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Geopolymer as Alternate Cementitious Material An Overview

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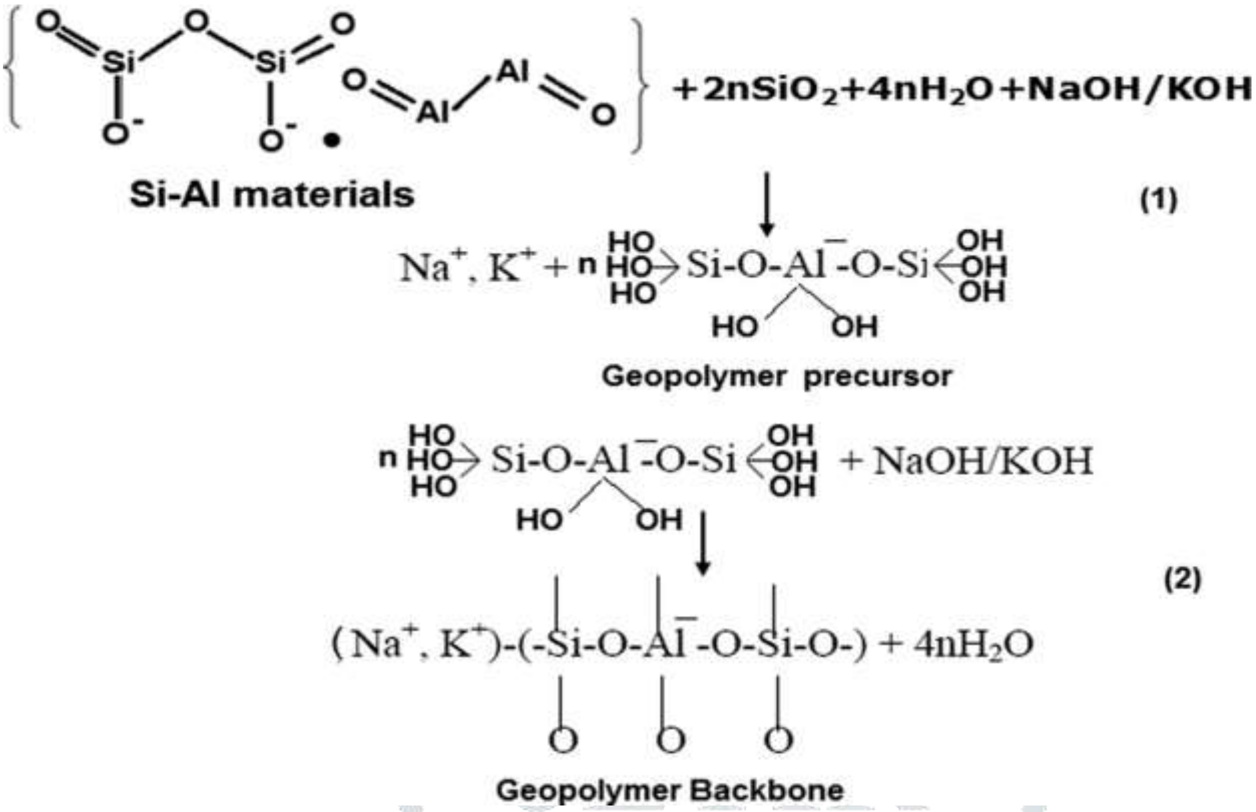
ABSTRACT

Concrete is supreme extensively used construction material around the world in which cement is foremost constitute. Production of cement consume huge quantity of energy and emits lot of carbon dioxide (Co_2) gas which is responsible for global warming, near about 7% of carbon dioxide (Co_2) is released from cement manufacture Industries. To grow a supportable forthcoming it is encouraged to limit the use of this construction material that can affect the environment. Geopolymers is appropriate substitute material to the cement, which is environment friendly material. Geopolymer is manufactured at room temperature and emits negligible quantity of carbon dioxide (Co_2). It is fabricated from by-products (waste) from different industries. Commonly used by-products are Fly-Ash (FA), Rice Husk Ash (RHA), GGBS (Ground Granulated Blast Furnace Slag). Geopolymer are fabricated using raw materials namely Fly-Ash, Metakaolin, Rice Husk Ash, Calcined clay, Zeolite by the activation of Alkaline solutions. Payable to their high mechanical properties and eco-friendly benefit, geopolymer cement and concrete seem as a future construction material and have applications in several areas. In present paper briefly review about manufacture, mechanical properties, durability and curing conditions of Geopolymer composites, Geopolymer concrete.

Keywords- Geopolymer, Rice Husk Ash, Geopolymer Composite, Carbon dioxide.

I. INTRODUCTION: -

From Past few decades' environment issues is major concern manly due the carbon dioxide release in atmosphere. Manufacturing of Portland cement required massive amount of energy and raw materials and release lot of Co_2 in the atmosphere which is responsible for global warming [1]. It is expected that the manufacturing of Portland cement 5.9 billion tons with more 4.8 billion tons release of Co_2 in 2020 all around the globe. This state will be worrying and thus there is a crucial need to decrease Co_2 emanations from the cement manufacturing industries [2]. There are two tactic which will be adopt **(i)** partial replace of Portland cement by Cementous material to overcome the energy and emission of carbon dioxide (Co_2) [3-5]. **(ii)** Producing cement without clinker. Alkaline activated binder (geopolymer cement) and geopolymer appeared to alternate to conventional concrete in past few years. Geopolymer is made by alkaline activator with aluminosilicate source materials like GGBS, RHA, Fly-Ash, Metakaolin (MK) etc. Geopolymer may be short out the problem of construction industries and waste generated. Geopolymer is first time introduced by Joseph Davidovits in 1978 [6]. Geopolymer is an inorganic polymer which is made through polycondensation of convinced waste comprising aluminosilicate with alkaline solution. The semi-crystalline 3-dimensional aluminosilicate framework structures of Geopolymers are formed by the combination of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedral. The mechanism of Setting and hardening of geopolymer is not understood till now. The geopolymerization process may start with dissolving of source materials comprising aluminosilicate in alkali solutions prominent to the development of monomers of aluminate and silicate. These are then transformed into oligomers and later to geopolymers. Water is add during dissolving and free in polymerization as given by Eqs.(1) and (2) [7].



Scheme 1. Schematic representation of formation of geopolymer materials [7].

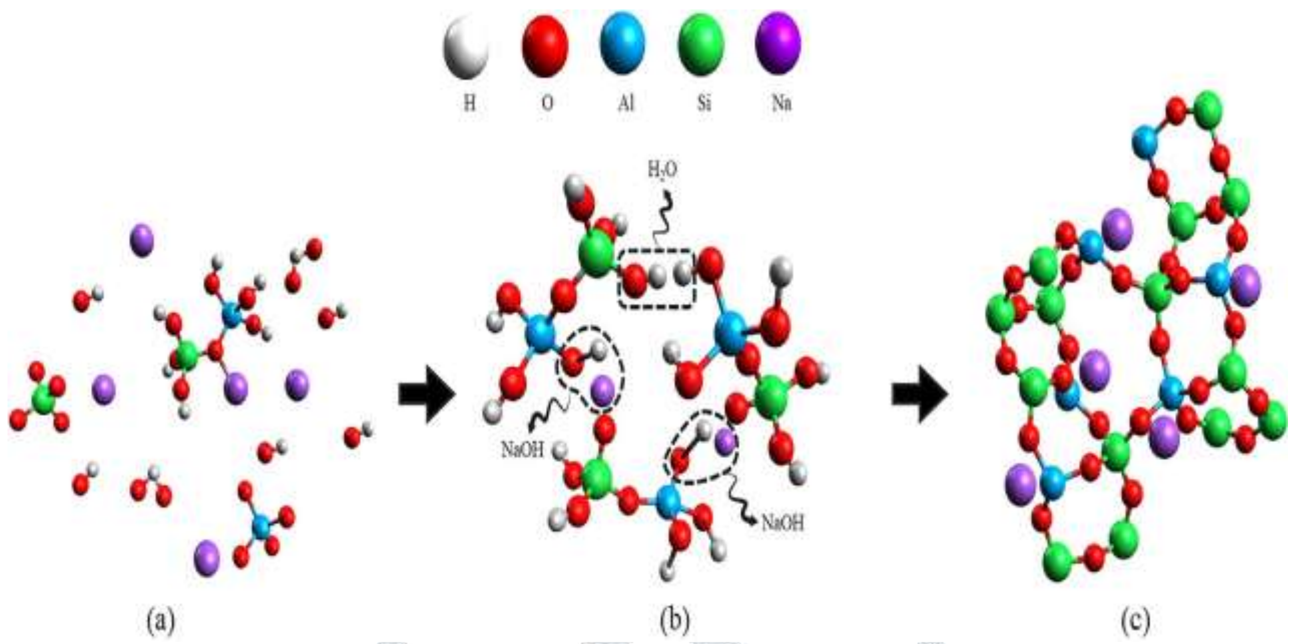
The concrete which is made from geopolymer cement is called geopoylmer concrete and it has good engineering properties [8-10], seems to be appropriate alternative to conventional concrete. Geopolymer concrete is non-toxic and release negligible amount of Co_2 so it a green concrete. [11-13]. It possibly will resolve the difficulties of cement industries and problems related to environmental contamination [14]. This article reviews the process of geopolymerization, mechanical properties, durability, heat curing methods of geopolymer concrete and geopolymer composites.

II. GEOPOLYMERIZATION PROCESS : -

Geopolymerisation is a multifarious heat-releasing procedure containing a chains of independent and concurrent steps comprising of dissolution-rearrangement -solidification reactions similar to zeolite synthesis. The source material which contain aluminium and silicon atoms is dissolve in a extremely alkaline solution, developing a 3-dimensional polymeric structure comprising of –Si-O-Al-O- bonds, signified as an empirical equation suggested by Davidovits [16]

$$\mathbf{M_n\ [-(SiO_2)_z–AlO2\ ]_n \cdot wH_2O}$$

Where, M= the alkaline component or cation namely potassium (K), sodium (Na) or calcium (Ca); the symbol – shows the existence of a bond; n is the degree of polycondensation or polymerization; z is 1, 2, 3, or higher. The particular reaction appliance which clarifies the setting and hardening of geopolymers is not yet fairly understood, even if it is endorsed to be reliant on the aluminosilicate source materials and configuration of alkaline activator. The Geopolymerisation mechanism proposed by Lee et al.[15] comprises the subsequent four stages, (i) disbanding of Si and Al from the solid aluminosilicate material in a strong alkaline aqueous solution, (ii) development of oligomeric sorts (geopolymer forerunners) comprising of polymeric bonds of Si-O-Si and/or Si-O-Al type, (iii) polycondensation of the oligomers to procedure a three dimensional aluminosilicate framework (geopolymeric framework) and (iv) attachment of the undissolved solid particles into geopolymeric framework and strengthening of the whole arrangement into a ending solid polymeric structure. Fig 2 show the process of Geopolymerization.



Scheme 2. Schematic illustration of geopolymerization process: (a) reorganization of aluminosilicate, (b) gel formation from oligomers condensation, and (c) polymerization

III. MODELS : -

Geopolymerisation is a multifarious heat-releasing procedure containing a chains of independent and concurrent steps comprising of dissolution-rearrangement –solidification Davidovits [16-17]. Barbosa suggest a new model this is modified version of Davidovits model, it describe complete geopolymer mechanism in three stage, (i) oligomerization, (ii) aggregation, and (iii) condensation. The models of molecular dynamics with Si/Al molar ratios of 2 were simulated and shown Fig 1. [7].

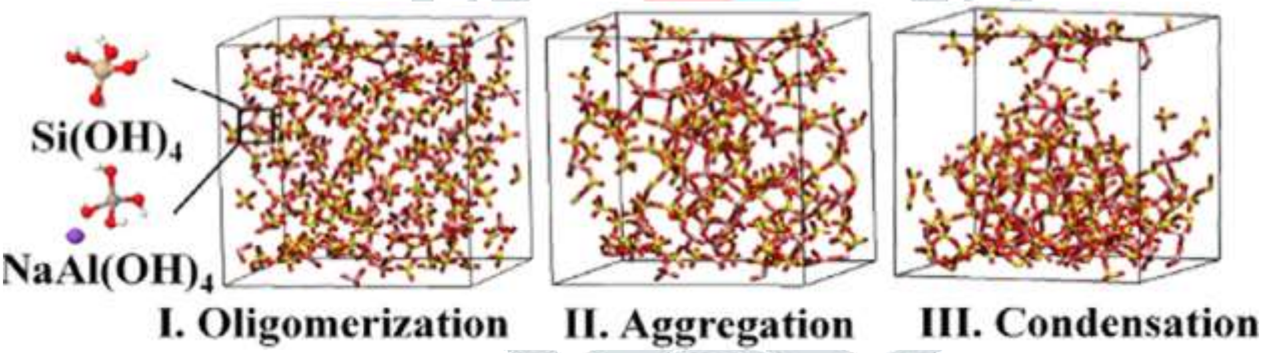


Fig 1. Molecular dynamics simulation model for geoplymerization at Si/Al = 2 [7]

IV. GEOPOLYMER CEMENT AND CONCRETE FABRICATION : -

Basically two type of component are required for fabrication of geopolymers [10,13,18,19]. The two component are represented in table given below.

Source Materials (Alumino silicate)	Alkaline Activator
Fly-Ash, Rice Husk Ash, Calcined Clay, Slag, Coper Mine Tailing, Waste Glass, Pure Al_2O_3–$2SiO_2$ Powder, Palm Oil Fuel Ash obtained from Malaysia.	KOH, NaOH, $Ca(OH)_2$, NaOH + Na2CO3, K_2CO3 + Ca(OH)2 Sodium Silicates (Other Silicates May be used)

Commercially, serval grade of sodium silicate solutions are available and alkali solutions of altered concentrations (8– 16 M) are used but ready at least 24 h ago. Sodium silicate can be substituted by rice husk ash and disbursed diatomaceous mud in NaOH or rice husk ash and sodium water glass in Sodium Hydroxide [20-22].

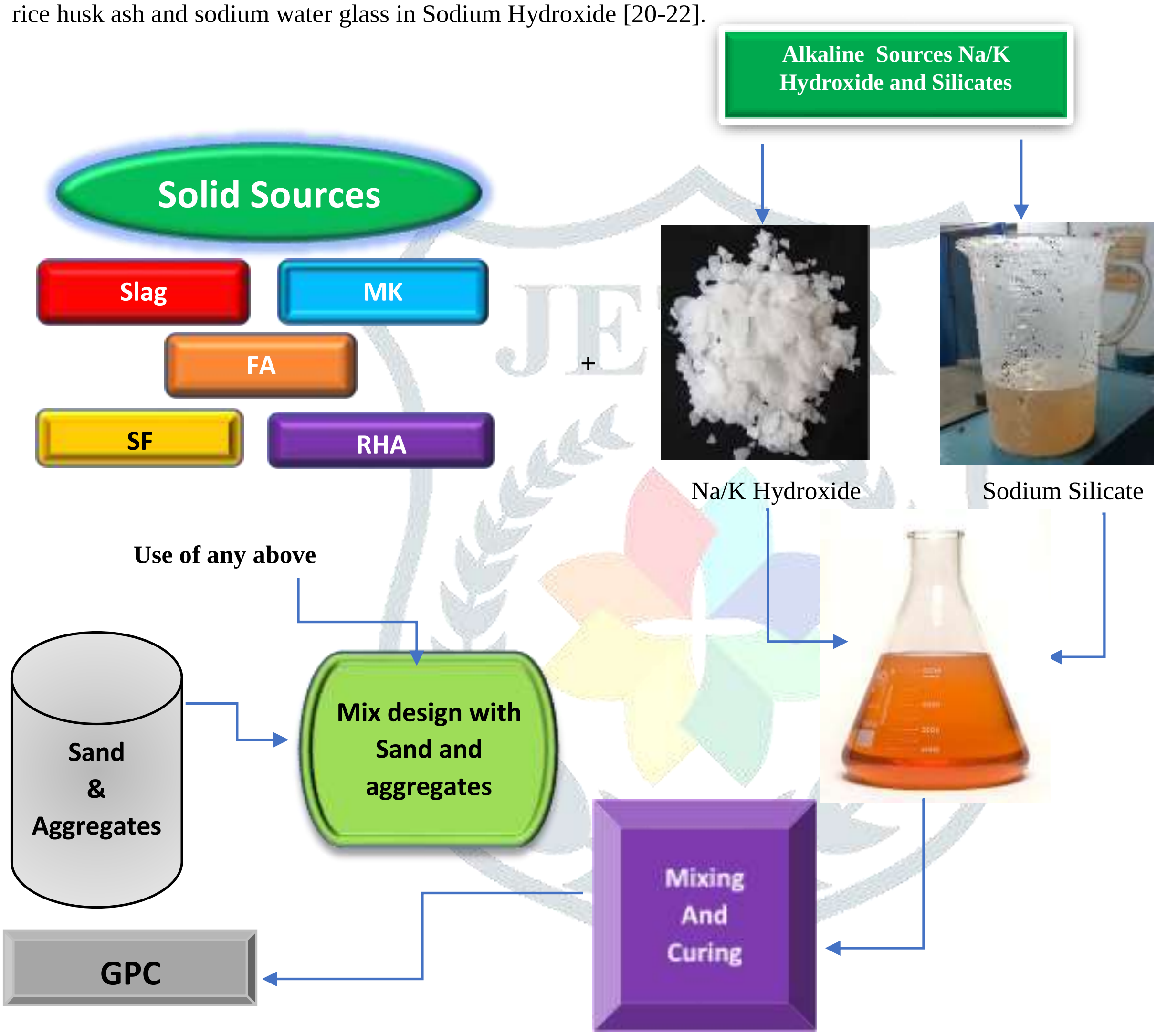


Fig. 2 Geopolymerization Process

Bottom coal ash and calcined paper sludge in combination is used as raw material in geopolymer. Paper sludge improved the reactivity of bottom coal ash through the development of polymerization [23]. For masonry applications waste paper sludge based geopolymer mortars can be used [24]. Fabrication of geopolymers using mixing of recycled sludge and Rice Husk Ash has been used for the light weight works [25]. The reactivity and the properties of geopolymers be governed by particle size of the source material [11,16]. There are three altered ways have been tried to create geopolymer cement [8].

Processes 1	**Processes 2**	**Processes 3**
FA(*s*) + **NaOH**(*l*) ↓ ***mixing*** **Sodium Silicates** (*l*) ↓ ***mixing*** Cement paste	**FA**(*s*) ↓ ***mixing*** **NaOH**(*l*) +**Sodium Silicates**(*l*) ↓ ***mixing*** Cement paste	**FA**(*s*) + **NaOH**(*l*) + **Sodium Silicates**(*l*) ↓ **Dry-** ***mixing*** **Water** ↓ ***mixing*** Cement paste

Fig. 3. Synthesis ways for geopolymers [8].

Processes 1 and 2 give high compressive strength as compare to the processes 3, (Fig.4) but in case of processes 3, high heat is releases, which increases the temperature and used is dry form as well.

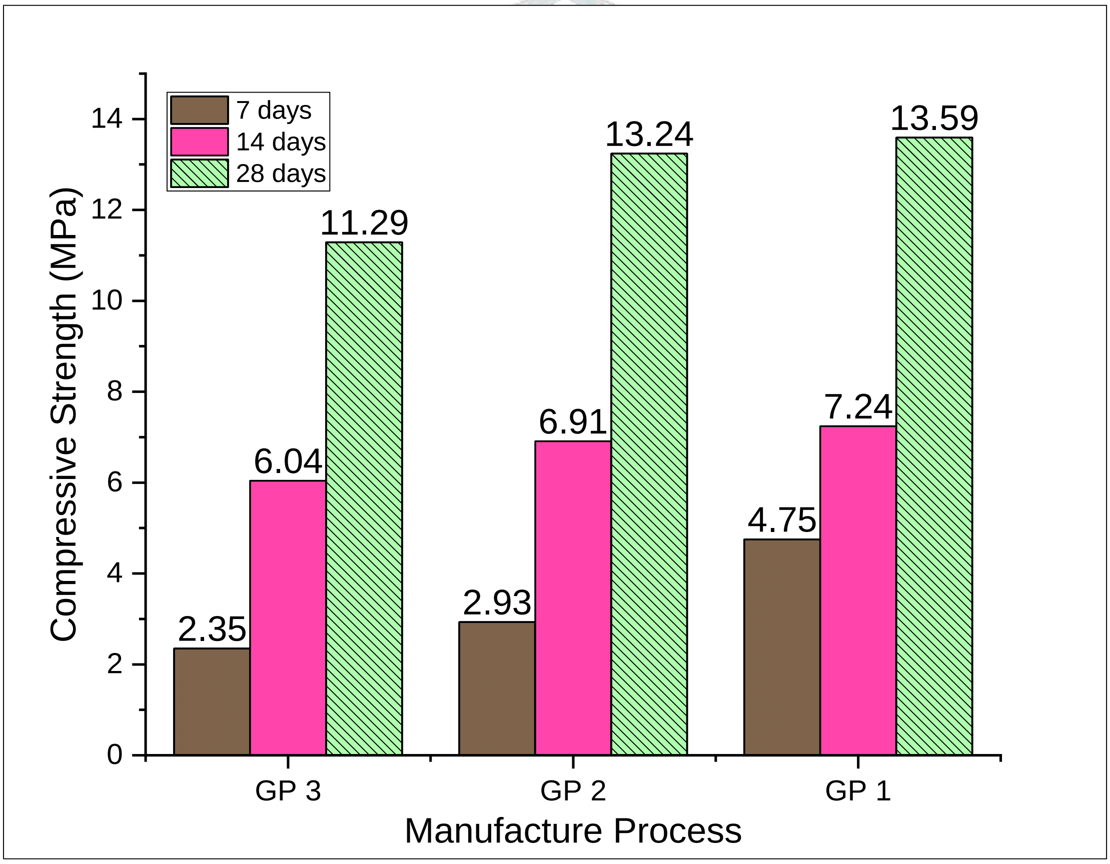


Fig 4. Compressive strength and process of synthesis [8].

Several parameters altered the production of geopolymers prominent to changes in properties. few of the parameters liable for property fluctuations are given below..

4.1 Effect of Na_2O and SiO_2/Na_2O on the compressive strength of fly ash based geopolymer.

As Na_2O content increases the compressive strength of fly-ash based geopolymer is increases Fig (5.a) [31]. It may be possible due to increased amount of reaction products. As amount Na_2O content increases, alumina and amorphous silica of (FA) is more dissolving phase. The dissolved ions take part in the reaction and rise the quantity of products. The variation of compressive strength with curing time at different SiO2/Na2O molar ratio at constant amount of Na2O (8%) and temperature are plotted in Fig. 5.b [26]. The results showed that compressive strength increases up to certain optimum value of SiO2/Na2O (SiO2/Na2O = 1.4) and after that decreases.

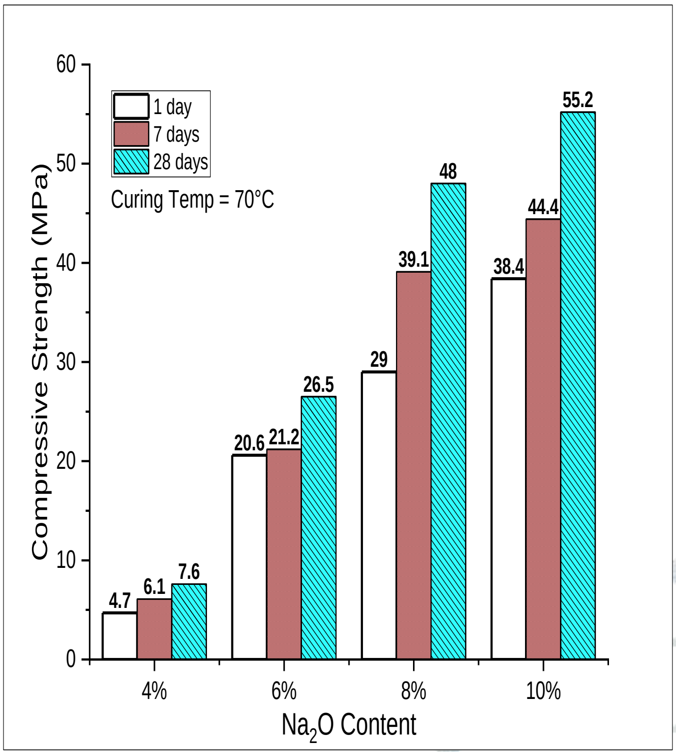


Fig. 5 (a)

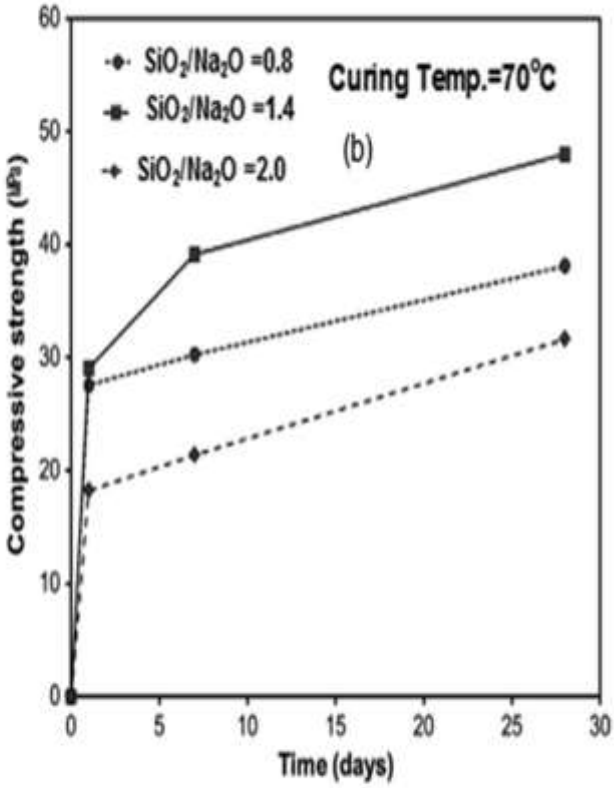


Fig. 5 (b)

4.2 Quantity of NaOH and mechanical properties:-

As the content of Sodium Hydroxide (NaOH) is increases it is predictable the compressive strength is increases because as NaOH increases the dissolving characteristic of Si and Si-Al of the source materials expected to increases with increases the geopolyerization. But higher concentration may increases the viscosity of NaOH causing rapid precipitation of aluminoslicate gel, result decreases in mechanical properties [27]. Commonly, the strength of geopolymer mortars is improved with increasing Na2O/Al2O3 ratio. Mortars with Na2O/Al2O3 ratio of 0.84 have shown highest compressive strength [28].

V. CURING OF GEOPOLYMER:-

It may be noted that the geopolymerization is commonly increases by the heat treatment and curing environment. Two method are commonly used conventional heat and microwave curing.

5.1 Heat Curing

Curing is an important parameter of geopolymer, because curing influence the mechanical and durability properties. It is noted that overheat is occur during curing of the specimen. The inside temperature of specimen grow above the boiling temperature of water when specimen is put in a furnace at 90°C. Although at the starting silicate solution has an initial boiling point that is much higher than water, cracks are produced due to internal stress. It weakens the structure giving mechanical strength much lower [26,27]. When healed in a microwave oven, geopolymer pastes gives higher compressive Strength [29]. Fig. 6
Solar curing is a innovative and eco-friendly way of curing. Oven dry method and ambient curing are limit methods. Microwave curing is another method for increases the procedure of hardening. Hot pressing is an alternate method [30]. The air trapped in pores of geopolymer matrix are removed due to hot pressing, subsequent growth in the density [30].

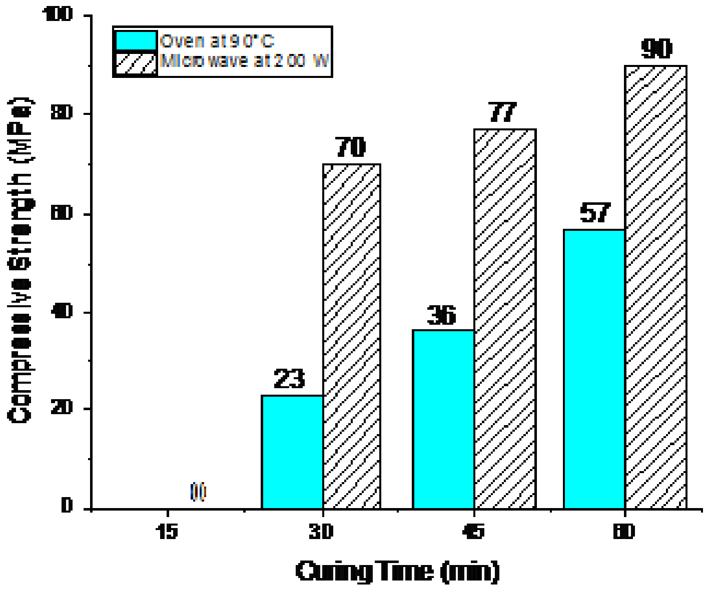


Fig. 6

VI. REPRESENTATION OF GEOPOLYMER BINDER : -

There are serval techniques has been used to characterization of geopolymers. Some of them are described below.

6.1 X- ray diffraction method (XRD):

It is understood that geopolymers is made from serval's raw material, with the help of XRD patterns we know that geopolymers manufactured from different raw materials are similar and amorphous in nature [31]. The hump of metakaolin pattern is broad between 2θ = 18-30° which decreases due to alkaline dissolution [31]. At the same time this seems the advent of new wide hump at 2θ = 7-13 and 20-35°. As soon as curing time enhance to 28 and 60 days the hump at low angle extinct. It is found that the pattern of geopolymer for 28 and 60 days curing is almost identical, showing that very few reaction might occur after 28 days.

6.2 Raman spectra:

For know about differentiate between various silicates glassy phase, Raman spectroscopy can be used. It is noted that band between 1200 and 800 c/m are found in Raman spectra of geopolymer. Basically bands are due to (Si_2O_5), (Si_2O_6), (Si_2O_7) and (SiO_4) symmetric stretching vibration were found between 1100 and 1050 c/m, 1000-950 c/m, 900 c/m, and 850 c/m respectively. The region of band from 700-400 c/m are associated with inter-tetrahedral Si-O-Si linkage.

6.3 SEM (Scanning Electron Microscopy) studies

SEM and EDX pattern of Fly-Ash shown on figure 5 given below. At different concentration of NaOH and temperature the SEM photomicrographs of synthesized of geopolymer samples are shown in figure a) to i) []. By the change of alkali concentration (6, 8 and 10 M) and curing temperature (27, 45 and 60º C) (eg. 6 M 27 = 6 M @ 27ºC), microstructure are changed. The degree of alteration increased with curing temperature.

6.4 Heat evolution

Kumar and Nath studied heat evolution profile during geopolymerization of Fly-Ash at different temperatures (34, 39, 45, 52, and 60ºC) in presence of 6, 8 and 10 M NaOH. The FA was mixed in the of 2:1 is NaOH solution. The rate of heat evolution (mWg^{-1}) with time (h) at different temperature in presence of 6, 8 and 10 M NaOH given in fig. (a-c) after data normalization. It is noted that as the temperature increases the peak intensity is also increases and shifted to lower time, show that high reactivity. At high concentration the shape of peak changed. Based on calorimetric, geopolymerization degree was determine at different temperatures and NaOH concentrations. Arrhenius equation is used to find out energy of activations and the values for 6, 8 and 10 M NaOH were found respectively 52.8, 87.9 and 104.6 $kJmol^{-1}$. At higher NaOH concentration, the energy of activation value was found higher because the amount of reaction product formed was higher.

6.5 IR spectral analysis of geopolymer

According to the C.A Rees the IR spectroscopy is used to investigated the geopolymers [32]. For the different linkages there are different vibrational band is present [33]. Due to asymmetric stretching of Si-O-Si or Al-O-Si the band at around 1075 c/m in case of fly ash. But asymmetric stretching shifted to lower value 997 c/m due to geopolymerization.
This is due to the AlO_4 partially replaces SiO_4 and change chemical environment of Si-O bond [34].

VII. PROPERTIES OF GEOPOLYMER CEMENT

7.1 Mechanical properties

There are several parameters in which compressive strength of geopolymer cement depend [28]. It is noted that the more the fineness of binding materials and nanosize additions affect the compressive strength to a considerable degree. Compressive strength at 3 days of geopolymer cement and Portland cement paste at different temperatures were compared in fig . Allowing to the P.Duan, C. Yang et al. the compressive strength of geopolymer cement paste was found to be much higher as compared to that of OPC cement [35]. When heated to 1000°C for 2h the change in dimensions is occur by measuring the change in dimensions the thermal stability of some geopolymer is determined.

7.2 Anticorrosive properties

In comparison to the Portland cement based product the geopolymer have better anticorrosive properties. Bar embedded in geopolymer concrete had low corrosion rate and good corrosion performance [36].

7.3 Efflorescence

Efflorescence is defined as deposit of salt on the surface of concrete, In generally the salt is whitish in colour. In case of geopolymer concrete it is deposited in form of $Na_2CO_3.nH2O$ (s) on the other hand in case of Portland cement concrete it is calcium carbonate. Efflorescence is not only the surface problem but it may be responsible for structural change result to lower the strength [37].

7.4 Fire resistant properties of geopolymer

It is important that building must be flamed and fire resistant. There are many materials which are fire and heat resistant [38]. Geopolymer are able to resist higher temperature and can be used as fire resistant materials. Saxena et al studies the effects of temperature on compressive strength [39]. For the different curing temperature with different mixes the compressive strength are show in fig. It is found that compressive strength increases up to 600°C and there after the value decreased in all the cases.

7.5 Geopolymer coating

The geopolymer materials are good coating material because it posses satisfactory fire resistant, corrosion resistant, heat resistant and high mechanical properties [40].

7.6 Effect of ground granulated blast furnace slag (GGBFS)

According to the S. Saha setting time of geopolymer paste were reduced when GGBFS is added to it [41]. As content of CaO is higher it may help to form C-S-H gel along with geopolymer at early time. When the sodium hydroxide content and amount of GGBFS is increased in geopolymer give higher value of compressive strength.

7.7 Effect of $Ca(OH)_2$ on geopolymerization

L. Prasittisopin et al concluded that $Ca(OH)_2$ accelerates process of geopolymerization [42]. In fly ash based geopolymer as amount of $Ca(OH)_2$ increases result decrease setting and increases compressive strength.

7.8 Effect of silica flume with high alkaline activation

The rheological behavior of GGBFS based geopolymer is a enhance by the slice flume [43]. For mortar with maximum aggregate size of 2 mm when warer/binder ratio reduced to 0.25 resulting in very high compressive strength value (> 150 MPa) after 28 days or even after 2 days cured at 60°C for 24 h [44]. In the case of rice husk ash based geopolymer this effect also be observed as well [45] but not as strong as in case of GGBFS based. But it is find that in both the cases the capillary porosity is lower than 2 vol%.

7.9 Addition of nanomaterials

Nanoparticles such as nanosilica (NS), nanotitania (NT), nanoalumina (NA), carbon nanotube and nano-clay is generally enhance the properties of geopolymer [46] but the studies are limited. The carbonation resistance of geopolymer is increases when the nano- TiO_2 is used [46]. Mechanical properties is improved when nano Al_2O_3 is used fig. [47]. The small quantity of rGo sheets used in geopolymer enhances mechanical properties and reduced the overall porosity of geopolymer [48].

Constituents	**Mixes**					
	A	B	C	D	E	F
Fly ash	200	200	0	0	0	0
GGBFS	0	0	0	0	200	200
Cc	0	0	200	200	0	0
Quarzitic sand	600	600	600	600	600	600
Silica flume	0	64	0	64	0	64
Sodium silicates	80	80	80	80	80	80
Sodium hydroxide	40	40	40	40	40	40
Extra water	0	5 ml	0	10 ml	0	5 ml

VIII. FIBER REINFORCED GEOPOLYMER CONCRETE

Concrete exhibits brittle behavior due to low tensile strength to overcome this problem fiber reinforced geopolymer concrete have been developed. When the fiber added to the geopolymer, change the behavior from brittle to ductile or quasi-ductile with considerable enhance in the tensile strength, toughness, tensile strain and absorption capacity, even fibers are either short or continuous [49]. It is also noted that when carbon fiber (CF) used is geopolymer it decreases electrical resistivity considerably fig. [50].

IX. DURABILITY OF GEOPOLYMER CEMENT

9.1 Durability in NH_4NO_3

The compressive strength of fly ash based geopolymer decreased during 28 days, when it exposed to 6 M NH_4NO_3. Decrease in compressive strength is due to the breaking of -Si-O-Al- bonds in aluminoslicate gel [51].

9.2 In acidic environment

The properties of concrete by which it resist weathering, abrasion and chemical attack is known as durability of concrete. The studies of durability in acidic medium of geopolymer is available in details [52,53]. Deteriorating is influenced by concentrations of acid and time of exposure [54]. Deteriorating is very little in case of sulfuric acid [55]. In sulfuric acid solution fly ash based geopolymer paste give high resistance at temperature 60-220°C [56]. It is find that 5% Na_2SO_4 solution did not have any deteriorating effect [57]. But in case of $MgSO_4$ severe decalcification of binder . Gypsum is formed due to $MgSO_4$ which deterioration of structure and dimensional integrity [59].
The collapse of mesoporous structure and leaching of geopolymer gel occur due to the concentration hydroxide solution [60]. Geopolymer concrete resist to chloride attack. When exposed to a short term , no major change in compressive strength is observed [61].

X. APPLICATION OF GEOPOLYMER CEMENTS

There are different area in which geopolymer cement is used [62].

10.1 Anti-microbial efficiency of geopolymer mortar

Normally mortar and concrete have a pH value of range from 10-12 due to it's high alkalinity it does not allow any microbe attack on surfaces. however, in the presence of CO2/H2S, the pH decreases with time and when it goes beneath 9, microbial assault starts. The formation of colonies (microbial) and capillaries on the surface result in damage on concrete surfaces thru bio- deterioration. When used in small quantities Silver NPs have anti-bacterial property [63].

10.2 Self- cleaning geopolymer concrete

For neat and clean environment and maintain building appearance self cleaning concrete is one of the best way to achieve it. The photocatalytic materials likes titania (TiO_2) and zinc oxide (ZnO) gives the self-cleaning properties of geopolymer concrete. The decomposition of organic matter in presence of UV in geopolymer concrete [64]. Compressive strength increases when nano-TiO_2 add in geopolymer , because formation of more geopolymer.

XI. EMISSION OF CARBON DIOXIDE

Compression of Carbon footprint of geopolymer and OPC concete is given by the Turner and Collins et al fig. [65]. There are 9 % less carbon footprint is found as compared to OPC [65].

XII. CONCLUSION

- **a)** Geopolymer technology is a appropriate approach to utilization of by wastes (by product) like-Rice husk ash, fly ash, GGBS etc from different industries.
- **b)** Geopolymer contain dense structures gives high early strength and better resistance to adverse environment.
- **c)** The properties and formations of geopolymers depends upon physical and chemical properties of raw material, curing conditions and alkaline activators.
- **d)** It is not clear understood the polymerization mechanism due to the impurities and different origins of raw materials.
- **e)** Geopolymer cement emits lower toxic gas CO2 gas so it is a green (eco-friendly) cement.
- **f)** Now a day geopolymer used as a alternative to the OPC to develop construction materials but new technologies has been developed by construction industry to solution of its green house problems.
- **g)** Mechanical properties of geopolymer increases with increase in SiO2 and Na2O content.
- **h)** The properties of geopolymer improve when nano-materials used in geopolymers.
- **i)** Addition of fiber in geopolymer concrete leads to increased tensile strength, toughness and tensile strain of geopolymers.
- **j)** Geopolymer used a self-cleaning concrete for better appearances and clean environment.
- **k)** In geopolymer technology the water used is negligible amount as compared to the OPC.

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