine aggregate comprises of 100% stone dust. The stone dust is, therefore, in a much larger quantity in the present study. Due to a high fraction of fine materials present in stone dust (Fig. 3.1), water demand would be more, which seems to be fulfilled at a higher moisture content (15%). The combined action of optimum moisture content (15%) and mixing sequence II resulted in the highest compressive strength value for mix Q2 (13.68 N/mm²).

The mix O1 belongs to mixing sequence-I and having a moisture content 12.5%. In mixing sequence-I, water is added to the binder materials (without stone dust) that results in a high liquid content in the binder. This can create the localized pockets of liquid in the binder and this may

decrease the compressive strength of the bricks. The effect was more visible at an intermediate mix O1.

One of the possibilities behind this observed behaviour can be as follows. The mixes prepared at lower water content (M1 and N1) might not have the enough water to create such localized pockets. Whereas, in the mixes prepared at higher water content, the negative effect of localized pockets might get compensated due to the improved hydration. The effect of improved hydration is clearly visible from the continuous increasing trend in the compressive strength of mixes (O1, P1 and Q1) at higher water content range. However, further studies are required to comment on the exact mechanism behind this observed behaviour.

Fig. 3.7 shows the SEM images of brick specimens. At 2500X magnification (Fig. 3.7 (a)), weak interfacial transition zone (ITZ) and unreacted particles can be observed in sample M1. Furthermore, at 5000X magnification (Fig. 3.7 (b)), voids and cracks can be observed at the ITZ of the stone dust particle and hydrated paste. Due to the presence of unreacted particles, the compressive strength of the final brick product is lower. The SEM image of mix Q2, at 2500X magnification (Fig. 3.7 (c)), shows that the hydrated paste has a better contact area and fewer voids in Q2 mix than M1 mix (Fig. 3.7(a,b)). Furthermore, at 5000X magnification (Fig. 3.7 (d)), hydrated paste is observed to be more homogenized than the M1 mix (Fig. 3.7(a)).



Fig. 3.7 SEM images of HLF bricks: (a) M1 mix at 2500X magnification; (b) M1 mix at 5000X magnification; (c) Q2 mix at 2500X magnification; and (d) Q2 mix at 5000X magnification

3.2.2 Dry bulk density, water absorption, percentage voids, and efflorescence

Table 3.4 presents the values of dry bulk density, water absorption, and percentage voids. A total of thirty Nos. samples for each parameter, three Nos. for each mix have been tested. It can be observed that the dry bulk density is largely dependent on the moisture content than the mixing sequence, as an increase in moisture content results in a more dense HLF brick. An increase in dry bulk density with an increase in moisture content may be due to the favourable conditions provided by high liquid content to assist the hydration reaction of binder and develop a properly compacted brick matrix. Another possible explanation can be that the increase in the water content contributes to better compaction which may have resulted in higher dry bulk density. An earlier study [282] showed that there is an increase in dry density with increase in moisture content up to an optimum moisture content corresponding to maximum dry density, further increase in moisture content resulted in decreased dry density. Since, in the current study, though the decline in dry density has not been observed until the highest moisture content, the optimum moisture content is 15% or more. It may be noted that in the current study bricks with higher moisture content could not be produced as a further increase in the moisture content resulted in bleeding. It can be observed from Fig. 3.8 that moisture content has a more dominant role than mixing sequence in the water absorption. The lowest value of water absorption and percentage voids was observed for Q2 mix (15% M_C), and the highest value was observed for M2 mix (10% M_C). As discussed in section 3.2.1, the lower liquid content in brick mixes inhibits the hydration reaction which results in a poor brick matrix. This poor brick matrix develops a high amount of voids, which increases the overall percentage of voids and water absorption of bricks. In higher liquid content, the water absorption characteristics of stone dust lower the effective liquid content to an optimum level, which facilitates the hydration reactions and restricts the pockets of imbalanced water. The hydration reaction products have an outward growing nature which fills

the voids and limits the ingress of water [283, 284]. The mixing sequence II with 15% moisture content provides such a favorable brick production method, which lowers the percentage void and water absorption of the brick.

Mix	Dry bulk density (kg/m ³)	Water absorption (%)	Percentage voids (%)
M1	1810.81 ± 11.10	17.44 ± 0.11	36.38 ± 0.33
M2	1821.12 ± 7.09	17.56 ± 0.07	36.39 ± 0.05
N1	1835.74 ± 5.75	16.79 ± 0.23	36.02 ± 0.43
N2	1874.15 ± 6.62	15.76 ± 0.19	33.86 ± 0.45
01	1871.73 ± 8.76	15.67 ± 0.34	34.79 ± 0.61
O2	1856.18 ± 12.51	16.37 ± 0.27	34.91 ± 0.48
P1	1866.94 ± 2.39	15.65 ± 0.20	35.14 ± 0.12
P2	1856.92 ± 5.70	16.15 ± 0.11	34.86 ± 0.26
Q1	1867.89 ± 13.39	15.46 ± 0.11	34.80 ± 0.17
Q2	1948.21 ± 11.04	10.93 ± 0.34	27.16 ± 0.30

Table 3.4 Dry bulk density, water absorption and percentage voids of HLF brick mixes



Fig. 3.8 Dry bulk density and water absorption of HLF brick mixes: (a) for mixing sequence I; and (b) for mixing sequence II



Fig. 3.9 Dry bulk density and percentage voids of HLF brick mixes: (a) for mixing sequence I; and (b) for mixing sequence II



Fig. 3.10 The visual appearance of the different sets of bricks after the exposure period for efflorescence

From the results shown in Figs. 3.8-3.9, the water absorption and the percentage voids have been found inversely related to the dry bulk density of bricks. This can be understood by the fact that at higher dry density, the brick matrix will be denser, and the number of voids will be less. Therefore, the possible explanation of compaction for correlating the dry density and moisture content may be applied to the correlation of water absorption and the percentage voids with moisture content.

As observed in Fig. 3.10, no efflorescence was observed in any brick specimen after the exposure period which satisfies the requirement of efflorescence rating (not more than moderate) as per IS 12894 [116]. A total of thirty Nos. samples, three Nos. for each mix have been tested. Therefore, it can be stated that the moisture content (10% -15%) and the mixing sequences considered in the present study do not cause any efflorescence in HLF bricks.

3.2.3 Dynamic modulus of elasticity

The dynamic modulus of elasticity for various brick mixes is presented in Fig. 3.11. A total of thirty Nos. samples, three Nos. for each mix have been tested. It can be observed that up to moisture content 11.25%, the mixing sequences have almost no effect on the dynamic modulus of elasticity. For mixes with higher moisture content (12.5%-15%), the dynamic modulus of elasticity is found higher (except the P series) for mixing sequence II. The highest value of the dynamic modulus of elasticity is observed for the Q2 mix (Fig. 3.11).



At lower moisture content, higher percentage voids lowered the UPV of brick matrix which resulted in low dynamic modulus of elasticity. For mix Q2, the lower value of percentage voids (Table 3.4) in the brick matrix leads to higher values of dynamic modulus of elasticity. Furthermore, the homogeneity of the brick matrix can be assessed by UPV based dynamic modulus of elasticity as the ultrasonic pulse velocity is lowered due to high heterogeneity of poorly distributed grains and incomplete hydration reactions in brick. From the results obtained, it can be stated that the higher moisture content (in the studied range) and proper mixing sequence (mixing sequence II in this study) can provide homogenous distribution of particles in the brick matrix.

3.2.4 Impact energy

Table 3.5 presents the impact energy value of different brick mixes. Fig. 3.12 shows the brick specimens before and after impact loading. A total of thirty Nos. samples, three Nos. for each mix have been tested. It can be observed from Table 3.5 that mixing sequence II is more suitable (except the N series) in improving the impact energy resistance of HLF

bricks. The first crack was always observed in the transient region of the brick. With the increase in the number of drops, the cracks start moving towards the center of the specimen. In a few cases, the crack propagation started from both the transient regions. Similar crack failure patterns were observed by Javan et al. [285] on interlocking bricks during impact loading.

The mixing sequences played an important role in the impact energy resistance of the HLF brick as compared to the moisture content. It can be observed from Table 3.5 that specimens of mixing sequence II endured higher impact energy as well as higher values of N_f . For impact energy, the contact area between hydration products and particles is the major factor in resisting the propagation of crack [286]. As discussed in previous sections, the specimens with higher moisture content and mixing sequence II can have a better contact area between hydration products and the stone dust particles (Fig. 3.7(c, d)). In mixing sequence II, the initial mixing of all raw materials together is the key aspect which resulted in the improved contact area between hydration product and particles. Another factor is that the higher amount of hydration products in the Q2 mix can result in improved hardness of HLF bricks. Considering the mix N1 and N2 as outlier case, approximately 20% more impact energy is observed for mixing sequence-I as compared to mixing sequence-II.

Mix	M1	M2	N1	N2	01	O2	P1	P2	Q1	Q2
N _i	28.33 ± 1.25	$\begin{array}{c} 34.00 \pm \\ 1.63 \end{array}$	33.67 ± 2.36	25.00 ± 1.63	23.00 ± 2.44	$\begin{array}{c} 28.00 \pm \\ 2.44 \end{array}$	25.33 ± 2.05	28.33 ± 1.24	$\begin{array}{c} 28.00 \pm \\ 2.16 \end{array}$	$\begin{array}{c} 35.00 \pm \\ 0.81 \end{array}$
N _f	$\begin{array}{c} 43.00 \pm \\ 1.41 \end{array}$	49.33 ± 1.89	58.33 ± 1.70	50.67 ± 3.09	24.33 ± 1.25	$\begin{array}{c} 38.00 \pm \\ 2.16 \end{array}$	44.00 ± 1.63	46.33 ± 2.87	39.33 ± 1.70	$\begin{array}{c} 44.67 \pm \\ 0.94 \end{array}$
Impact energy (J)	277.95 ± 12.24	333.54 ± 16.02	330.27 ± 23.12	245.25 ± 16.02	225.63 ± 24.03	274.68 ± 24.03	248. 52 ± 20.16	277.95 ± 12.24	274.68 ± 21.19	$\begin{array}{r} 343.35 \pm \\ 8.01 \end{array}$

 Table 3.5 Impact energy values for HLF bricks



Fig. 3.12 Typical failure patterns observed on three samples of one set of HLF bricks; (a) before impact loading; and (b) after impact loading

3.2.5 Drying shrinkage

The values of drying shrinkage for HLF bricks are presented in Table 3.6. A total of thirty Nos. samples, three Nos. for each mix have been tested. All the brick mixes have drying shrinkage values within the limit (<0.15%) specified by IS 12894 [116]. The lowest drying shrinkage is observed for the Q1 mix (15% M_c), whereas the highest drying shrinkage is observed for N1 mix (11.25% M_c).

From the results of drying shrinkage (Table 3.6), it can be observed that the moisture content has a significant effect on the drying shrinkage of the bricks. As discussed in section 3.1.2, drying shrinkage is defined in terms of the percentage change in length during the drying of the bricks from the saturation state to dry state. Drying shrinkage of bricks is usually affected by the amount of water lost during the evaporation, which can be associated with the amount of water present at the saturation state. The higher amount of water lost during the drying resulted in the higher drying shrinkage which can be correlated with the higher values of water absorption at corresponding mixes (Fig. 3.13, considering the results of the Q2 mix as an outlier value, it has been excluded from the reported data in the figure). It may be noted that similar observation was drawn by Searle and Grimsha [287] for the changes in the physical state of ceramic materials on removal of free water.

Other than the water absorption, drying shrinkage depends on factors such as rigid skeleton matrix of bricks, flocculation of particles due to improper mixing, pore size and pore distribution over the surface as well as inside the brick which may result in an inconsistent trend [287]. The inconsistent trend of drying shrinkage observed for mixing sequence-II may be due to the change in dominating factor with the change in the moisture content in the mix.

It can be observed that up to 11.25% moisture content, the drying shrinkage for mixing sequence II is lower than corresponding mixing sequence I, which can be attributed to the stronger brick matrix. The stronger brick matrix can be justified with the corresponding results of compressive strength, as shown in Fig. 3.6.

For high moisture content (12.5% -15%), the values of drying shrinkage for mixing sequence I are lower than those of corresponding mixes of mixing sequence II. As discussed earlier, stronger brick matrix is associated with lower drying shrinkage. Another aspect is that the formation of localized pockets due to improper mixing or the presence of unreacted binder content may result in reduced drying shrinkage due to the flocculation effect [287]. The observed trend can be justified by the combined effect of flocculation and a strong brick matrix.

Mix		M1	N1	01	P1	Q1
Drying	shrinkage	113.58 ± 2.51	126.24	58.35	24.86	23.7
$(10^{-3}, \%)$			± 1.51	± 0.86	± 1.51	± 0.46
Mix		M2	N2	02	P2	Q2
Mix Drying	shrinkage	M2 89.83	N2 50.27	O2 95.42	P2 44.12	Q2 74.75

Table 3.6 Drying shrinkage values for HLF bricks



Result of Q2 mix excluded as an outlier value

Fig. 3.13 Correlation between drying shrinkage and water absorption for different brick mixes

Discussion

In a previous study by Pimraksa and Chindaprasirt [24], maximum compressive strength was observed at an intermediate water content whereas, similar to present study, the highest dry density was observed in the bricks of highest compressive strength. It is noted that those bricks were compressed at much lower hydraulic pressure (3.5 MPa) as compared to the present study (17 MPa) which might decreased the dry density at higher water content rather than bleed out from the mix. In the present study, bricks with higher moisture content were not cast due to visual bleeding observed during compression.

In another study by Wattanasiriwech et al. [32], water content was varied in the range 15%-20% and found the optimum properties at highest moisture content. It is to be noted that those bricks were compressed at 25 MPa during that study.

Apart from moisture content, similar effect of mixing sequence was studied for reactive powder concrete (RPC) by Hiremath and Yaragal [97]. They observed that mixing sequence has significant influence on performance of RPC mixes. They have observed the better flow properties, and therefore better mechanical properties using a four-stage mixing sequence where the diluted superplasticizer is added to the binders only and remaining dry ingredients are added at a later stage.

In another recent study by Hou et al. [288], effect of mixing sequences of nano-silica on hydration and hardening properties of cement basedmaterials were observed. They reported that compressive strength is closely related to the mixing sequence of raw materials.

Similar study on influence of mixing sequence were carried out on different flowable mixes, specifically the mixes containing nano-additives with superplasticizer [289]. However, in the present study, mixing sequence is studied for lime based compressed mix without any superplasticizer, the results of which are difficult to compare directly with the reported works.

3.3. Summary

Experimental studies were carried out to observe the effect of mixing sequences at different moisture contents on the properties of HLF bricks and to subsequently identify the most effective approach to produce HLF bricks within the selected parameters. All brick mixes (except mix O1 with strength values, 9.94 N/mm²) passed the criteria of minimum strength values (10 N/mm²), maximum water absorption (20%), maximum shrinkage (0.15%) and efflorescence (not more than moderate) specified for Class 10 laid down by IS 12894 [116]. The following key observations can be drawn based on the results of the performed experiments.

- A combination of high moisture content (15% in the present study) and mixing sequence II (a two-stage mixing procedure discussed in the study) resulted in the highest compressive strength (13.68 N/mm²) that can be taken as optimum production method to ensure the quality of HLF bricks.
- Microstructure investigation revealed that mixing sequence II and high moisture content (15% in the present study) resulted in improved interfacial transition zone and fewer voids between

stone dust and binder paste, which resulted in increased compressive strength of HLF bricks.

- 3. The water absorption and percentage voids are influenced by the moisture content than the mixing sequence. Furthermore, water absorption and percentage voids inversely correlate to bulk density. Mixing sequence II and high moisture content (15% in present study) resulted in the highest bulk density (1948.21 kg/m³) due to improved matrix as observed in microstructure investigations. Additionally, moisture content (10%-15%) and mixing sequences considered in the present study do not cause any efflorescence in HLF bricks.
- 4. The HLF bricks made with mixing sequence II at high moisture content (15% in present study) showed the highest dynamic modulus of elasticity (8.47 GPa). The HLF bricks made with mixing sequence II showed approximately 20% higher impact energy due to a better distribution of particles and a homogenized brick matrix as observed from microstructure investigations.
- 5. The drying shrinkage is found correlated with the water absorption value of the brick. Higher values of drying shrinkage are observed in the bricks having higher water absorption.

Chapter 4

Characterisation of Stone Processing Waste for Value Addition in Unfired Bricks

Background and chapter Organization

Lime stabilised fly ash bricks (a type of unfired bricks) have an inherent grey colour, which makes it difficult to compete against red coloured fired clay bricks in the consumer market, especially in rural areas. While fly ash bricks can be imparted colour using synthetic pigments, the significantly high cost of such pigments cannot fit into the budget of the low-cost composite materials used for fly-ash bricks (generally not more than INR 1.0 per kg; 1 USD \approx INR 70.0). Stone processing wastes being inherently coloured present an attractive option to develop the coloured bricks which will give two-fold advantage of the improved aesthetics of fly ash bricks as well as efficient disposal of stone processing waste.

In this chapter, a detailed mineralogical characterization of four different type of stone processing wastes is presented using the XRD patterns, FT-IR frequencies, and Raman spectra, and their suitability for utilization in the coloured bricks is evaluated. To realize the coloured bricks, stone waste mixed GGBS based geopolymer mortars are produced and their compressive strengths are compared.

4.1. Experimental details

In the present study, four different stone waste samples have been collected from the western part of India. A detailed characterization data of these stone waste is presented in terms of the mineralogical composition by analysing their X-ray diffraction patterns, FT-IR spectra (without thermal treatment), and their Raman spectra both before and after thermal treatment at 1000 °C. The coloured composite mortars have been developed by fusing the stone wastes in GGBS-based geopolymer mortar and their compressive strengths are compared to assess their individual potential for developing bi-layered bricks.

4.1.1 Materials

A total of four different types of sludge stone wastes in their dry powdered form have been collected from the stone processing industries situated in Rajasthan, a state in the western part of India. These powdered stone wastes are produced during the processing of different dimensional stones, namely, Dholpur stone, Jaisalmer stone, Kota stone, and Makrana stone. Henceforth in the text, these are designated as S-I, S-II, S-III, and S-IV, respectively. During processing, a large amount of slurry waste is generated, which is passed through a series of sedimentation tanks (situated at different heights) to separate the fine and the coarse aggregates. The sludge waste is the waste collected at the last stage of the sedimentation process in which the fine particles (typically $< 150 \mu m$) remain in suspension. This sludge is pumped out through tankers and dumped at a designated area outside the city. In this study, these last-stage sun-dried wastes have been collected directly from the industry to avoid any external contamination. Subsequently, these stone wastes have been dried in a hot air oven at ~100 °C to remove moisture. Post-drying, a wooden hammer is used to break the small lumps manually, and the resulting powder has been passed through a 150 µm sieve. These powdered stone wastes passing from 150 µm sieve have been characterized in their dry form. In physical appearance, the stone wastes S-I, S-II, S-III, and S-IV are pink, yellow, greyish white, and white in colour, respectively. Fig. 4.1 shows the digital images and

the corresponding SEM micrographs of these powdered stone wastes. The SEM images have been obtained at a magnification factor of 2500X using Nova NanoSEM 450, FEI. The SEM micrographs show that all the powdered stone wastes have angular-shaped particles and do not vary significantly in shape.



Fig. 4.1. Digital images and SEM micrographs of different types of powdered stone wastes: (a) Dholpur stone (S-I); (b) Jaisalmer stone (S-II); (c) Kota stone (S-III); and (d) Makrana stone (S-IV)

The particle size distribution of different types of stone wastes is shown in Table 4.1. The chemical composition of stone processing wastes is determined using the energy-dispersive X-ray (EDX) spectroscopy (attached facility with SEM), as shown in Fig. 4.2, and detailed in Table 4.2. Note that the EDX spectrum reveals the chemical composition only in the elemental form rather than in the compound form. Therefore, elemental compositions obtained from EDX have been used to estimate the probable compounds; this data is used as corroborating evidence for the exact mineral composition, which has been determined using advanced characterization techniques such as XRD, FT-IR, and Raman spectroscopy.

Sieve size	Cumulative J	ve particles retained on respective sieve (%)				
(µm)	S-I	S-II	S-III	S-IV		
300	0.0	0.0	0.0	0.0		
150	0.0	0.0	0.0	0.0		
75	4.5	7.5	0.3	4.5		
45	13.5	13.0	3.5	12.5		

Table 4.1 Particle size distribution of different types of stone wastes

 Table 4.2 Elemental chemical composition of different types of stone wastes (%)

Element	Type of stone wastes						
_	S-I	S-II	S-III	S-IV			
Si	38.61	0.55	7.91	4.59			
Ca	0.00	30.54	35.38	33.02			
С	11.27	34.07	13.54	20.56			
0	40.02	34.84	40.86	33.65			
K	5.06	0.00	0.00	2.62			
Al	5.03	0.00	1.62	2.15			
Mg	0.00	0.00	0.69	3.41			



Fig. 4.2. EDX spectra of different types of stone wastes: (a) Dholpur stone (S-I); (b) Jaisalmer stone (S-II); (c) Kota stone (S-III); and (d) Makrana stone (S-IV)

4.1.2 Methodology

The mineralogical characterization of powdered stone wastes has been performed using three different techniques, namely, XRD, FT-IR, and Raman spectroscopies. An automated multipurpose X-ray diffractometer (Smartlab, Rigaku) has been used to record the XRD patterns in a continuous scanning mode at a scan rate of 0.2 s/step with a step size of 0.01° . Each sample has been scanned by varying the 2θ between 10° and 90° to record the XRD pattern. FT-IR spectra have been recorded in the absorbance mode using the FT-IR spectrometer (Spectrum two, Perkin Elmer). The powdered samples have been scanned for their FT-IR spectra over the range of 400-2000 cm⁻¹. The Raman characterization of powdered samples has been carried out using a Raman spectrometer (Labram HR, JY- Horiba) in the backscattering geometry with a 785 nm laser source. Raman spectra of the powdered samples have been acquired in two states: without thermal treatment and after thermal treatment at 1000 °C. To obtain the latter state, approximately one gram of sample has been placed in the muffle furnace for 30 minutes at 1000 °C and then left for cooling under ambient conditions until it reaches room temperature. These samples are referred to as thermally treated powdered stone wastes. As such, no definite guidelines are available in literature for the firing duration. Therefore, the firing duration has been chosen as per the closest technical standard IS 1727 [221]. Raman spectrum obtained after thermal treatment is useful for estimating the amorphous phases present in the sample as many of the amorphous phases get crystallized during the heatingcooling cycle and show their characteristic peak in the Raman spectrum [189, 290–292]. Besides, the luminescence due to amorphous carbon can be avoided as it gets released in the form of CO₂ during thermal treatment. The additional amorphous phases present in the sample can be determined by identifying the additional peaks that appear after thermal treatment.

Production and testing of coloured composite mortars

The coloured geopolymer mortars are realized by fusing the stone wastes S-I, S-II, S-III, and S-IV individually with ground granulated blast-furnace slag (GGBS). GGBS is preferred as a precursor over fly ash because fly ash is dark grey in colour that results in diminished colour properties. The compressive strength of different coloured composite mortars is assessed to evaluate their individual potential for developing coloured bricks.

Five different geopolymer mortars have been prepared: one without the stone waste, which serves as the baseline case, and four others with four different stone wastes, i.e., Dholpur, Jaisalmer, Kota, and Makrana. Indian standard IS 1727 [221] specifies the method to determine the lime reactivity of pozzolanic materials. In the absence of a technical standard for comparing the geopolymer reactivity of solid precursors, the same has been adopted with suitable modifications to compare the reactivity of stone wastes in GGBS based geopolymer matrix. For baseline case, GGBS has been used as a solid precursor, and standard sand confirmed to IS 650 [223] has been used as a fine aggregate. The latter has been selected to eliminate the effect of minor variations in the gradation of fine aggregates. A mixture of 10M sodium hydroxide and sodium silicate has been used as the liquid solution to enable geopolymerization. The ratio of liquid to solid precursor has been kept constant at 0.8, and the ratio of solid precursor to fine aggregates (*i.e.*, standard sand) has been kept fixed at 1:3. To produce the coloured composite mortars, stone wastes have been fused as the solid precursor, and 50 wt. % of GGBS has been replaced with the respective stone waste. The control mortar with 100% GGBS (without stone waste) and the mortars having blended solid precursor (50% GGBS + 50% stone waste) corresponding to stone waste types S-I, S-II, S-III, and S-IV are designated as M-0, M-I, M-II, M-III, and M-IV respectively. The compositions of these mortars are detailed in Table 4.3.

Mix	GGBS	Stone waste		NaOH	Na ₂ SiO ₃	Standar d sand	
	(g <i>)</i>	Туре	Amount (g)	(g)	(g)	(g)	
M-0	100	-	-	40	40	300	
M-I	50	S-I	50	40	40	300	
M-II	50	S-II	50	40	40	300	
M-III	50	S-III	50	40	40	300	
M-IV	50	S-IV	50	40	40	300	

 Table 4.3 Compositions of various stone waste and GGBS-based coloured geopolymer mortars

For the compressive strength test, 50 mm mortar cubes have been filled layer-by-layer in three steps and compacted using a tamping rod after each layer. Subsequently, the cubes have been sealed using incombustible plastic bags and set aside for curing in a drying oven for the first 24 hours [94]. As such, no well-defined curing temperature is specified in the literature. Researchers have kept the temperature between 50 °C - 80 °C for different types of solid precursors [293–295]. In the present study, the cubes have been cured at 50 °C. The oven-cured mortar cubes have then been left under ambient conditions until they have been tested. These mortar cubes have been tested for their 3-days compressive strength using a 50 T capacity compression testing machine at a loading rate of 3.43 MPa/min. [221] and compared with each other to evaluate their relative potential for developing coloured bricks.

4.2. Results and Discussion

The mineralogical characterization of stone wastes has been performed using three different techniques: XRD, FT-IR, and Raman spectroscopy. The XRD patterns and the FT-IR frequencies of stone waste samples have been recorded without any thermal treatment, whereas the Raman spectra of stone waste have been recorded for the samples both before and after the thermal treatment. Further, the compressive strength results of different coloured composite mortars are discussed.

4.2.1 XRD analysis

Fig. 4.3 shows the XRD patterns of the four stone wastes, namely, Dholpur stone (S-I), Jaisalmer stone (S-II), Kota stone (S-III), and Makrana stone (S-IV). Based on the peaks observed in the XRD patterns, the minerals are estimated by comparing them with the reference powder diffraction files (PDF) as per the ICCD-2003 database [224]. The X`pert high score plus software along with the reference powder diffraction files (ref. no. mentioned in Table 4.4) is used to analyse the XRD patterns. Table 4.4 shows the estimated mineral phases along with their semi-quantitative composition, respective 2θ angle, peak intensity, and the corresponding value of full width at half maximum (FWHM) of the major peak observed for the respective mineral. Since the value of FWHM depends on the crystallite size, it gives a measure of the amorphous nature of the mineral phase [225]. In the XRD pattern of stone waste S-I (Fig. 4.3a), quartz (SiO₂) and microcline (KAlSi₃O₈) are estimated as the major minerals, which corroborates with the chemical composition obtained from its EDX spectrum (Fig. 4.3a). In XRD pattern of stone waste S-II (Fig. 4.3b), different variants of calcium rich carbonate minerals such as calcite, magnesian $(Mg_{0.1}Ca_{0.9}CO_3)$, kutnahorite $(Ca_{1.11}Mn_{0.89}(CO_3)_2)$, and vaterite (CaCO₃) are estimated. It may be noted that Mn and Mg could not be detected in the EDX spectrum (Fig. 4.2b). It is well known that the EDX spectrum shows the particle specific composition, whereas XRD detects the bulk composition of the sample. The undetected Mn and Mg in EDX spectra are possibly due to the low presence or absence of these elements in the particle that are focused on obtaining the EDX spectra. Another possible reason for the peaks representing calcite, magnesian, and kutnohorite appear in the XRD pattern of stone waste S-II is the presence of some other minor impurities. Therefore, at this stage, XRD pattern can only estimate that the stone waste S-II is rich in calcium carbonate minerals and the impurities are present in either amorphous form or as intrinsic impurities calcium carbonate minerals. In the XRD pattern of stone S-III (Fig. 4.3c), only calcite (CaCO₃) and quartz (SiO₂) mineral phases are estimated, which are in-line with the chemical composition observed in the EDX spectrum (Fig. 4.2c). The elements Al and Mg that are additionally observed in the EDX spectrum (Fig. 4.2c) indicate the possibility of these elements being present in their highly amorphous phase. The presence of amorphous Al and Mg may accelerate the formation of reaction products during the geopolymerization process [296, 297], where the amorphous mineral phases dissolve to form monomers and morph into the long-chain polymers. In the XRD pattern of stone S-IV (Fig. 4.3d), calcite (CaCO₃), dolomite (MgCa(CO₃)₂), berlinite (AlPO₄), and silicon (Si) are estimated, which are again in agreement with the elemental composition of stone waste S-IV detected using the EDX (Fig. 4.2d); except the presence of phosphorus (P). Surprisingly, silicon is estimated in its elemental form. In addition, potassium (K) is detected in the EDX spectra, which indicates the possible presence of potassium compounds in their amorphous form. This is expected as it is well known that the compounds that are present either in their amorphous phase or in minor quantities can go un-detected by XRD.

In geopolymers, the reactivity of a solid precursor depends on its amorphous nature [298]. As the first important step in geopolymerization (of any solid precursor) is the dissolution of its amorphous phases to form monomers, it is imperative to determine the extent to which a mineral phase is amorphous or crystalline. Highly amorphous compounds are not detected using XRD; however, for crystalline compounds, the FWHM value obtained from the XRD patterns provides a qualitative impression about the amorphousness of the mineral phase. As shown in Table 4.4, for the stone waste S-I, a peak corresponding to the quartz mineral phase has the highest relative peak intensity. For stone waste S-II, a peak corresponding to calcitemagnesian has the highest relative peak intensity, whereas, for stone wastes S-III and S-IV, calcite has the highest relative peak intensity. This indicates the presence of a major crystalline compound in all four stone waste samples. The crystalline nature of the stone waste may slow down the reaction when used as a partial replacement for the solid precursor in the geopolymer mortar. Besides, the stone wastes S-II, S-III, and S-IV are also found to be rich in calcium carbonate mineral phases.

In comparing the corresponding FWHM value of calcium carbonate mineral phases (calcite) in these stone wastes (see Table 4.4), it is highest for S-III. This indicates that S-III has the maximum amorphousness, and therefore, S-III may be best suited in facilitating geo-polymerization. As seen from the above discussion, there is a possibility of the presence of minor phases or the additional amorphous phases in the stone wastes. In Chapter 2, for characterization of industrial ash, FT-IR spectra were used to confirm the minerals estimated in the XRD patterns and obtain additional information about the amorphous phases. Following the same methodology, the FT-IR spectra of stone wastes are analysed in the present study to gather additional information about amorphous phases.

Stone	Minerals	Semi-quantitative		PDF reference		
waste		composition (%)	2θ (degrees)	Peak intensity (a.u.)	FWHM (degrees)	no.
S-I	Quartz	74%	26.6702	21431.77	0.1378	01-085-1053
	Microcline	26%	27.5036	2109.15	0.1378	01-076-0918
S-II	Calcite, magnesian	39%	29.9160	5194.39	0.1680	01-071-1663
	Kutnahorite	10%	23.5950	338.59	0.1680	01-084-1291
	Vaterite	51%	27.1409	446.18	0.0960	01-074-1867
S-III	Calcite	75%	29.4099	4281.53	0.2160	01-083-0578
	Quartz	25%	26.5935	1276.52	0.1440	01-083-0539
S-IV	Calcite	83%	29.3083	7432.51	0.1200	01-072-1937
	Dolomite	6%	30.8278	2593.33	0.0960	01-083-1766
	Berlinite	8%	26.4922	964.08	0.0960	01-076-0226
	Silicon	3%	28.4092	308.01	0.0960	00-027-1402

Table 4.4 Mineral phases estimated in different types of stone waste



Fig. 4.3 XRD patterns of different types of stone wastes: (a) Dholpur stone (S-I); (b) Jaisalmer stone (S-II); (c) Kota stone (S-III); and (d) Makrana stone (S-IV)

4.2.2 FT-IR analysis

FT-IR spectra of four types of stone wastes are presented in Fig. 4.4. The peaks observed in the FT-IR spectra are compared with the peaks reported in the previous studies (see Table 4.5) to confirm the minerals estimated from their XRD patterns reported in section 4.2.1. Some additional peaks (other than the minerals estimated from their XRD patterns) are also observed, as shown in Table 4.6. In the FT-IR spectrum of stone waste S-I (Fig. 4.4a), the peaks observed at 451 cm⁻¹, 518 cm⁻¹, 694 cm⁻¹, 777 cm⁻¹, and 796 cm⁻¹ are due to the presence of quartz mineral phase, while the characteristic peaks observed at 583 cm⁻ ¹, 647 cm⁻¹, 730 cm⁻¹, and 1151 cm⁻¹ correspond to the microcline mineral phase. Additionally, a few other peaks of the microcline phase (in the range 994-1010 cm^{-1} and 1050-1088 cm^{-1}) are most likely masked by the broad peak at 1031 cm⁻¹. Microcline mineral is a member of the K-feldspar mineral family. The peak at 1031 cm⁻¹ indicates the partial presence of other minerals of the same family, such as sanidine and orthoclase [299].

In the FT-IR spectrum of stone waste S-II (Fig. 4.4b), peaks observed at 712 cm⁻¹, 872 cm⁻¹, 1088 cm⁻¹, 1396 cm⁻¹, and 1795 cm⁻¹ correspond to the calcite phase. Recall that the XRD analysis for S-II showed the presence of vaterite mineral phase. Vaterite and aragonite are the polymorphs of calcite, and the occurrence of peaks at 469 cm⁻¹ and 855 cm⁻¹ can be attributed to the presence of these polymorphs [300, 301]. Another compound that was detected in the XRD pattern of S-II is kutnahorite, which is not observed in the FT-IR spectra. Other small and broad peaks observed at 526 cm⁻¹, 773 cm⁻¹, 798 cm⁻¹, and 1037 cm⁻¹ denote the presence of additional amorphous phases that go undetected in the XRD pattern of S-II.



Fig. 4.4 FT-IR spectra of different types of stone wastes: (a) Dholpur stone (S-I); (b) Jaisalmer stone (S-II); (c) Kota stone (S-III); and (d) Makrana stone (S-IV)

In the FT-IR spectrum of stone waste S-III (Fig. 4.4c), peaks observed at 712 cm⁻¹, 873 cm⁻¹, 1094 cm⁻¹, 1415 cm⁻¹, and 1794 cm⁻¹ can be attributed to calcite mineral phase, while the peaks at 467 cm⁻¹, 520 cm⁻¹ ¹, 696 cm⁻¹, 780 cm⁻¹, and 799 cm⁻¹ can be attributed to quartz. Additionally, the shoulder peaks at 848 cm⁻¹ and 1164 cm⁻¹ show the presence of additional phases. The FT-IR spectrum of stone waste S-IV (Fig. 4.4d) shows calcite peaks at 713 cm⁻¹, 875 cm⁻¹, 1089 cm⁻¹, 1417 cm⁻¹, and 1795 cm⁻¹, and berlinite peaks at 417 cm⁻¹, 452 cm⁻¹, 465 cm⁻¹ ¹, and 1220 cm⁻¹. Other peaks of berlinite are possibly hidden under the broad peaks of other minerals. Another reason can be the low signal to noise ratio due to the poor crystal contact of natural berlinite in the ATR FT-IR [302]. Further, the peak at 729 cm⁻¹ is a characteristic peak for dolomite mineral to distinguish it among the family of carbonate mineral phases [301], which confirms the presence of dolomite mineral phase in S-IV and is also corroborated by the XRD pattern (Fig. 4.3d). Ankerite $(Ca(Fe, Mg, Mn)(CO_3)_2)$ is another mineral of the dolomite mineral family, which often appears along with dolomite and kutnohorite [301]. While the calcite peak usually appears at 872 cm⁻¹, a shifted peak is observed in the present case at 875 cm⁻¹ indicated the possible presence of dolomite phases (dolomite, ankerite and kutnohorite) as intrinsic impurities along with the calcite phases.

FT-IR spectrum of S-IV (Fig. 4.4d) shows quartz peaks at 452 cm⁻¹, 510 cm⁻¹, 774 cm⁻¹, and 798 cm⁻¹. The peaks at 774 cm⁻¹ and 798 cm⁻¹ appear as doublet due to the presence of silicate phases, which is in-line with the appearance of silicon in the EDX spectrum (Fig. 4.2d) and the XRD spectrum (Fig. 4.3d). The first peak in the doublet typically lies in the range of 776-778 cm⁻¹ and has approximately the same intensity as observed in the case of other stone wastes, *i.e.*, S-I and S-III. The shifting of the peak may be due to oxygen deficiency, which may have resulted in the detection of elemental silicon during the XRD analysis of stone waste S-IV (Fig. 4.3d). Another possibility is the presence of carbonate mineral alumohydrocalcite, which shows characteristic peaks at 798 cm⁻¹ and 1007 cm⁻¹. The small FT-IR peaks observed at 798 cm⁻¹ and 1006

cm⁻¹ (Fig. 4.4d), the absence of phosphorus in the EDX spectrum (Fig. 4.2d), and the presence of berlinite peaks partially in the FT-IR spectrum (Fig. 4.4d) indicate the possible presence of alumohydrocalcite instead of berlinite.

Additionally, a broad band is observed with some low-intensity peaks at 926 cm⁻¹, 1062 cm⁻¹, and 1165 cm⁻¹. The broad band between the 926 cm⁻¹ and 1165 cm⁻¹ may be due to the presence of multiple amorphous phases, which constitute several small peaks and difficult to estimate accurately. Also, some mineral phases are FT-IR inactive, and therefore, they may go undetected. To confirm the presence of amorphous phases that are detected by FT-IR and to reveal the additional phases that are IR inactive, the Raman spectroscopy of stone wastes (without and after thermal treatment) is performed, as described in the next section.

Stone waste	Mineral phase	Peaks observed in the present study	Peaks observed in the previous studies	Reference
S-I	Quartz	451, 518, 694,777,796	458-464, 509-514, 690-695, 776-780, 795-800, 1104	[228, 303]
	Microcline	583,647, 730, 1151	535, 576-584, 646-648, 725-726, 769-772, 994-1010, 1050-1088, 1130	[299, 304]
S-II	Calcite and its other polymorphs469, 712, 855, 872, 1088, 1396, 1795		469, 712, 850, 871, 1086, 1404, 1796	[301, 305]
S-III	Calcite	712, 873, 1094, 1415, 1794	712, 871, 1086, 1404, 1796	[305]
	Quartz	467, 520, 696,780,799	458-464, 509-514, 690-695, 776-780, 795-800, 1104	[228, 303]
S-IV	Calcite	713, 875, 1089, 1417, 1795	712, 871, 1086, 1404, 1796	[305]
	Dolomite	729	729	[301]
	Berlinite	417, 465,1220	416, 448, 473, 648, 696, 752, 874, 1029, 1111, 1233	[302]
	Quartz	452, 510, 774, 798	458-464, 509-514, 690-695, 776-780, 795-800, 1104	[228, 303]

 Table 4.5 Mineral phases confirmed using the FT-IR spectra of different stone wastes

Stone waste	S-I	S-II	S-III	S-IV
Additional peaks (cm ⁻¹)	1031	526, 773, 798, 1037	843, 1164	926, 1006, 1062, 1165

Table 4.6 Additional peaks observed using FT-IR spectra for different stone wastes

4.2.3 Raman analysis

Raman spectra of different stone wastes, without thermal treatment and after thermal treatment, are presented in Fig. 4.5-4.8. Peaks observed in the spectra are compared with the data in the existing literature (see Table 4.7) to confirm the presence of minerals estimated using the XRD pattern and FT-IR spectrum of respective stone wastes. In the Raman spectrum of stone waste S-I without thermal treatment (Fig. 4.5), clear peaks of quartz mineral phase are observed at 126, 263, 356, and 464 cm⁻¹. The broad peaks of anatase (TiO₂) mineral phase are also observed at 146 cm⁻¹, 194 cm⁻¹, 409 cm⁻¹, 511 cm⁻¹, 612 cm⁻¹, and 801 cm⁻¹ [306], which indicate the possibility of its significant presence in the amorphous phase. A broad peak is also observed at 283 cm⁻¹, which can be attributed to the microcline phase [307]. For thermally treated stone wastes S-I (Fig. 4.5), a high-intensity peak of Anatase is observed at 147 cm⁻¹ along with the other characteristic peaks at 199 cm⁻¹, 401 cm⁻¹, 511 cm⁻¹, and 634 cm⁻¹. A peak with high intensity (at 147 cm⁻¹) probably diminished the peaks and only a peak at 461 cm⁻¹ could be attributed to the quartz mineral phase.


Fig. 4.5 Raman spectra of Dholpur stone waste (S-I) without and after thermal treatment

For stone waste S-II without thermal treatment (Fig. 4.6), the Raman spectrum shows clear peaks of the calcite mineral phase at 154 cm⁻¹, 280 cm⁻¹, 713 cm⁻¹, and 1087 cm⁻¹. Besides these peaks, a bunch of small staggered-peaks is observed at 101 cm⁻¹ and 196 cm⁻¹, and some broad peaks are observed at 1192 cm⁻¹ and 1272 cm⁻¹, which are possibly due to the presence of amorphous phases. Calcite mineral phases undergo decarbonation at ~700 °C and get converted into CaO. As shown in previous studies [308], CaO does not reflect any peak in the first-order Raman spectrum. As expected, in the Raman spectrum of thermally treated stone waste S-II, peaks of calcite mineral phase have not been observed (Fig. 4.6).



Fig. 4.6 Raman spectra of Jaisalmer stone waste (S-II) without and after thermal treatment

For stone waste S-III without thermal treatment (Fig. 4.7), clear peaks of calcite are observed at 155 cm⁻¹, 280 cm⁻¹, 713 cm⁻¹, and 1087 cm⁻¹. However, the characteristic peaks of quartz mineral phase are not observed. The absence of characteristic peaks of quartz mineral phase may be due to the high spectral intensity of calcite minerals. Other than a small peak at 197 cm⁻¹, some broad peaks are observed at 1223 cm⁻¹, 1274 cm⁻¹, 1408 cm⁻¹, and 1526 cm⁻¹, which again may be due to the presence of amorphous phases. In thermally treated stone wastes S-III (Fig. 4.7), clear peaks of quartz mineral phase are observed at 125 cm⁻¹, 263 cm^{-1} , 355 cm^{-1} , 456 cm^{-1} , and 469 cm^{-1} , along with the additional peaks of K-feldspar (probable orthoclase) at 148 cm⁻¹, 283 cm⁻¹, 512 cm⁻¹ ¹, 747 cm⁻¹, 811 cm⁻¹, 990 cm⁻¹ and 1128 cm⁻¹. The peaks of K-feldspar appear after thermal treatment, which confirms the presence of amorphous silica in untreated samples [309]. The peaks of the calcite mineral phase have not been observed in the Raman spectrum of thermally treated stone waste S-III (Fig. 4.7) for similar reasons as explained in case of stone waste S-II.



Fig. 4.7 Raman spectra of Kota stone waste (S-III) without and after thermal treatment

Raman spectrum of stone waste S-IV without thermal treatment (Fig. 4.8) shows clear peaks of calcite mineral phase at 155 cm⁻¹, 281 cm⁻¹, 711 cm⁻¹, and 1087 cm⁻¹, while the small and broad peaks observed at 100 cm⁻¹, 192 cm⁻¹, 264 cm⁻¹, and 421 cm⁻¹ can be attributed to the additional amorphous phases. A continuous lump that appears in the range 400-700 cm⁻¹ in the Raman spectra of S-IV can be attributed to the presence of a glassy phase. To reveal such glassy phases, Raman spectra of the samples after heating at 1000 °C are analysed. In the thermally treated Raman spectra of stone S-IV (Fig. 4.8), clear peaks of quartz are observed at 126 cm⁻¹, 204 cm⁻¹, 262 cm⁻¹, 354 cm⁻¹, 462 cm⁻¹, and 1078 cm⁻¹, which confirm the presence of amorphous silicon in the untreated sample. The peaks of the calcite mineral phase have not been observed in the Raman spectrum of thermally treated stone waste S-IV (Fig. 4.8) for similar reasons as explained in case of stone waste S-II. Finally, in the thermally treated samples, several other small peaks are observed, as shown in Table 4.8, which possibly appear due to the formation of oxides of various amorphous elements in stone wastes during their thermal treatment.





Table 4.7	Raman peaks of the mineral phases characterized in different
	stone waste samples, with and without heat treatment

Mineral	Peaks observe		
pnases -	Present study	Previous studies	Reference
Quartz	125-126, 204, 262-263, 354-356, 456-469, 1078	128, 206, 265, 355, 465, 809, 1081	[129, 257]
Anatase	146-147, 194-199, 401- 409, 511, 612-634, 801	145, 198, 399, 516, 640	[306]
Microcline	283	283-285	[309]
Calcite	154-155, 280-281, 711- 713, 1087	156, 278, 714, 1087	[129, 257]
K-feldspar (Orthoclase)	148, 283, 512, 747, 811, 990, 1128	156, 282, 455, 477, 513, 748, 811, 989, 1123	[309]

Stone waste	S-I	S-II	S-III	S-IV
Additional peaks (cm ⁻¹)	293, 1316	106, 116, 200, 249, 350, 557, 699, 706	67, 107, 177, 197, 406, 649	393, 671, 1267, 1496, 1765, 1918

Table 4.8 Additional peaks observed in the Raman spectra of thermally treated stone wastes

The appearance of K-feldspar and quartz mineral phases in the thermally treated stone waste S-III and S-IV indicates the potential for high reactivity when incorporated in the geopolymer mortars. To confirm this, the stone wastes are incorporated partially in the GGBS geopolymer mortars, and the compressive strength results of coloured composite mortars are compared with the control GGBS geopolymer mortar that has no stone waste.

4.2.4 Compressive strength of coloured composite mortars

The 3-days compressive strength of various coloured composite mortars is presented in Fig. 4.9, which shows that the addition of stone waste as a partial replacement of GGBS decreased the compressive strength of the geopolymer mortar. A total of fifteen samples, three for each mix have been tested. Stone waste S-I is rich in silicon, whereas the stone wastes S-II, S-III, and S-IV are rich in calcium. For Ca-rich stone wastes (S-II, S-III, and S-IV), the compressive strength reduces by ~30-35% to 24-26 MPa, whereas for Si-rich stone wastes (S-I), the compressive strength reduced even more, by ~60%. Central Public Works Department (CPWD), Government of India recognizes and adopts the bricks of class designation 10 for construction [310]. The minimum compressive strength required for class designation 10 is 10 MPa as per IS 12894 [116]. The compressive strength for all the coloured composite mortars is greater than 10 MPa, which indicates the high potential of using stone waste blended GGBS as a solid precursor to produce the coloured bricks.



Fig. 4.9 A comparison of the compressive strength of different coloured geopolymer mortars

Although the strength is getting reduced by incorporating the stone dust, the mix reported in the study still showed a potential to produce the bricks of M10 designation with an improved aesthetics. One can optimize the blending composition of colored stone waste and GGBS balancing out between the individual's requirement of compressive strength and the aesthetics.

Discussion

Quartz and microcline minerals observed in S-I (present study) were previously reported in sandstone [311]. In a recent study carried out by Dong et al. [312], sandstone powder is used with silica fume to produce alkali activated mortar in a wide range of compressive strength (1.0 - 40.1 MPa). However, in present study, silica fume could not be used as primary aim is to produce the coloured mortar. In another recent study [313], Si-rich mudstone is used along with GGBS and red mud stone and obtained light wood-colored samples. They produced different composites up to 23.48 MPa. In a previous study by Ling and Poon [314], GGBS was used as a partial replacement of white cement to produce architectural mortar. They could replace up to 60% of white cement in the mix with a loss of only 8% brightness and a 22% decrease in the compressive strength of the architectural mortar. They recommended the large volume of GGBS for eco-friendly advantages in the architectural mortar. As compared to that, in the present study, GGBS is used without white cement to produce colored mortar using the colored stone waste. Additionally, TiO₂ was reported to increase the brightness of the architectural mortar [314], which has been identified as an inherent mineral in S-I stone waste.

In another study by Mármol et al. [177], granite dust was calcined at (700-900 °C) to produce reddish pigment and attempted to produce colored cement-based mortar. However, in present study, colored stone wastes have been used without any pre-processing in GGBS-based geopolymer mortars. Calcite and dolomite rich stone waste were used in alkali activated slag-based paste [315]. In the present study, similar minerals were present in stone waste S-IV.

4.3. Summary

A detailed characterization of four different stone processing wastes, namely, Dholpur (S-I), Jaisalmer (S-II), Kota (S-III), and Makrana (S-IV), is performed using XRD, FT-IR, and Raman spectroscopy to detect mineral phases. Following the characterization, the stone wastes are fused in GGBS based geopolymer matrix and suitability of stone wastes for producing coloured bricks is evaluated. Following key observations are drawn based on the results:

- Based on the XRD patterns, it is estimated that different crystalline minerals such as quartz and microcline are present in the Si-rich stone waste S-I, whereas calcite, kutnahorite, vaterite, dolomite, berlinite, quartz, and silicon are estimated as crystalline phases in other Ca-rich stone wastes (S-II, S-III, and S-IV).
- FT-IR analysis of stone wastes confirmed the presence of additional amorphous phases, which were not estimated by the XRD analysis.
- 3. The additional presence of anatase and orthoclase minerals was identified using the Raman spectra, which confirmed the

presence of amorphous Ti and Si in stone wastes S-I and S-III, respectively.

- 4. Raman spectra of stone waste S-III and S-IV indicated the high reactivity in geopolymer solution due to the presence of amorphous and elemental phases, which are further confirmed by the compressive strength results of stone waste incorporated geopolymer mortars (M-III and M-IV).
- 5. The coloured composite mortars produced with Ca-rich stone waste had higher compressive strength compared to the ones produced with Si-rich stone waste.

Chapter 5

Raman Imaging for Measuring Homogeneity of Dry Blended Mix

Background and chapter organization

Previously, in Chapter 3, dry blending of solids and their homogenous distribution throughout the matrix (focus of mixing sequence-II) was found effective to ensure the quality of unfired bricks. In porous materials like unfired bricks, existing tools for measuring the micro-level chemical homogeneity have certain limitations for industrial scale implementation. Expanding the capabilities of Raman scattering as a tool for unfired brick manufacturing industries can optimize the technological output immensely.

In this chapter, Raman spectromicroscopy has been established for the studying the homogeneity of a dry binary blended mix. A three staged procedure has been adopted to demonstrate Raman spectromicroscopy as a microscopic tool to clearly "see" the homogeneity of a mixture. Two powdered stone wastes (S-I and S-II, same as in previous Chapter 4), have been characterized as a case: (i) in separate heaps; (ii) by simply making a physically separated and identifiable boundary; and (iii) in their blended form. Chemical imaging using Raman spectroscopy has been demonstrated to be used as a simple tool in form of Raman area map to understand the homogeneity of binary blended mix which was not possible by other simple techniques. The demonstrated tool can be useful for industrial scale implementation in unfired brick industries.

5.1 Experimental details

In the present study, Raman chemical imaging has been established as a simplified and reliable tool to identify two distinct materials based on representative chemical bonds. The Raman area maps are developed to check the homogeneity of the dry binary blends adopting a three-stage procedure.

5.1.1 Materials

Two different waste stone powders (S-I and S-II, same as in previous Chapter 4) have been used that are collected from dimensional stone processing units in western Indian stone fields. The collected stone waste powders, S-I stone waste belongs to the waste generated during the processing of "Dholpur stone", whereas S-II stone waste belongs to the waste belongs to the waste generated during the processing of "Jaisalmer stone". The names are assigned based on the names of places "Dholpur" and "Jaisalmer" in the western state of "Rajasthan" in India. Both the stone powders defer in their colour; S-I is pinkish whereas S-II is yellowish in colour.

5.1.2 Methodology

The Raman characterization of powdered samples in dry form has been carried out using Raman spectrometer (Model: Labram HR; Make: JY-Horiba) in backscattering geometry with a 633 nm excitation laser source. The experiment has been planned in the following three stages. In first stage, the characteristic peaks of individual material have been identified using independent spectra of each material. In second stage, the materials have been brought together and allowed to form a common material boundary. In the third stage, both the materials have been blended gently, and Raman area mapping has been done in the selected area. The various arrangements of stone powders are as shown in Fig 5.1.

Samples have been oven-dried at 50°C till constant weight has been achieved and pre-screened from 150 μ m sieve. For characterization in separate heaps (Fig. 5.1a), both powders have been directly taken on

glass slides separately and their individual spectra have been collected. For characterization in junction arrangement (Fig. 5.1b), a separator has been used, and solid powder samples have been arranged at different sides of the separator. After placing the powdered samples, separator has been removed and pressed gently against each other with another glass slide for levelling and better resolution of the spectra. Spectra have been taken across the junction made on a line passing through both the materials at multiple points. For characterization in blended form, both solid powders have been gently but thoroughly mixed for sufficient time and a pinch of powder has been pressed in the same manner as above (Fig. 5.1c). The spectra of blended mix have been collected at multiple points in a selected area. Such spectra have been taken at five randomly selected regions, and two-dimensional (2-D) chemical Raman spectral mapping has been obtained to verify the chemical homogeneity through confirming the presence of both the individuals in the blended mix.



Fig. 5.1 Actual images of stone powders used for characterization: (a) in separate heaps; (b) separated by physical boundary; and (c) in blended/mixed form

5.2 Results and Discussion

5.2.1 Raman characterization of stone powders in separate heaps

Stone powders (S-I and S-II) have been characterized using Raman spectra that show distinct spectral features (Fig. 5.2a, 5.2b). In stone powder S-I, a clear sharp peak at 463 cm⁻¹ is observed, representing the presence of quartz mineral phase [119] whereas in stone powder S-II, a sharp peak at 1086 cm⁻¹ has been observed which can be attributed to calcite mineral phase [257]. In cementitious mixes, calcium silicate

hydrate (CSH) is the major reaction product which contributes mainly to the mechanical and durability properties to the hardened product [283, 316]. The raw materials to produce CSH may be supplied through two different source materials, namely Ca- source and Si- source. Hence, the selected stone powders predominantly resemble the field of building construction materials. With a broader goal to image these two materials, a Raman point map (Fig. 5.2c) has been recorded by collecting Raman spectra (Fig.5.2a & 5.2b) from six different points (three each from S-I and S-II). The obtained map (Fig. 5.2c) can be correlated with the constituents' representative Raman spectra which is represented as a line pixel on the map. A correlation between the spectra and map clearly shows the presence of calcite-rich mineral from point 1-3, whereas presence of quartz-rich mineral from point 4-6. It means that a mapping truly represents the spectroscopic information related to the chemical composition and makes it simple for analysis. Characterization done in the separate heap has been found important to define the representative characteristic peak for the further stage of experiments.



Fig. 5.2 Stone powders in separate heaps: (a) Raman spectra of S-I; (b) Raman spectra of S-II; and (c) corresponding Raman point map at multiple selected points on separate heaps

5.2.2 Raman characterization of stone powders separated by a physical boundary

Proceeding a step further towards development of the Raman mapping tool, Raman map of the sample through Raman scanning on a line as well as an area crossing the sample boundary (Fig. 5.1b) has been recorded. The scheme along with actual images (through naked eye and microscope) of the sample, on which Raman measurements have been carried out, are shown in Fig. 5.3a. The Raman line map (Fig. 5.3b) resembles the one obtained from the case when it was collected from samples separated as heaps (Fig. 5.2c) with the only difference in the yaxis where the line scan shows the distance scanned by the Raman probe. Here again the two materials show a very clear boundary in the Raman map near y=325 μ m (Fig. 5.3b) highlighting the region separating the two materials, silica-rich (S-I) and calcite rich (S-II). A line scan of two different powders separated by a thin boundary clearly establishes that Raman spectra of selected materials collected at different sides of the boundary did not show any mutual interference indicating that there was no effect of the material present on the other side of the junction. Further, to confirm the same once again, Raman spectra were obtained by scanning the Raman laser probe on an area across the boundary as shown in the scheme (Fig. 5.3a). The corresponding Raman area image (Fig. 5.3c) shows the Raman micrograph with a clear boundary separating the two samples (S-I and S-II). The green portion on the Raman image highlights the presence of silica-rich material (S-I) as identified by a 463 cm⁻¹ peak. On the other hand, the red portion on the Raman image highlights the presence of calcite-rich material (S-II) as identified by 1086 cm⁻¹ peak. The area scan re-establishes the fact that there was no mutual interference of selected materials separated by thin junction during the collection of Raman spectra. It may be noted that Raman mapping of the selected area, developed in the present study, is easy to understand even for non-technical persons involved in the unfired brick manufacturing industry to identify the two different materials separated by a thin boundary. It is worth mentioning here that the materials' arrangements as discussed in above two situations, do not belong to the actual case where they are actually mixed in the desired ratio to get the necessary strength of the material. The applicability of the above-mentioned Raman mapping tool has been studied on actual blended mix of two chemically different materials at the micro-level that are of technological importance.



Fig. 5.3 Stone powders S-I and S-II kept by forming a boundary: (a) actual photograph and corresponding microscope image; (b) Raman line scan; and (c) Raman area scan

Hence, in the next stage, a binary blend comprising of S-I and S-II in equal quantities has been prepared and subjected to the Raman scan.

5.2.3 Raman characterization of stone powders in blended form

Finally, Raman image from the blended mix, the final ready-to-use form, is captured from the materials obtained after mixing the two (Fig. 5.1c) from an area shown in the optical photograph (Fig. 5.4a) as seen under the Raman microscope. Five different areas are selected randomly on the sample for analysis and validation purposes. The mix is expected to have both the materials (S-I & S-II) present. The distinct presence of constituents in the Raman microscopic image will be advantageous as the optical images (Fig. 5.1c & 5.4a) are unable to distinguish the constituents of the mix. Raman micrograph from one location (selection in Fig. 5.4a) confirms the presence of both the materials at the microlevel (Fig. 5.4b). The red and green regions on the Raman image (Fig. 5.4b) correspond to S-I and S-II rich areas, respectively. It is important here to mention that the same could not be distinguished through an optical microscope (Fig. 5.4a) or naked eye. Furthermore, to identify the presence of individual samples (S-I or S-II) in the selected region Raman image has been filtered to show individual constituent as can be identified through the two uni-colour Raman images (Fig. 5.4c & 5.4d). The filtered uni-colour Raman image of the blended mix for S-I (Fig. 5.4c) and S-II (Fig. 5.4d), clearly confirms the presence of both the materials in the selected area. To further elaborate, four different areas are clearly marked in Fig. 5.4(b) as α , β , γ , and δ .

The area α denotes the calcite rich region, whereas the area β denotes the silica rich region. The presence of both the elements at one location results in yellowish colour, which is marked as the area γ in Fig. 5.4(b). Some dark areas can also be seen, which are marked as the area δ in Fig. 5.4(b). Such areas represent the low-intensity region, probably due to the poor focus of laser at that point as the z-focus was not used to capture the Raman image. Areas marked as α , β , γ and δ can also be confirmed in the filtered images Figs. 5.4(c) and 5.4(d).

The presence of both the materials at all the locations represents the homogeneity of the binary blend at micro level. Such filtered images can be used to confirm the presence of a particular ingredient in the multi-ingredient mix.



Fig. 5.4 Dry blend of two different powders S-I and S-II: (a) optical image and selected portion for Raman image; (b) complete Raman image; (c) filtered Raman image highlighting silica-rich region; and (d) filtered Raman image highlighting calcite-rich region

To validate the observation, similar area maps from different regions on different samples have been taken and four such dual-colour Raman micrographs (Fig. 5.5-5.8) have been shown for reference. Results (Fig. 5.5-5.8) show observations like the one observed in Fig. 5.4 confirming the ability of Raman imaging in the homogeneity investigations.



Fig. 5.5 Dry blend of two different powders S-I and S-II: (a) optical image and selected region-I for Raman image; (b) complete Raman image; (c) filtered Raman image highlighting silica-rich region; and (d) filtered Raman image highlighting calcite-rich region



Fig. 5.6 Dry blend of two different powders S-I and S-II: (a) optical image and selected region-II for Raman image; (b) complete Raman image; (c) filtered Raman image highlighting silica-rich region; and (d) filtered Raman image highlighting calcite-rich region



Fig. 5.7 Dry blend of two different powders S-I and S-II: (a) optical image and selected region-III for Raman image; (b) complete Raman image; (c) filtered Raman image highlighting silica-rich region; and (d) filtered Raman image highlighting calcite-rich region



Fig. 5.8 Dry blend of two different powders S-I and S-II: (a) optical image and selected region-IV for Raman image; (b) complete Raman image; (c) filtered Raman image highlighting silica-rich region; and (d) filtered Raman image highlighting calcite-rich region

The point, line and area Raman micrographs from the samples mixed in three different ways unambiguously reveal the information about the presence of different constituents and their nature of intermixing. Raman image could distinguish the different constituents which were otherwise not possible to be seen separately using optical micrograph or naked eye. This three-stage experimentation helped to develop Raman mapping as a chemical characteristic-based homogeneity measurement tool which can represent the true homogeneity even at the micro-level and the separate materials can be actually "seen".

In unfired brick industries, dry blending is an important operation performed during the production of bricks. Raman mapping successfully investigates the homogeneity of dry blended mixes which can be useful for industrial scale implementation in unfired brick manufacturing industries. Since the developed tool has been proven as an easy though effective way to check the homogeneity in dry blended mix, application for the hardened bricks can be easily explored. It may be noted that Raman spectra allow the data collection in wet materials too due to poor little interference caused by water. The possible data collection in wet mix through Raman spectroscopy can be further extended for on-line quality monitoring of wet brick mixes.

Discussion

In a previous study by Kuity and Das [317], homogenous distribution of filler was checked using SEM image analysis which involved the complex sample preparation of cutting, grinding and polishing operations, vacuum conditions and gold coating for measurement and a long numerical based image analysis procedure to comment on homogeneity. Da silva et al. [318] used AC impedance spectroscopy analysis to characterize the material homogeneity based on the response of polarization. As compared to these, in present study, homogeneity of mix is directly visible through the dual-colored Raman images directly prepared in non-vacuum conditions without much sample preparation.

The Raman scattering experiments mentioned here can be easily used and are affordable for research purposes. At present, the application of the demonstrated technology may not to be affordable for continuous quality monitoring purposes in small scale industries like the unfired bricks manufacturing industries or the small-scale construction projects.

However, in many large-scale industries such as cement industry and other construction chemical industry, where the dry blending is an important operation performed on daily basis can have the better economic viability and can afford for a limited sample size and limited number of samples.

Now a days, various companies are launching their portable hand-held Raman spectroscopy in the market with basic features in a price range of ~ INR 25 Lacs. The application of demonstrated methodology may be affordable in future with the possibility of upcoming low-cost models of Raman spectroscopy.

5.3 Summary

A step-by-step analysis of Raman scattering experiments from individual constituents to a binary blended mix establishes Raman imaging as a simple yet confirmative tool to be used for confirming the homogeneity of brick mixes. The following key observations can be made.

- The three-stage experimentation performed by using two constitutes, stone processing wastes (S-I, Dholpur stone waste and S-II, Jaisalmer stone waste) collected from Indian stone fields, in separate heaps, in a thin boundary arrangement and in the blended form, well demonstrated the stage-wise efficacy of developed homogeneity tool for the dry blended mix.
- The experimentation performed here exploits the chemical composition specific Raman characteristic peaks to identify the representative materials and accordingly has potential to "see" (in-) homogeneity of brick mixes using Raman spectroscopy reliably.

- 3. A micro-level Raman map very can clearly identify the different constituents of brick mixes which are otherwise unidentifiable optically.
- 4. The developed tool has shown the ability to represent the true homogeneity of the blended brick mix at micro level based on the chemical characteristic of the ingredient materials.

Chapter 6

Manufacturability and Economic Viability of Coloured Bi-layered Bricks

Background and chapter Organization

Previously, in Chapter 4, stone processing wastes were found to show potential to produce coloured bricks. However, costly chemical binders used for developing coloured composite mortar seems uneconomical as compared to conventional fly ash bricks.

In this chapter, the bi-layered bricks are conceptualized to make the coloured bricks economically viable. This study presents a first-of-itskind detailed study to produce coloured bi-layered bricks using stone processing wastes. Their manufacturability is demonstrated at the laboratory scale via a four-step process in an existing industrial set-up (used for conventional fly ash bricks). The economic viability of these bi-layered coloured bricks is evaluated, and a cost comparison is made with the conventional single layered fly ash bricks. These new bricks combine the desired features of aesthetics and durability, and therefore, show a great promise as a cost-effective alternative to conventional lime stabilized fly ash bricks.

6.1 Experimental details

In present study, the bi-layered bricks are conceptualized to make them economically viable, where the coloured mortar (developed in Chapter 4) is adjusted for the mix composition to use as a top-layer (of limited thickness) of the brick, while the bottom layer (remaining thickness) is made using the same material (optimized in Chapter 3) as that of the conventional fly ash bricks. In this way, a systematic manufacturing procedure to produce coloured bi-layered bricks is presented, and their manufacturability is demonstrated at a lab-scale. Further, the economic viability of the proposed coloured bi-layered bricks is discussed and compared with the conventional fly ash bricks, while accounting for the finishing cost of the wall construction. Fig. 6.1 shows a comparison of the fired clay bricks, unfired fly ash bricks, and the coloured bi-layered bricks proposed in this study.



Fig. 6.1 A qualitative comparison of fired clay brick, unfired fly ash brick, and the coloured bi-layered brick

6.1.1 Materials

Coloured bi-layered bricks are developed through the monolithic casting of two different mortars. The top layer mortar comprises of different coloured composite mortar, whereas the bottom layer mortar is the same as that used in the conventional lime-based fly ash bricks. The top layer mortar used the same solid precursor (50% GGBS: 50% stone waste) which is attempted for developing coloured composite mortar in Chapter 4. For the top layer, the liquid content of the coloured composite mortars has been adjusted to obtain a low-moist mortar that is suitable for compressed bricks. A mixture of 10M sodium hydroxide and sodium silicate has been used as the liquid solution to enable geopolymerization. The liquid content has been adjusted to 15% by weight of the total dry solids, and the natural sand passing from the 1.18 mm sieve has been used as the fine aggregates. These mortars are designated as TLM-I, TLM-II, TLM-III, and TLM-IV, where TLM stands for top layer mortar mix and the following numeric I, II, III, and IV represent the blended solid precursor corresponding to the stone waste types S-I, S-II, S-III, and S-IV, respectively.

For bottom layer mortar, a mixture of hydrated lime and fly ash (30:70 wt. %) has been used as the binder, and the stone dust passing from a 4.75 mm sieve has been used as fine aggregates. The water content is kept as 15% of total dry solids. The same Q2 mix, as optimized in Chapter 3 is used as bottom layer mortar to develop coloured bi-layered bricks. The bottom layer mortar mix is designated as BLM and is kept the same in all the bi-layered bricks. The composition of the mortars for the top and the bottom layers of one bi-layered brick are detailed in Table 6.1 and Table 6.2, respectively.

Mix	Stone waste		GGBS River		NaOH	Na ₂ SiO ₃
_	Туре	Amount (g)	(g)	(g)	(g)	(g)
TLM-I	S-I	111.11	111.11	111.11	25.0	25.0
TLM-II	S-II	111.11	111.11	111.11	25.0	25.0
TLM-III	S-III	111.11	111.11	111.11	25.0	25.0
TLM-IV	S-IV	111.11	111.11	111.11	25.0	25.0

Table 6.1 Composition of top layer mortars for one bi-layered brick

Mix	Hydrated lime (g)	Fly ash (g)	Stone dust (g)	Water (g)
BLM	200	466.66	2000	400

Table 6.2 Composition of bottom layer mortar for one bi-layered brick

6.1.2 Methodology

Methodology for developing coloured bi-layered bricks

Compressed bi-layered bricks have been developed using the same brick manufacturing facility that is used in previous Chapter 3 for casting the conventional lime-based fly ash bricks. Bi-layered bricks have been produced in the standard modular size (90 mm \times 90 mm \times 190 mm) as per IS 12894 [116]. Four different bi-layered bricks have been produced by varying the stone waste for the top layer mortar (see Table 6.1). The bottom side hydraulic press has been used in the manual mode, and loose mortars have been filled manually. However, a rotary-type or top-side hydraulic press can also be used, and automatic filling of two different mortars can be realized by integrating an additional feeder in the existing industrial plant used for single-layered conventional fly ash bricks. Filling of mortar in the mould has been done in two steps by maintaining the required loose thickness for each mortar. Loose thickness is the thickness up to which the mortar must be filled to obtain a brick of the required thickness after compression (under a certain pressure). In practice, the loose thickness is calculated for each mix in the industry based on the trials. However, it is continuously monitored and fine-tuned by the machine operator throughout the production for each lot of the mix received in the feeder hopper as a regular quality monitoring check.

Methodology for evaluating economic viability of coloured bi-layered bricks

The bi-layered bricks are compared in cost with the lime stabilized fly ash bricks. The market rates have been taken from M/s Abhishek bricks, which is a leading brick manufacturer in central India, having its manufacturing facility at Indore (Madhya Pradesh, India). For bi-layered bricks, a combination with a 10 mm thick top layer and an 80 mm thick bottom layer is considered. The top layer comprises coloured composite mortar, while the bottom layer is the same as the lime stabilized fly ash bricks. The total dry weight of raw materials (GGBS, stone waste, and river sand) for the 10 mm thick top layer of proposed composite mortar is assumed as 0.333 kg (neglecting the difference in specific gravity of different raw materials), considering the weight of a 90 mm thick conventional lime stabilized fly ash brick is 3 kg. Although the stone wastes are available free of cost, their freight on delivery and other costs are considered while calculating the procurement cost per unit of stone wastes at the manufacturing facility of M/s Abhishek Bricks. For calculating the per-unit rates for procuring stone wastes, INR 2.00/ton/km is taken as the freight rate, and a procurement distance of 600 km is considered. Along with transportation, loading, unloading, and other charges are considered as INR 0.20 per kg. In this way, the overall procurement cost of stone waste is taken as INR 1.40 per kg. The material cost of water is considered nil as groundwater is used in industries, and the corresponding electricity cost is included in other costs.

6.2. Lab-scale manufacturability of coloured bi-layered bricks

Two different mortar mixes have been prepared separately for the top and the bottom layer. Fig. 6.2 shows a sequential process of manufacturing coloured bi-layered bricks at a lab-scale. Firstly, the bottom punch is moved down to an intermediate level, and the coloured mortar is filled uniformly (step-1). Secondly, the bottom punch is moved further down to the final level, and the normal mortar is filled in the additional space created in the second step (step-2). In the third step, the surface lock is applied from the top, and hydraulic pressure of ~17 MPa is applied from the bottom side at once and maintained for ~10 s to ensure proper compaction (step-3). In the final step, the compaction pressure is released, the surface lock from the top is removed, and the bottom punch is moved up to eject the compressed brick out of the mould (step-4).



Fig. 6.2 A schematic diagram showing a step-by-step method for manufacturing of coloured bi-layered bricks.

In this way, the coloured brick has been produced through a monolithic casting comprising of two different layers: a coloured layer on the top and a layer like the lime-based fly ash bricks on the bottom. Using the same method as described in Fig. 6.2, different bi-layered bricks have been manufactured in the laboratory incorporating the coloured composite mortar comprising of different stone wastes (S-I, S-II, S-III, and S-IV) in the top layer (Fig. 6.3).



Fig. 6.3 Actual photographs of bi-layered bricks produced using different types of stone wastes: (a) Dholpur stone (S-I); (b) Jaisalmer stone (S-II); (c) Kota stone (S-III); and (d) Makrana stone (S-IV)

A key feature of these bricks is that their coloured top layer can be used as a facing surface during the construction of masonry walls for getting a coloured building façade.

6.3. Economic viability of coloured bi-layered bricks

The material cost of a typical fly ash brick of size 90 mm \times 90 mm \times 190 mm is calculated as INR 2.78 (1 USD \approx INR 70.0), as shown in

Table 6.3 which includes the cost of raw materials such as hydrated lime, fly ash, and stone dust.

Raw material	Weight (kg)	Unit rate (In INR per kg)	Total Cost (In INR)
Hydrated lime	0.225	6.00	1.35
Fly ash	0.525	0.80	0.42
Stone dust	2.250	0.45	1.01
Total raw material	2.78		

Table 6.3 Raw material cost analysis of 90 mm thick lime stabilized fly ash bricks

Table 6.4 Cost analysis of 10 mm thick top layer mortar

Raw material	Weight (kg)	Unit rate (In INR per kg)	Total Cost (In INR)
GGBS	0.111	2.50	0.278
Stone waste	0.111	1.40#	0.155
River sand	0.111	1.65	0.183
Sodium hydroxide pellets*	0.010	50.0	0.500
Sodium silicate solution*	0.025	20.0	0.500
Total raw material cost (in I	1.616		

*For cost calculations, unit rates of commercial-grade sodium hydroxide pallets and sodium silicate solutions have been considered.

[#] While stone wastes are available free of cost, freight on delivery and other costs are considered in calculating the rates per unit

Therefore, proportionately, the cost of raw materials for a 10 mm thick layer of conventional lime based fly ash brick can be calculated as INR 0.31. On the other hand, a 10 mm thick layer of coloured composite mortar will cost approximately INR 1.62 per brick (Table 6.4). Therefore, the resultant increase in the use of coloured composite mortar would be approximately INR 1.31 per brick. Further, the cost of coloured composite mortar can be reduced by procuring the stone waste from a nearby location.

Cost head	Fly ash bricks	Cost per brick (In INR)	Bi-layered bricks	Cost per brick (In INR)
	Single layer (90 mm thick)		Bottom layer (80 mm thick)	
	Hydrated lime	1.35	Hydrated lime	1.20
Raw material	Fly ash	0.42	Fly ash	0.37
cost	Stone dust	1.01	Stone dust	0.90
			Top layer (10 mm thick)	
			Coloured composite	1.62
Total raw material cost		2.78 -	→ Increase in - cost	→ 4.09
(A)			(~INR 1.31)	
Other cost (B)		0.65		0.65
Overall manufacturing		3.43 -	→ Increase in - cost	→ 4.74
$\cos t (A + B)$			(~INR 1.31)	
Plaster and paint work cost (C)		3.80		Nil
Net cost per brick (A + B +		7.23 -	Saving per brick	→ 4.74
C)			(~INR 2.49)	

Table 6.5 Economic feasibility of Bi-layered fly ash bricks

It may be noted that the paint and plaster would not be needed in the case of proposed bi-layered bricks. Assuming the cost of plaster and paint work as INR 20 per sq. ft., the corresponding cost-saving per brick for a façade surface of 90 mm \times 190 mm size would be approximately INR 3.8 per brick surface. This will result in an approximate net saving of INR 2.49 per brick surface, as shown in Table 6.5, which is 35% of the overall cost. Therefore, the proposed bi-layered bricks are a viable solution for improving aesthetics and simultaneously reducing the overall cost.

6.4. Summary

In this chapter, the bi-layered bricks are conceptualised to make them viable, and their manufacturability is demonstrated at the laboratory scale. The following key observations are drawn.

- A four-step process adopted can be used to produce coloured bilayered bricks in an existing industrial set-up (used for conventional fly ash bricks).
- Based on the market rates of commercial-grade raw materials and the actual production cost, the bi-layered bricks are shown to be economically viable.
- Since the bi-layered bricks eliminate the need for paint or plaster, the construction using these bricks is estimated to provide a net saving of INR 2.49 per brick surface of 90 mm × 190 mm; amounting to a cost saving of ~35 %.

Chapter 7

Conclusions, Recommendations, and Scope for Future Work

Unfired brick manufacturing industries have huge potential for industrial scale utilization of wastes. The utilization of local industrial wastes in unfired bricks addresses the sustainability of unfired brick manufacturing industries. In the present thesis, a comprehensive methodology has been established primarily for the characterization of industrial ashes originated in different manufacturing set up. The qualitative potential of local industrial ash (biomass and coal ashes) has been accessed for their utilization in unfired bricks.

The knowledge explored about optimum production parameters will help in enhancing the industrial scale implementation of research outcomes related to waste incorporated bricks. The present thesis reports the optimum mixing sequence and moisture content for waste incorporated unfired bricks that will help the industry in selecting the appropriate production methodology while incorporating the waste industrial ash in unfired bricks. The dry blending of solids and homogeneous distribution throughout the matrix is another important aspect for optimized quality of unfired bricks. In this thesis, Raman spectroscopy has been established as a simple and reliable tool for measuring the micro-level chemical homogeneity of dry blended mix, which will pave the way in future to develop the quality monitoring tools of the blended recipe for industrial scale production of waste blended unfired bricks. Apart from production parameters, in this thesis, an alternate approach to utilize the high-volume of stone waste has been demonstrated by conceptualizing the colored bi-layered bricks for improved economic viability of waste incorporated bricks. The stone wastes have been characterized using the same methodology adopted for industrial ash and evaluated primarily to improve the aesthetics of unfired bricks. The manufacturability and economic viability of stone waste incorporated coloured bi-layered bricks have been evaluated against conventional lime-based fly ash bricks.

Major conclusions of the research work reported in this thesis are being summarized below along with the limitations of present study, recommendations to the end user, and scope for future extension of the work.

7.1 Conclusions

- A comprehensive characterization methodology comprising the macro-level tests (LOI and lime reactivity test) and micro-level characterization techniques (XRD, FT-IR, Raman spectroscopy and lime reactivity test) has been found suitable for characterization of industrial ashes and instrumental to suggest a qualitative potential of the industrial ash to use in lime-based masonry products.
- In the macro-level tests (LOI and lime reactivity test), high lime reactivity has been observed for industrial ashes (A-III and A-V) having high LOI (10.80% -12.18) as compared to the industrial ashes (A-IV and A-VI) having low LOI (2.22% - 7.83%). This behavior required the micro-level characterization for the necessary explanation.
- The micro-level characterization techniques revealed the inherent presence of Ca-rich reactive mineral phases such as calcium aluminum oxide and anhydrite in industrial ashes (A-III & A-V) which explained the reason behind the high pozzolanic reactivity of these industrial ashes.

- 4. The micro-level characterization of biomass ashes (A-I and A-II) revealed the presence of both reactive minerals such as portlandite and aphthitalite, as well as the rocking CH2 bonds that restricts the pozzolanic reactivity of the ashes. The macro-level tests are essential for such industrial ashes to be conclusive about their pozzolanic reactivity and the governing factor. The results of macro-level tests such as high LOI (23.16% 60.38%) and low lime reactivity (0.08 -0.39) brought the clarity about the governing factor (i.e., presence of rocking CH2 bonds) behind the low pozzolanic reactivity of these biomass ashes.
- 5. The evaluation based on the adopted comprehensive methodology suggested the possible utilization of irregular shaped coal-based industrial ashes (A-III & A-V) locally in lime-based fly ash bricks without any treatment rather than transporting the low LOI ashes from a distant thermal power plant. Industrial ash utilization in unfired brick manufacturing industries can resolve the ash disposal issue and provide a low-cost resource to the brick manufacturing industries.
- Raman spectroscopy has been found instrumental to analyze the trio of amorphous, crystalline and carbon bands present in the industrial ashes.
- A combination of high liquid content and mixing sequence II (a two-stage mixing procedure) is the optimum production method for achieving higher compressive strength of unfired bricks.
- The bricks made with a two-stage mixing procedure achieve higher dynamic modulus of elasticity due to better distribution of particles and a homogenized brick matrix.
- 9. The drying shrinkage is correlated with the water absorption value of the bricks. The bricks with higher water absorption result in higher drying shrinkage in the bricks.
- 10. The comprehensive methodology proposed for ash is found suitable to draw the useful inferences, also while characterizing the coloured stone wastes. Moreover, Raman spectroscopy has

been found instrumental in characterization of Si-rich and Carich stone wastes.

- 11. Coloured composite mortars produced with Ca-rich stone waste achieve higher compressive strength and, therefore, they are preferable than the ones produced with Si-rich stone waste for producing coloured composite mortars. The locally available colored stone waste can be utilized for value addition in unfired bricks balancing out between the aesthetics and the desired performance parameters.
- 12. The three-stage experimentation performed for two constituents well demonstrated the efficacy of developed homogeneity tool to be used for dry blended brick mixes. Raman spectroscopy has been found suitable to determine true chemical homogeneity of the dry binary brick mixes.
- 13. Manufacturing of coloured bi-layered bricks is feasible in conventional plants (used for manufacturing of single layered bricks) with minor alterations.
- 14. Stone waste incorporated bi-layered bricks combine the desired features of aesthetics and durability, and therefore, show a great promise as a cost-effective alternative to conventional fly ash bricks.

7.2 Limitations of present study, recommendations to the end user, and scope for future work

Limitations of present Study

The present work has been kept limited to characterize the representative ash samples of some selected industries. In the present study, while studying the optimum mixing method, physical characteristics and microstructure of unfired bricks have been majorly studied. The current scope of the study does not include the durability parameters on unfired bricks. The scope of the study has been kept limited to analyze the effect of an important mixing parameter such as mixing sequence on unfired bricks. Besides, Raman imaging-based homogeneity tool has been used to demonstrate the homogeneity of dry binary blended mixes. The demonstrated lab-scale manufacturability and economic viability of stone waste-based coloured bi-layered bricks opens a new area for the detailed investigations on the bi-layered bricks that are affordable and have improved aesthetics against conventional lime-based fly ash bricks. The study explored the viability of selected local wastes such as industrial ash and stone processing wastes for industrial scale implementation in unfired bricks.

Recommendations to the end user

Within the scope of the thesis, the following is recommended to the end user.

- 1. A comprehensive characterization methodology comprising both the macro-level tests (LOI and lime reactivity test) and micro-level characterization techniques (XRD, FT-IR, Raman spectroscopy and lime reactivity test) is essential to understand the complex chemical characteristics of industrial ashes, and should be analysed together to suggest the qualitative potential of industrial ashes for utilization in lime based unfired bricks.
- The mixing of all the dry ingredients before adding the water, and the high moisture content in the workable range results into the optimum mechanical properties of lime-based fly ash bricks. The same should be adopted by the unfired brick manufacturing industries.
- 3. The methodology demonstrated here using Raman spectroscopy, is suggested to study the chemical homogeneity of dry binary blended mix. The large-scale industries such as cement industries, and construction chemical industries should use for their industrial application where the dry blending operation is of the primary importance.
- 4. The use of locally available coloured stone waste is suggested to get the cost-effective colored bi-layered bricks with improved aesthetics. Moreover, the Ca-rich stone waste should be

preferred over the Si-rich stone wastes to get the better mechanical properties.

Scope for future work

The future research can be carried out in the following areas.

- The work can be extended to analyse more types of industrial ashes to; (i) develop a generic protocol for characterizationbased waste utilization in unfired bricks and, (ii) to create a large-set database for easy incorporation of industrial ashes in local brick manufacturing industries.
- Studies can be extended to analyse the variation in the chemical phases formed in lime-ash mixtures due to variation in the mixing sequence and moisture content.
- Like the mixing sequence, studies can be carried out to optimize the other mixing parameters such as type of mixing equipment and mixing time.
- 4. The studies can be extended to investigate the suitability of the developed homogeneity tool for wet mixes and the hardened building construction products.
- 5. Future work can be directed towards a full-scale quantitative evaluation of the mechanical properties and durability of the bilayered bricks, which show great promise as a cost-effective alternative to conventional fly ash bricks.
- 6. Since locally sourced wastes may have better economic feasibility, in future, waste maps can be prepared like the other geographical maps for enhancing the industrial scale utilization of local wastes in unfired brick industries.
- 7. Studies can also be carried out to investigate the optimized curing strategy for coloured bi-layered bricks.
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