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NOVEL GEOPOLYMERIC BUILDING MATERIALS THROUGH SYNERGISTIC UTILISATION OF INDUSTRIAL WASTE

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Abstract. Synergistic utilisation of major industrial wastes generated in India, namely fly ash, blast furnace slag and red mud, has been explored to develop novel building components using geopolymerisation. These include: (a) high strength cements (b) self glazed wall tiles, and (c) pavement tiles. Fly ash was used as main source of silico-aluminate for geopolymerisation. Granulated blast furnace slag (GBFS) and red mud were used individually or in combination with fly ash to tailor properties of the developed components. Chemical and mechanical activation have been judiciously incorporated in the processing schemes through an understanding of processing-structure-property relationships. Improvement in the reactivity of fly ash by mechanical activation using high-energy mills was found to results in the formation of a compact micro-structure during geopolymerisation leading to high compressive strength (above 100 MPa) in geopolymer cements. The cements also exhibited improved setting time and a very low autoclave expansion. In self-glazed wall tiles, the hard impervious glazed surface was obtained at temperature lower than 150°C by controlling the particle size distribution of solid reactants, viscosity of slurry and reaction atmosphere. The self-glazed surface showed the presence of gismodine (Na-plagioclase) phase which was absent in the main body of the tiles. In pavement tiles, fly ash and granulated blast furnace slag were used to give structural framework, whereas red mud was used to supplement the iron oxide for colouring effect and alkalis. The setting and hardening occurred due to formation of cementitious A-S-H and C-S-H gel ($A = Al_2O_3$, $S = SiO_2$, $C = CaO$, $H = H_2O$). The technologies have been developed at bench scale and efforts are underway for scaling up to pilot plant level.

1 Introduction

The concept of industrial ecology is based on integration of byproduct and waste streams across industries leading to production of useful product(s) with near zero flow of material to the environment. Building industry is one of the most dynamic sectors with enormous potential of industrial symbiosis and



synergistic utilisation of industrial wastes. With increasing environment awareness, there is growing concern worldwide for updating production processes, as well as development of green building materials. The green material can be defined as products made from waste, recycled or by-products to conserve natural resources, circumvent toxic and other emissions, saves energy, and contribute towards a safe and healthy environment.

Geopolymers, silico-aluminate materials formed through mimicking natural rock forming process, are fast emerging as new class of green building construction materials [1]-[5]. In the process of geo-synthesis, silicon (Si) and aluminium (Al) atoms react to form molecules that are chemically and structurally comparable to those binding natural rock and allows for novel products synthesis that exhibit the most ideal properties of rock-forming elements, i.e., hardness, chemical stability and longevity. Fly ash, blast furnace slag and red mud are the three major industrial wastes in India [6]. Presently over 100 million tonnes of fly ash, 12 million tonnes of blast furnace slag and nearly 4 million tonnes of red mud are generated. It is estimated that production of these wastes will double in foreseeable future due to rapid expansion coal based power generation, and increase in the production of iron & steel and aluminium through primary processing. These waste materials contain SiO_2 and Al_2O_3 , along with Fe_2O_3 , CaO , MgO , MnO , etc, and have immense potential as man made raw materials for geopolymers.

During geopolymerisation process, the alumino-silicate fraction reacts with alkaline media and transform into a solid geopolymer product, via a dissolution-polycondensation-structural reorganisation mechanism, to develop strength [7]. Blast furnace slag behaves differently during geopolymerisation as compared to fly ash and clay. This is attributed to its higher reactivity due to mostly glassy structure which, leads to faster dissolution of Si and Al during geopolymerisation. The CaO portion of the slag particles does not necessarily participate in polycondensation, but reacts with water and may undergo hydration reaction [8]. It has also been reported that addition of blast furnace slag in the conventional silico-aluminate geopolymer cement and concrete improves setting characteristics [9]. Use of red mud in geopolymers appears to be an attractive proposition from the point of view of its high alkaline content. However, there have very limited attempts in this direction [10].

This paper is based on our recent research on the development of a wide variety of geopolymeric products using fly ash as the main raw material along with granulated blast furnace slag (GBFS) and red mud. The focus is on: (a) high strength cement, (b) self-glazed tiles, and (c) pavement



tiles. Processing, structure and properties of the products are highlighted. The commercialisation prospects of the products are also discussed.

2 Materials & methods

The fly ash and GBFS used in the study were obtained from a cement grinding unit at Chattisgarh State, India, The red mud was obtained from a Aluminium Plant at Orissa State, India. The chemical analysis and physical properties of the fly ash, GBFS and red mud are given in Table 1. The $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ content of the fly ash was $> 70\%$ and it was a Class F fly ash as per ASTM. The basicity of the slag (CaO/SiO_2 ratio) was 1.06. The batch composition of the each product was selected based on chemical, physical and mineralogical characteristic and reactivity. The composition of the products, in terms of the amounts of fly ash, blast furnace slag and red mud used are indicated in the ternary diagram shown in Fig.1.

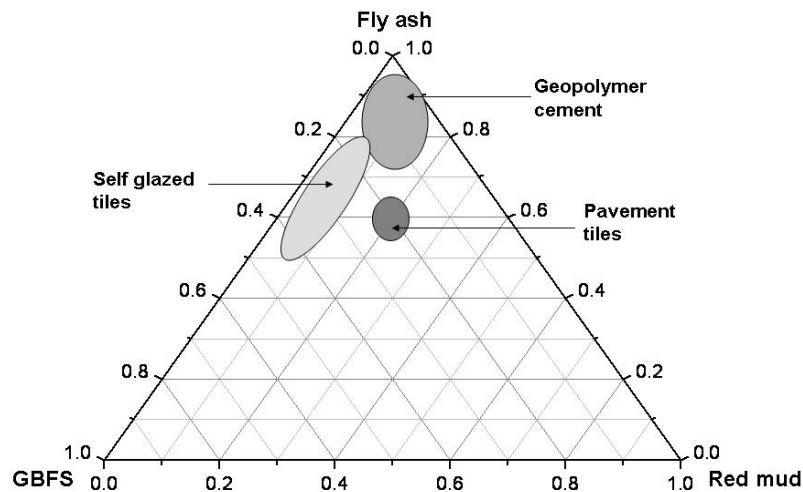


Fig. 1. Composition of geopolymer cement, self glazed tiles and pavement tiles.

The geopolymer cements were prepared using the raw as well as pre-processed fly ash. The techniques used for pre-processing include air classification and mechanical activation. Air classification was carried out using a HOSOKAWA ALPINE (Germany) air classifier 50 ATP. Mechanical activation of fly ash was carried out using an attrition mill (Model PE-075, NETZSCH Feinmahltechnik GmbH, Selb, Germany) and a vibratory mill (SIEBTECHNIK, ESM 234, Germany). Sodium hydroxide was dissolved in water at least 24 hours before use. In case of geopolymer cement, geopolymerisation was carried out by keeping the samples in controlled humidity for 24 hours at 27°C followed by thermal curing at 60°C for 24 hours.



For self glazed tile, fly ash and a ball milled granulated blast furnace slag (GBFS) were used as main materials. The batch composition was thoroughly mixed with alkaline activator and then casted in tile mould. Colour pigments were added into the slurry before casting to get the desired colouring effects. The casted tiles were then edged for 24 hours at 27°C followed by heat treatment in the range of 150-300°C using different thermal cycle. In pavement tiles, red mud was intimately mixed with fly ash and ball milled GBFS. The batch was prepared by adding coarse, medium and fine aggregates and alkaline activator. The slurry was casted in rubber moulds and allowed to set at ambient temperature. In all the cases, physical properties were tested as per standard procedures discussed elsewhere [11]. The heat evolution during reactions was monitored using an isothermal conduction calorimeter (TAM AIR, Thermometric AB, Jarafalla, Sweden). XRD patterns of samples were recorded on a Siemens Diffractometer (Model D500) using CoK_α radiation. The morphology of the samples was examined using JEOL 840 Scanning Electron Microscope (SEM) with EDS attachment for micro-analysis.

Table. 1. Chemical analysis and physical properties of the fly ash, GBFS and red mud.

Chemical analysis			
Constituents	Fly ash	GBFS	Red Mud
SiO ₂	60.48	32.97	7.4
Fe ₂ O ₃	4.52	0.72	47.4
Al ₂ O ₃	28.15	17.97	20.4
CaO	1.71	35.08	3.2
MgO	0.47	10.31	-
SO ₃	Traces	0.72	-
Na ₂ O	0.14	-	4.8
K ₂ O	1.41	-	-
L.O.I.	1.59	0.58	13.1
Physical properties			
Glass content	43	93	-
Major crystalline phases	Quartz, mullite, hematite	Gehlinite	Gibbsite, hematite, aluminogoeite, hitequartz, sodalite



3 Geopolymerisation of waste

Most proposed mechanisms of geopolymerisation consist of dissolution of aluminosilicate phase, polymerisation and re-precipitation of gel phase, and transformation of the gel phase into geopolymer of varying crystallinity and structure. Depending upon experimental conditions, the different stages of geopolymer formation may overlap and even merge with each other. Isothermal conduction calorimetry was used to study the geopolymerisation of fly ash, mixture of (GBFS+fly ash), and the mixture containing (fly ash+GBFS+red mud). The calorimetry was carried out under following conditions:

- (i) 27°C for 24 h (Fig. 2a)
- (ii) 60°C for 24 h after keeping the sample at 27°C for 24 h (Fig. 2b)

The calorimetric response in Fig. 2a for the alkali fly ash mixture at 27°C is expected to represent dissolution polymerization and initiation of gel formation. Response in Fig. 2b signifies the conversion into geopolymer via gel formation step. Based on conduction calorimetric results, the following observations were made:

- (i) at 27°C (Fig.2a), the initial exothermic peak I in all the cases indicates that reaction started as soon as the starting powders was mixed with NaOH solution. In the case of (fly ash + GBFS + red mud) mixture, a minor peak was observed at the start, which after a short induction period of 30 min accelerated to stronger exothermic peak. No such induction and acceleratory period was observed in other samples. In terms of maximum reaction rate, (fly ash + GBFS + red mud) mixture has shown maximum reaction rate followed by (fly ash + GBFS) and fly ash.
- (ii) at 60°C, after edging the sample at 27°C for 24 h (Fig. 2b), two peaks were observed in all the samples. First endothermic peak, observed during 0–250 min, corresponds mainly to dehydration that occurred owing to the evaporation of water formed or water remained unused during gel formation. The area under the endothermic peak for (fly ash + GBFS) sample showed a higher area, indicating greater amount of gel formation. After the endothermic peak, the broad flat exothermic peak, observed during 240–1200 min, corresponds to polycondensation. This peak started and flattens earlier in fly ash. Whereas in other cases, the peak took longer time to flattens possibly due to presence of GBFS, which resulted into formation of C-S-H gel.



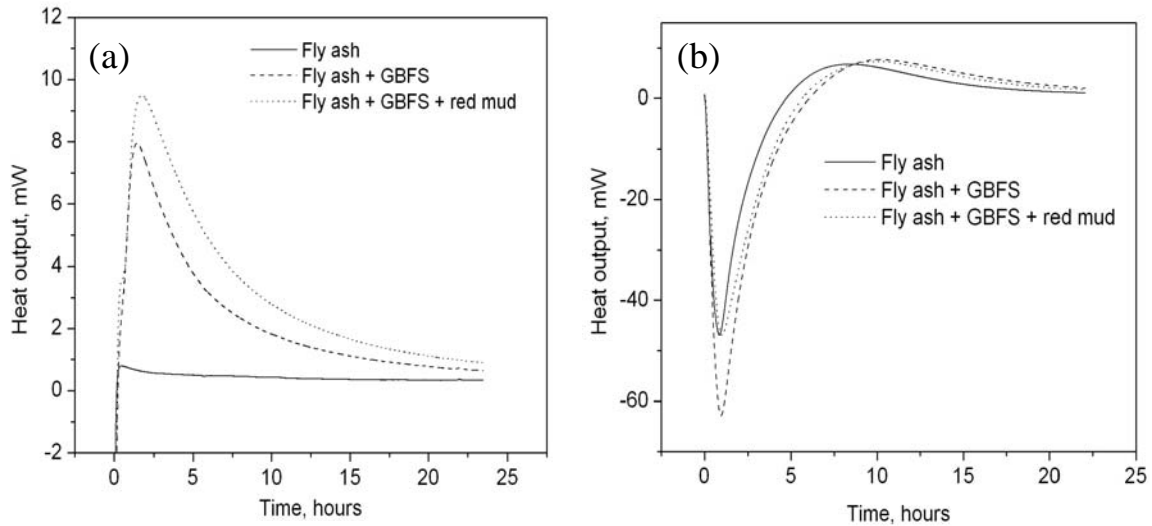


Fig. 2. Isothermal Conduction Calorimetry curve showing (a) dissolution of samples at 27°C, and (b) geopolymerisation at 60°C after 24 hour dissolution at 27°C.

4 Development of novel building materials

4.1 Geopolymer cement

Low reactivity of fly ash has often restricted the use of fly ash for geopolymer cements due to slow strength development [12]. The reactivity of fly ash depends on its vitreous phase content, which participates in geopolymerisation reaction [13], [14]. The remaining constituents takes longer time for reaction due to poor reactivity and leads to slow setting and strength development in geopolymers [12], [15]. Various methods such as chemical activation [16], mechanical activation [17]-[20] and size classification [21]-[23] of fly ash has been suggested as a means to improve the reactivity. Recently observations were made by the present authors that use of mechanically activated fly ash leads to high compressive strength in geopolymers [24]-[27]. Two different approach were adopted to enhance reactivity of fly ash: (a) air classification to separate finer fractions, and (b) mechanical activation in attrition and vibratory mills. Small size cenosphere cools faster during their formation in coal combustion process and separation of finer fraction by air classification results in increase in the glass contents vis-à-vis raw fly ash. Mechanical activation results due to combined effect of particle breakage (surface area) and other bulk and surface physicochemical changes induced by the process of milling.



The change in reactivity of fly ash due to increased glass content and mechanical activation was assessed vis-à-vis raw fly ash. Fig.3 shows typical particle size distribution of raw fly ash (RFA), classified fly ash (CFA), attrition milled fly ash (AMFA) and vibratory milled fly ash (VMFA). Based on median particle size (X_{50}), the samples can be arranged in following descending order: RFA ($36.2 \mu\text{m}$) > VMFA ($5.99 \mu\text{m}$) > AMFA ($4.85 \mu\text{m}$) > CFA ($2.79 \mu\text{m}$).

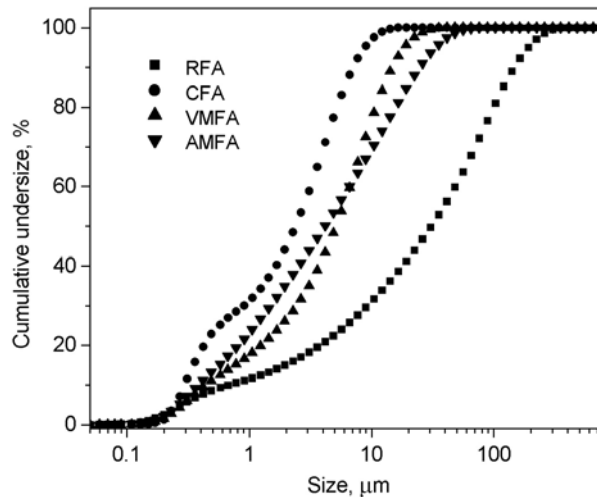


Fig. 3. Particle size distribution of RFA, CFA, AMFA and VMFA.

Figure 4(a) shows XRD pattern of RFA, CFA, AMFA and VMFA based geopolymers. Similar nature of XRD patterns suggests formation of same phases in all the samples. The XRD patterns show a broad peak in the range of $10\text{--}16^\circ$ corresponding to aluminosilicate gel. In addition, presence of hydroxyl-sodalite phase is observed indicating geopolymerisation. The most compact microstructure was obtained in VMFA based geopolymers with high proportion of reaction product (Fig. 3b). Based on the relative amount of geopolymer product formed and compactness of microstructure, the reactivity of fly ash samples decreases in following order: VMFA > AMFA > CFA > RFA. In spite of higher particle size of VMFA and AMFA ($5\text{--}6 \mu\text{m}$) as compared to CFA ($\sim 3 \mu\text{m}$), higher reactivity of mechanically activated samples was interesting.

The physical properties of the geopolymer cement are given in Table 2. The higher strength in AMFA and VMFA is attributed to higher reactivity due to mechanical activation that leads to enhanced geopolymerisation and more compact microstructure. Significantly higher strength of samples prepared using VMFA over corresponding AMFA samples highlights the importance of mechanical activation device. The other properties, such as setting time,



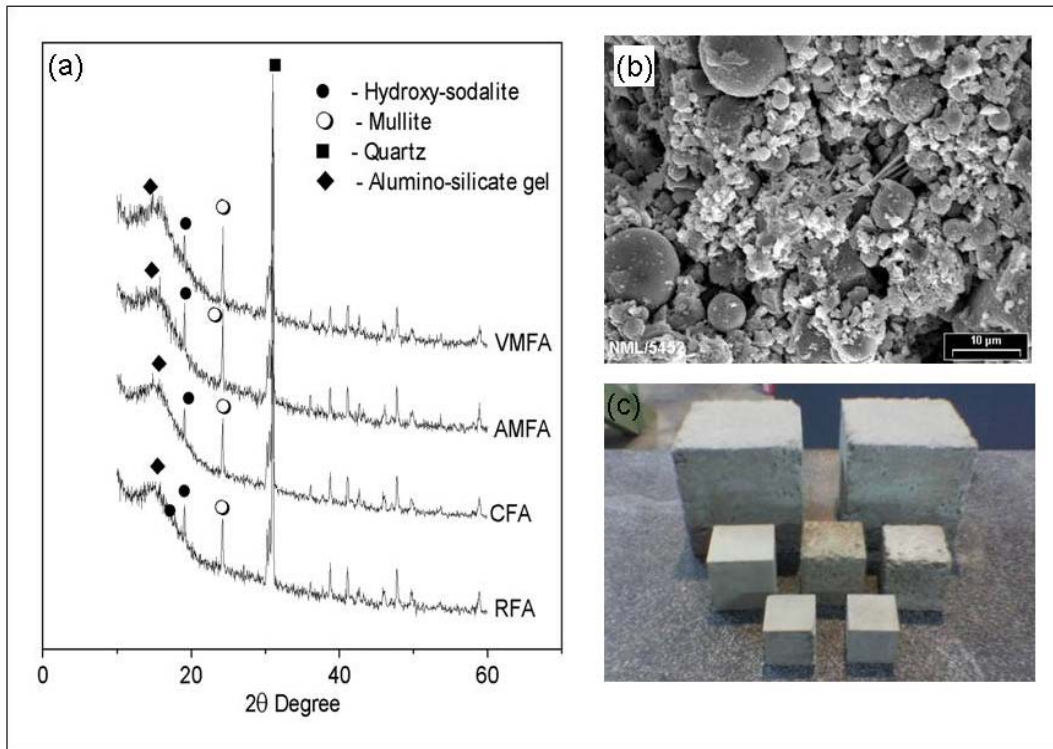


Fig. 4. (a) XRD pattern of RFA, CFA, AMFA and VMFA based geopolymers showing formation of alumino-silicate gel and hydroxysodalite, (b) SEM micrograph showing compact structure observed in VMFA based geopolymers, and (c) Geopolymer cement and concrete cubes.

Table 2. Properties of geopolymer cement.

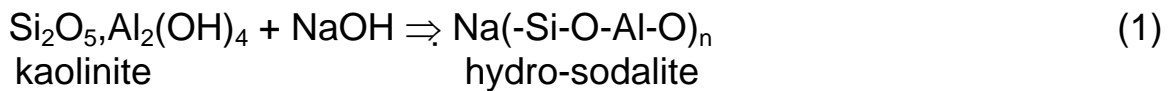
Properties	Geopolymeric material			
	RFA based	AMFA based	VMFA based	CFA based
Compressive strength (MPa)	10.0	18.6	36.0	16.0
1 day	43.0	70.0	120.0	48.0
3 day	64.0	77.0	125.0	67.0
28 day				
Setting time (minutes)	60	55	55	60
Initial	180	120	105	170
Final	<0.02	<0.02	<0.02	<0.02
Autoclave expansion (%)	Excellent	Excellent	Excellent	Excellent
Acid resistance				



autoclave expansion, etc. indicate that the developed geopolymer cements meet the specifications drawn for hydraulic cements like ordinary Portland cement, Portland slag cement and Portland pozzolana cement [27].

4.2 Self glazed wall tile

Conventionally ceramic tiles are produced by high temperature sintering/vitrification of aluminosilicate and silicate minerals such as clay, quartz, feldspar, etc. The strength and other properties of tiles are developed due to formation of ceramic bonds. Development of stoneware tiles at 250-400°C by geopolymerisation of aluminosilicate minerals has been reported [28]. The processing involved reaction between aluminosilicate mineral kaolinite and NaOH at 100°C-150°C resulting into the formation of hydro-sodalite



In the alkali activation of fly ash and slag mixture at ambient temperature, fly ash/slag ratio is the most relevant factor on the strength development [29]. The main reaction product is a hydrated calcium silicate with high amount of tetra-coordinated Al in its structure. The additions of calcium content increase the degree of geopolymerisation at elevated temperature and results into higher strength [30], [31]. Beneficial effect of slag on fly ash geopolymerisation was exploited in the development of self glazed wall tiles.

The glazed surface and the body of tiles showed distinctly different microstructure as revealed by SEM micrographs shown in Fig.5a and Fig. 5b, respectively.

The glazed surface is characterized by well knitted grains giving rise to compact microstructure with very low porosity (Fig.5a). The morphology of the tile body shows the well reacted porous body. XRD studies indicated the presence of gismodine (Na-plagioclase) phase in the glazed surface (Fig.5c). Two type of bulk reaction products were identified by EDX studies: (a) a low-crystalline calcium silicate hydrate rich in Al, which includes Na into its structure and results from the alkali activation of slag, and (b) an amorphous alkaline aluminosilicate hydrate resulting from the alkali activation of fly ash. Critical control on particle size distribution, chemical composition, rheology of slurry and reaction environment is necessary for the formation of required phases in the glazed surface.

The properties of glazed geopolymer tile are summarised in Table 3. The tiles developed conform to the European Nation (EN) specification for wall tiles. The natural colour of the tiles was light grey but different colour and designs were produced using colour pigments. Unlike the fired ceramic tiles,



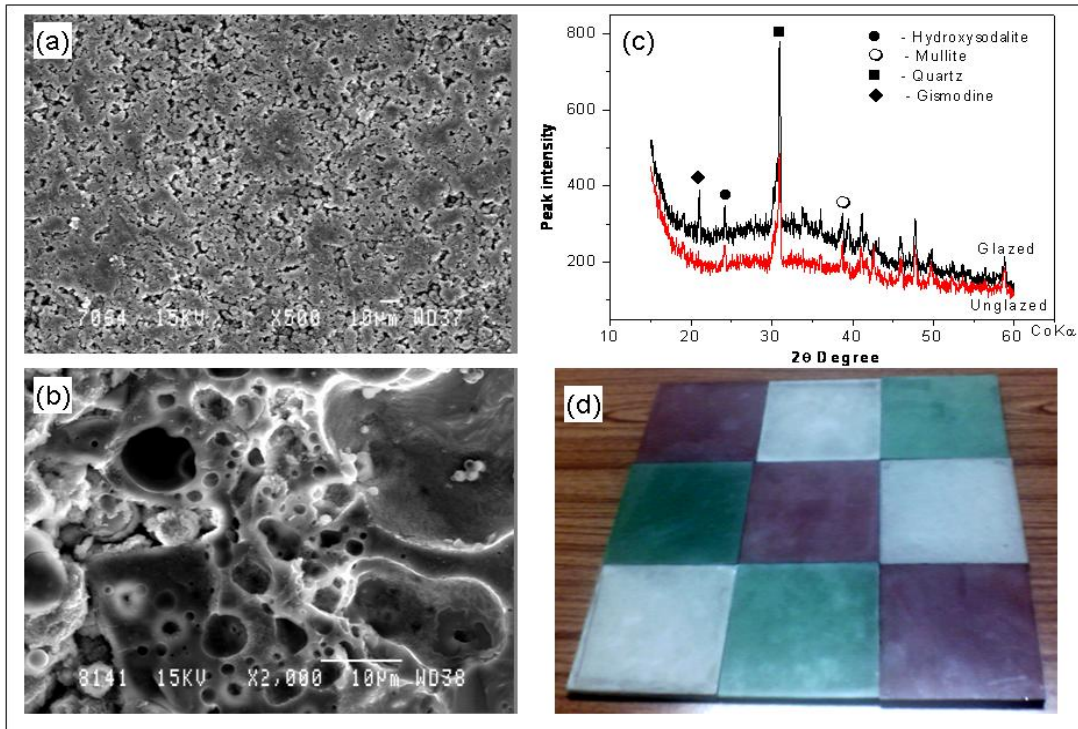


Fig. 5. (a) Closely knitted microstructure of glazed surface, (b) well reacted microstructure of tile body, (c) XRD pattern of glaze and body of tile, and (d) tiles of different colour.

Table 3. Properties of geopolymer tile.

Properties	EN specification	Geopolymer tiles
Dimension tolerance	± 0.5%	As per specification
Thickness tolerance	± 0.5%	As per specification
Straightness of sides	± 0.5%	As per specification
Rectangularity	± 0.6%	As per specification
Surface flatness	± 0.5%	As per specification
Surface quality	95% free from visible defects	As per specification
Water absorption, % Gr.III	14-16	13-17
Scratch hardness (Moh's)	Min. 5 >22	As per specification >25
Compressive strength (MPa)	To conform class AA	Confirms class AA
Chemical resistance		



no crazing and other glaze defects were observed [32]. Although the surface of the tile was impervious, the porosity of body was 13-17%, which is good for bonding with cement.

4.3 Pavement tiles

Pavement tiles are small cement structures in geometrical shapes that are usually laid on pathways or on any open ground as a solid platform. As these tiles are not cemented and only laid closely over a bed of loose sand, they can be easily removed, stored and reused as many times as possible. In India, the pavement tiles are mostly vibro-cast and/or pressed cement mortar or concrete hydrated for 28 days. The strength is obtained due to hardening of cement. Earlier research on alkali-slag-red mud-cement (ASRC) has indicated high early and ultimate strength together with excellent resistance against chemical attacks [33]-[37]. This was achieved by introduction of solid composite alkali activator into slag-red mud mixture system instead of liquid water glass. The hydration products of ASRC cement were mostly C-S-H gel with low Ca/Si ratio in the range of 0.8 to 1.2.

In the present work fly ash, GBFS and red mud was used to develop cementitious phases by alkali activation at ambient temperature. Red mud was used to give colouring effect to the tiles from presence of iron oxides, and also partly supplement alkalies for reaction. Similar to self glazed tiles, two major reaction products were identified in XRD (Fig.6a) and EDX studies. C-S-H gel with Na in its structure from the activation of GBFS, and amorphous alkaline alumino-silicate hydrate resulted from the activation of fly ash. Also presence of iron oxide and hydroxide resulted from addition of red mud. The SEM studies (Fig.6b) have shown a dense microstructure including numerous fibrous structures corresponding to C-S-H gel with Na in structure.

The physical properties of these tiles are given in Table 4. The tiles, although produced at ambient temperature (27-35°C), exhibits good compressive and flexural strength [38].

5 Synergistic use of industrial wastes

Synergistic use of industrial waste is an emerging concept whereby combination of two or more wastes is used to develop a useful product. The main advantage of the synergy is the deficiency of constituents from one waste is compensated by using second or third waste, which is rich in deficient constituent. Synergistic use also includes industrial symbiosis where



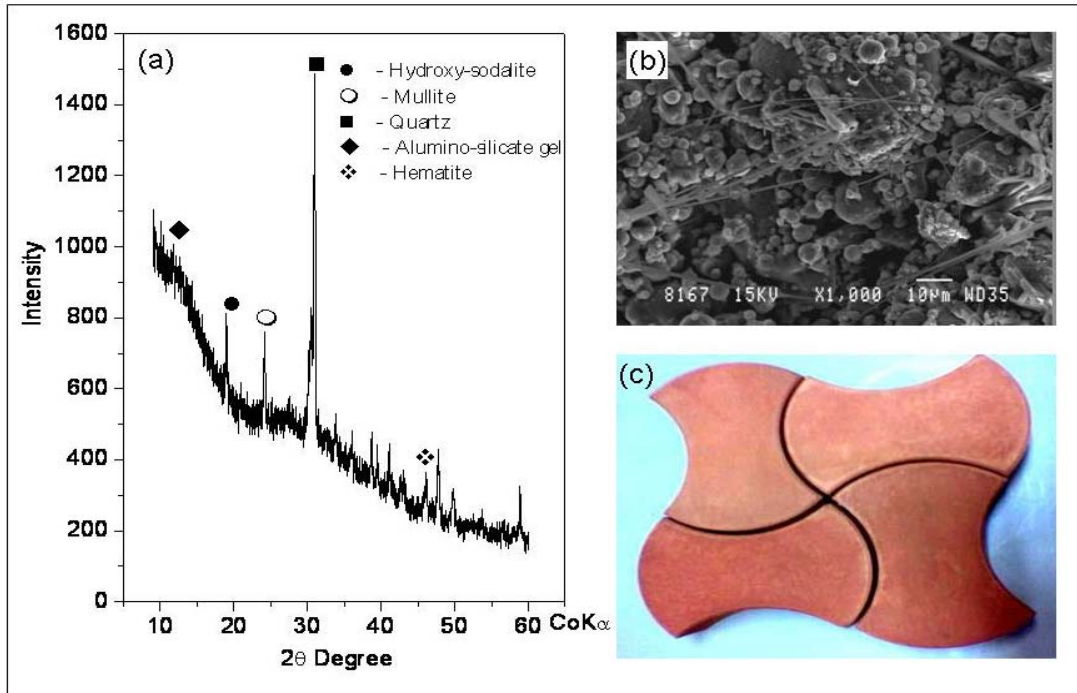


Fig. 6 (a) XRD pattern of pavement tiles, (b) dense microstructure with numerous fibers, and (c) pavement tiles.

Table 4. Properties of pavement tile.

Properties	Pavement tiles
Compressive strength (MPa)	40
Flexural strength (MPa)	5
Bulk density, gm/cc	2.8
Water absorption, %	6-7
Coefficient of friction	0.6
Youngs Modulus, GPa	3.51

physical exchange of waste/by-products between geographically close industries is exploited. In the present work, waste from three industries, fly ash from thermal power plants, fly ash and granulated blast furnace slag from Steel Plants, and fly ash and red mud from Aluminium plants, has been used. Fly ash was used for the development of geopolymers cement (product 1), combination of fly ash and blast furnace slag was used for self glazed tiles (product 2) and all three wastes fly ash, GBFS and red mud was used for pavement tiles (product 3). From the point of view of zero or minimum flow into environment, product 1 is best suited for thermal power plant, where fly ash is the main by-product. Product 2 and product 3 are more suitable for iron & steel and aluminium industry respectively. Fig.7 shows the synergy map of these wastes.



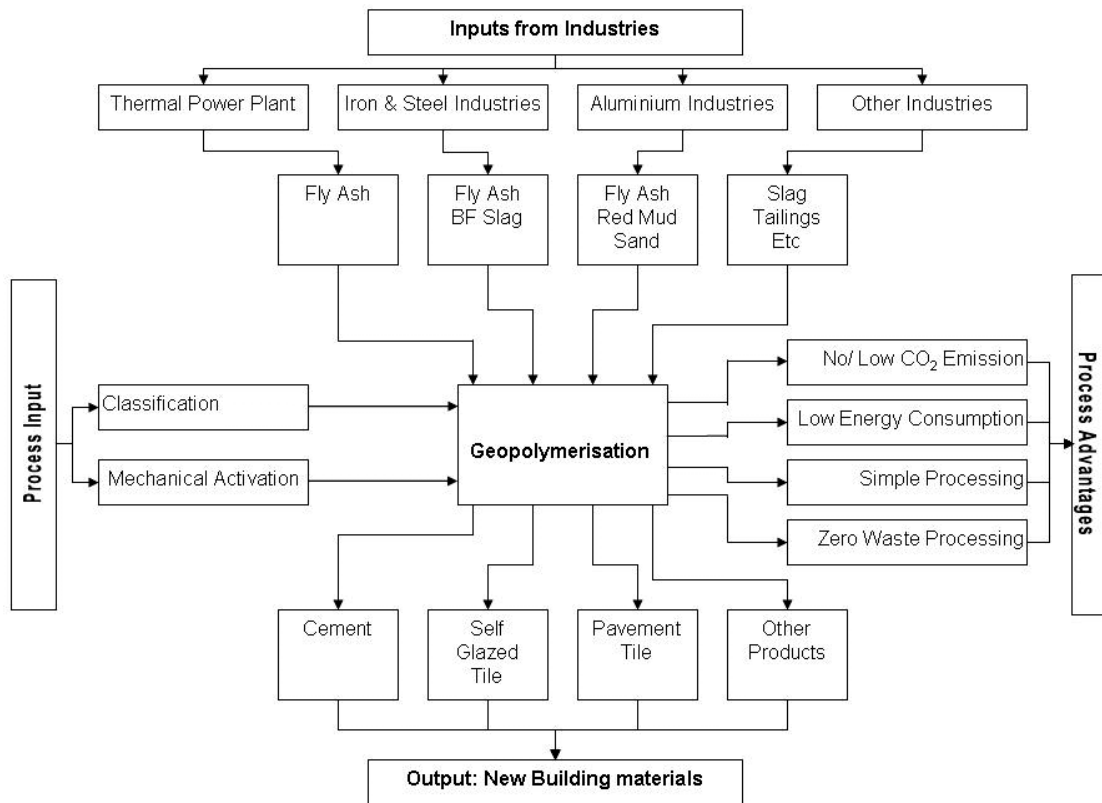


Fig. 7. Synergy map for the utilization of different type of industrial wastes.

6 Economics and commercial potential

The cost of most industrial production is increasingly influenced by the operations required for the adequate disposal of by-products. The disposal cost as per regulations may add 5-10% of the production cost depending on volume and nature of waste generated. The major benefit of synergistic use of industrial waste is reduction in product cost. The geopolymerisation process is low temperature process and thus the potential for energy savings is substantial. Cement clinker is normally produced at $\sim 1400^{\circ}\text{C}$ and ceramic tiles are produced at $950\text{-}1200^{\circ}\text{C}$. Whereas the geopolymers cement and self glazed tiles require $60\text{-}150^{\circ}\text{C}$ temperature. This significant reduction in temperature is expected to save upto 70% in energy cost. In addition, there will be enormous saving in capital cost as no high temperature processing kilns are required. Producers of geopolymers products may also benefit from raw-material costs because the main reagents are waste material. In India, fly ash and red mud are free of cost and only transportation cost is involved. The cost of granulated blast furnace slag is around Rs. 400-500 per ton. Based on the various inputs, a techno-economic calculation was carried out as follows:



Table 5. Techno-economics for the production of geopolymers products.

Plant Capacity (minimum viable plant)	10,000 MT / Year
Capital Cost	Rs. 100 Lakhs
Operating Cost	Rs 125 Lakhs
Profitability	Rs 85 Lakhs
Return on Investment	~80-90%

All figures are indicative and in Indian Rupees (1 \$ ~ Rs. 44)

The techno-economics based on laboratory results indicate high commercialization potential. Efforts are underway in this direction through setting up of a pilot plant to optimize manufacturing parameters and properties on a larger scale.

7 Conclusions

The following conclusions can be drawn:

1. Due to their ability to polycondense Si and Al into solid monolithic ceramic like structure during alkali activation, geopolymers have the potential of utilization of industrial wastes rich in silico-aluminates such as fly ash, GBFS, red mud, etc.
2. Novel building materials such as high strength geopolymers cement can be developed by additional processing such as mechanical activation, and self glazed tile and pavement tiles can be developed by synergistic use of industrial waste namely fly ash, GBFS and red mud.
3. The developed geopolymer products qualify as new members in the spectrum of eco-friendly construction materials due to easy and simple processing, low energy requirement and no CO₂ emission. The products have good commercialisation potential with significant returns.

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