

ABSTRACT

The production of Portland cement has been swelling manifold throughout the world due to the mounting demands of the construction industry. However, this huge production of Portland cement is highly internal- energy-intensive and causes emission of green house gas, CO₂. The pollution involved in the manufacture of cement hampers the image of concrete as a sustainable material. Efforts are continuously being made to make concrete environmentally friendly. Concrete is the most commonly used construction material without proper substitute so far. With the increase in construction activities, there is heavy demand on its ingredients, particularly for cement. Many such alternates for cement have been tried by different scientists worldwide, but the best choice of a substitute material to cement has been agreed to be the Geopolymer paste. Also, cement is manufactured by the calcinations process of a hefty quantity of lime stone and this large quantity of lime stone is explored from the lime quarries, which in turn creates an imbalance in the mineral wealth of our planet. In spite of the easy availability of Portland cement in the market at present, concrete made out of it is found to be less durable in some of the very severe environmental conditions due to the presence of free calcium. Therefore, arrival of any new alternate material of construction immediately should be assessed for both strength and durability. The complex phenomenon of aggressive chemical attack and the associated damage to concrete considerably reduces the strength and stiffness of reinforced concrete members leading to premature failure. Failure does not only mean structural collapse but also includes loss of serviceability characterized by cracking, spalling, debonding or excessive deflection. Keeping all the above aspects in mind, a detailed experimental investigation on the manufacturing process, serviceability under loads, durability against various severe disturbing agents are inevitable as far as a new material is concerned. Geopolymer concrete is a firsthand development in the world of concrete in which cement is wholly replaced. Geopolymer concrete is a versatile and embryonic material in the construction industry. In this regard, Geopolymer concrete can be considered as a potential candidate material to replace cement concrete which does not generally have free lime which attributes an inherited property of acid resistance. Geopolymers are ceramic materials that are produced by alkali activation of alumina-silicate raw materials, which are transformed into reaction products by polymerization in a high pH environment and hydro thermal conditions at relatively low temperatures. As relatively new material, extensive studies are still needed to explore its applicability as a construction material. In this research, anthracite coal burnt low calcium fly ash from Tuticorin Thermal Power Station, Tamilnadu, India has been used to synthesize Geopolymer concrete. This work is state-of-the-art and the first of its kind in India to evaluate the applicability of Indian fly ash in Geopolymer concrete as source material for manufacturing alumina-silicate concrete under heat curing, with the aid of an exclusively designed Heat-curing chamber in the Geopolymer concrete laboratory of Thiagarajar College of Engineering, Madurai, Tamilnadu, India. The present research has been organized into four primary sectors namely achievement of normal strength (30 N/mm²) and high strength (50 N/mm²) Geopolymer concretes, durability study on plain Geopolymer concrete cubes and cylinders, comparative study on the flexural behavior of reinforced cement concrete and reinforced Geopolymer concrete beams of various sizes, and durability study on reinforced Geopolymer concrete beams exposed to sulfuric acid attack, chloride attack, sodium sulfate and magnesium sulfate. Under the prime sector, using low calcium class F Indian fly ash, M30 and M50 grade Geopolymer concrete cubes and cylinders were manufactured and tested for resistance to sodium sulfate, sulfuric acid, and chloride and water absorption according to the procedure given in ASTM C 642. Durability aspects such as visual appearance, change in mass and change in compressive strength were noted and compared with ordinary Portland cement concrete cubes and cylinders of same grades subjected to the above tests. From the test results, it was observed that Geopolymer concrete exhibited very good resistance to all exposures, whereas OPC concrete got deteriorated very much. Reinforced cement concrete and reinforced Geopolymer concrete beams were cast and tested for load at first crack, ultimate load, ultimate moment and maximum deflection. The experimental

results of reinforced cement concrete and reinforced Geopolymer concrete beams were compared. It was observed that with the same percentage of tensile reinforcement, reinforced Geopolymer concrete beams showed higher ultimate moment resistance which exceeded by reinforced cement concrete beams with exemplary ductility. Finally, small reinforced Geopolymer concrete beams were cast. The specimens were subjected to durability tests such as resistance to chloride attack, sulfuric acid attack, sodium sulfate and magnesium sulfate. Of all the permeability tests on these durability parameters, it was observed that there was marginal reduction in the weight of the specimen subjected to acid attack and the weight loss was negligible in the case of specimen subjected to sodium sulfate attack. But the deposits found on the elements exposed to magnesium sulfate solution not only increased the weight marginally but also enhanced the flexural strength. Study of these durability tests reveals that Geopolymer concrete has the potential and could well be implemented into prefabricated structural applications particularly in aggressive environmental conditions.

KEYWORDS: Geopolymer concrete, ASTM C 642, M50 grade Geopolymer concrete, Geopolymers, metakaolin clay.

INTRODUCTION

Geopolymer concrete, an unindustrialized material in India, is going to be a revolution not only in the research field but also in the construction industry. Geopolymers, an unique class of inorganic polymers are new promising binders and are manufactured by the activation of a solid state alumino-silicate with a highly alkaline activating solution using thermal drive. In the recent past, Geopolymer binders have been found to be the best alternate to cement binders due to its environmental pleasantness. Its performance in aggressive environment is promising and these binders could become a replacement for cement concrete in aggressive situation where cement concrete is vulnerable. Cement is the most sought after material by the concrete industry throughout the world. Day by day, the requirement of cement in the concrete industry and in the construction field is increasing quite alarmingly. The production of such huge quantity of cement leads to the emission of 80% of that quantity of CO₂, the greenhouse gas, into atmosphere. The production of 1 tonne of rock based Geopolymer cement requires 3.5 times less energy than that of Portland cement. It generates 0.184 to 0.218 tonnes of CO₂, from combustion carbon-fuel, compared with one tonne of CO₂ for Portland cement (Joseph Davidovits 2010). This emission of green house gas into atmosphere is the prime reason for global warming, a worrisome factor for the humankind and Scientists across the globe are trying hard to find an alternative to disturbing factors like emission of green house gases into the atmosphere. Such hard work by Scientists has led to the invention of Geopolymers and Geopolymer concrete which are more suitable in the construction industry. Even high strength prefabricated structural elements of the desired size could be manufactured using this novel material.

GEPOLYMER TECHNOLOGY

Geopolymers

The production of Portland cement exhausts the resources and also it is an energy intensive process that releases large amounts of the green house gas CO₂ into the atmosphere. Approximately 2.8 tons of raw materials, which include fuel and other material, are required to manufacture 1 ton of Portland cement (Nugteren et al 2005). It has now become mandatory mixing pozzolonic material like fly ash to cement to partially replace Portland cement. Recently, another cementitious material, manufactured from an alumino-silicate precursor activated in a high alkali solution has been developed and this cementitious material is termed as Geopolymer. Geopolymer has recently emerged as a novel engineering binder material with environmentally sustainable properties (Palomo et al 2004). It is also well known that alkali activation of alumino-silicates can produce X-ray amorphous alumino-silicate gels, or Geopolymers, with excellent mechanical and chemical properties. These gels can be used to bind aggregate, such as sand or natural rock, to produce mortars and concretes. Geopolymers are inorganic binders that function as the Portland cements. The Geopolymer gel network is comprised of tetrahedral alumino-silicate structures charge-balanced by alkali cations. In the first stage of Geopolymerisation, (Van Jaarsveld et al 2003) the activating agents of the reacting slurry attack the solid alumino-silicate components, releasing aluminate and silicate monomers to the solution. These monomers and small oligomers polycondense and crosslink to form a three-dimensional alumino-silicate gel network (Joseph Davidovits 2008). From the term Geopolymer, it should not be concluded that polymers are used to manufacture Geopolymer concrete. A source material, like Fly Ash, metakaolin clay, Rice Husk Ash etc, rich in silica and alumina belong to geological origin. Upon mixing the source material with alkaline solution, polymerization takes place to get Geopolymer gel under thermal energy. Hence, taking Geo form geological origin and polymer from polymerization, Prof. Davidovits, a French chemist coined the term Geopolymer in 1978.

Geopolymerisation: The polymerization process involves a fast chemical reaction under alkaline conditions on silicon-aluminium minerals that results in a three dimensional polymeric chain and ring structure. The ultimate structure of Geopolymer depends largely on the ratio of Si to Al (Si:Al), with the materials having a ratio of Si:Al between 2 to 3.5 for use in concrete application (Joseph Davidovits 2008). A critical feature is that water is added only for workability and this water does not become a part of Geopolymer structure. In other words, water is not involved in the chemical reaction and is expelled during curing and drying. In the hydration process of OPC, the resultant products are predominantly calcium silicate hydrate (C-S-H) gel and calcium hydroxides. Whereas in the case of Geopolymer, these do not form. CSH is a gel of hydrated CaO-SiO₂, which normally contributes mechanical strength to cement. In contrast, the formation of three dimensional amorphous alkali alumino-silicate network with a general formula of (Na/K)_n-((-Si-O)₂-Al-O)_n.wH₂O which attributes the binding properties to Geopolymeric gel in terms of their elemental composition is calcium. If excess calcium is added, some forms of C-S-H gel will be obtained. But it has significantly lower Ca/Si ratio than the CSH gel formed from hydration of Ordinary Portland Cement (Van Jaarsveld et al 2003).

MATERIALS INVESTIGATION

INTRODUCTION

Samples of each and every constituent material are tested in laboratory for their physical and chemical properties.
 ORDINARY PORTLAND CEMENT

Ordinary Portland cement was used to produce a control mix concrete in this research. The total requirement was calculated and was purchased from local dealers and stored in a dry place inside casting yard and kept covered with tarpaulin sheets, to avoid clotting. RAMCO 43-grade cement has been used throughout this investigation. The physical properties of the cement obtained from the tests conducted as per relevant IS codes are shown in Table 4.1.

Table 4.1 Physical properties of cement

Sl. No.	Physical property	Tested value	Reference Code
1.	Specific gravity	3.10	Le-Chatelier flask IS : 1727-1967
2.	Standard consistency	30%	IS : 4031-1968 part 4
3.	Setting time Initial Final	57 minutes 4 hours	IS : 4031-1968 part 5 IS : 4031-1968 part 5
4.	Soundness test	0.95 mm	Le-Chatelier's apparatus
5.	Compressive strength (28 days)	44.37MPa	-----

The cement has magnesium oxide (MgO), sulfuric anhydride (SO₃), free lime and alkaline oxide below the permissible limit specified by AS 3972 and ASTM C150. Excessive content of those chemicals could change the cement soundness. Magnesium oxide and sulfuric anhydride in excessive levels contribute to a long-term expansion of cement. High alkaline oxide content in the cement is prone to cause alkali-silica reaction with reactive aggregates in the mixture. Chloride found in the cement is normally added to accelerate early strength and reduce setting time. The chemical composition of the OPC cement is presented in Table 4.2

Table 4.2 Chemical characteristics of Ramco 43 grade Portland cement (manufacturer's data)

Chemical Compound	Average %	Permissible limits
Silica (SiO ₂)	20.99	-----
Alumina (Al ₂ O ₃)	6.05	6%, max (ASTM C150)

Ferric oxide (Fe ₂ O ₃)	6.01	6%, max (ASTM C150)
Calcium oxide (CaO)	62.74	-----
Magnesium oxide (MgO)	1.33	5% max (BIS)
Sulphuric anhydride (SO ₃)	1.82	3.5% max (AS 3972)
Loss on ignition (LOI)	1.14	5%, max (BIS)
Alkalies	0.8	1.5%, max(BIS)
Chlorides	0.015	-----
Lime saturation factor(LSF)	0.88	0.66-1.02, max(BIS)

FINE AGGREGATE

The fine aggregate used in this investigation was clean river sand passing through 4.75 mm sieve with fineness modulus 3.0, the specific gravity 2.60 and the bulk density was 1.72 and 1000 gm of sample was taken for test. The particle size distribution is given in Table 4.3. The tests on sand were carried out as per IS: 2386-1963(III). The sand used belonged to Zone II. The grading curve is given in Figure 4.1.

Table 4.3 Sieve analysis of fine aggregate

Sieve size (mm)	Weight of material retained (gm)	% Weight of material retained	Cumulative % weight of material retained	% Weight of material passing
4.75	0	0	0	100
2.36	74	7.4	7.4	92.6
1.18	367	36.7	44.1	55.9
0.60	132	13.2	57.3	42.7
0.30	317	31.7	89	11
0.15	110	11	100	0

COARSE AGGREGATE

Locally available crushed blue granite metal aggregate of size 20 mm and below was used and various tests were carried out to ascertain the physical properties of coarse aggregate which are listed in Table 4.4.

Table 4.4 Physical properties of coarse aggregate

Sl. No.	Physical property	Tested value	Reference code
1.	Specific gravity	2.75	IS: 2386-1963 part 3
2.	Fineness modulus	7.12	IS: 2386-1963 part 3
3.	Percentage voids	39.02%	---
4.	Crushing value	27.07%	IS: 2386-1963 part 4

FLY ASH

Fly ash is pozzolonic and reactive mineral admixture generated by combustion of coal in thermal power plants, and comprises of fine particles that rise with the flue gases and assumes the prime role in the manufacture of Geopolymer concrete



Figure 4.2 Picture of Indian fly ash use

WATER

Potable water was considered throughout this study for diluting NaOH flakes, for manufacturing OPC concretes and for preparing aggressive liquids. The amount of solids was below the permissible limits as specified by

Table 4.6 Results of water quality analysis

Serial No.	Description of test	Water sample	Maximum permissible limit
1.	pH value	8.9	6.0-9.0
2.	Hardness (ppm)	403	1000
3.	Sulphate (ppm)	100	400
4.	Chlorides(ppm)	137	500

HEMICAL ADMIXTURES

In order to improve the workability of stiff and fresh concrete to some extent, a high-range water-reducing Ligno-sulphonated normal super plasticizer for the manufacture of M30 grade Geopolymer concrete and a high performance Polycarboxylic ether based super plasticizer purchased from BASF under trade name GLENIUM B233 for the manufacture of M50 Geopolymer concrete were used. Though the addition of plasticizer does not improve workability of Geopolymer concrete, (Chindapasirt *et al* 2007, Daniel Kong *et al* 2010), it is still mixed in Geopolymer concrete to match with OPC concrete mix.

MIXTURE PROPORTIONS

OPC Concrete Mix Design

Ordinary Portland cement (OPC) concrete was produced for certain tests and all the OPC concretes produced were taken as reference concrete. The mixture was designed according to IS Code method of design. The target strength of the OPC concrete control mix was 30 MPa for normal strength concrete and 50 MPa for high strength concrete. The same amount of superplasticizer was added in the mixtures to match with Geopolymer concretes

Geopolymer Concrete Mix Design

The Geopolymer concrete mixtures were originally designed referring GCI report (Hardjito et al 2005) and assuming some parameters such as aggregate content, alkaline/fly ash ratio and sodium silicate/sodium hydroxide ratio. The calculation was used to obtain the quantity of fly ash, aggregate, solid sodium hydroxide, sodium silicate, and water. The primary difference between Geopolymer concrete and Portland cement concrete is the binder. The silicon and aluminium oxides in the low- calcium fly ash react with the alkaline liquids to form the Geopolymer paste that binds the loose coarse aggregates, the fine aggregates and other un reacted



4.17 FINISHED GEOPOLYMER PRODUCTS READY FOR TESTING



Geopolymer concrete cubes (G50)



Geopolymer concrete cubes (G30)

- Based on these extensive investigations, the following set of conclusions is drawn:
This research has paved the way for the incorporation of promising Geopolymer concrete in structural applications and has led to the total elimination
- The fly ash, once considered as waste material, has found usefulness through Geopolymer concrete in construction industries and become a valuable material. Cement from concrete which ultimately becomes “Green Concrete”
- The average tensile strength of 14M, G30 Geopolymer concrete exceeded the tensile strength of its counterpart OPC concrete M30 by 13.20% and 14M, G50 exceeded M50 by 3.5%.
- Geopolymer concrete cubes exposed to 5% sodium sulfate solution showed no visible sign of surface erosion, cracking or spalling of the specimens upto 4 weeks and little erosion of surface could be noticed after 8 weeks. The increase in mass of specimens soaked in sodium sulphate solution was approximately 1.2% after 4 weeks and 1.72% after 8 weeks of exposure.
- All Geopolymer concrete specimens exposed to sulfuric acid invariably had lost strength by about 4.1% in 4 weeks and 9.7% in 8 weeks whereas OPC specimens had substantial weight loss of about 19% in 4 weeks and 22% in 8 weeks.

REFERENCES

- [1] Ailar Hajimohammadi, John L. Provis, Jannie S.J. van Deventer, “Time-resolved and spatially-resolved infrared spectroscopic observation of seeded nucleation controlling geopolymer gel formation”, *Journal of Colloid and Interface Science*, Vol.357, pp. 384-392, 2011.
- [2] Alvarez-Ayuso, X., Querola, F., Planaa, A., Alastueya, N., Moreno, M., Izquierdo, O., Fonta, T., Moreno, S., Dieza, E., Vázquez, M. and Barrab, “Environmental, physical and structural characterisation of geopolymer matrixes synthesised from coal (co-)combustion fly ashes *Journal of Hazardous Materials*”, Vol.154, pp.175-183, 2008.
- [3] Anjan K. Chatterjee, “Indian Fly Ashes: Their Characteristics and Potential for Mechanochemical Activation for Enhanced Usability”, *Journal of Materials in Civil Engineering*, Vol. 23, No. 6, pp. 783-788, 2011.
- [4] Anuradha, R., Sreevidhya, V., VenkataSubramani, R. and Rangan, B.V., “Modified Guidelines for Geopolymer Concrete Mix Design Using Indian Standard”, *Asian Journal of Civil Engineering (Building and Housing)* Vol.13, No.3, pp.353-364, 2012.
- [5] Anurag Mishra, Deepika Choudhary, Namrata Jain, Manish Kumar and Nidhi Sharda, “Effect of Concentration of alkaline liquid and curing time on strength and water absorption of geopolymer concrete”, *APRN Journal of Engineering and Applied sciences*, 2008.
- [6] AS 3972-Australian Standards for General Purpose and Blended Cement.
- [7] ASTM C-1202-09-Standard test method for electrical indication of concrete’s ability to resist chloride ion penetration: *Annual Book of ASTM standards* (Philadelphia).

-
- [8] ASTM C-150-Standard specifications for Portland Cement: Annual Book of ASTM standards(Philadelphia)
 - [9] ASTM C-494-Standard specifications for Chemical Admixtures for Concrete: Annual Book of ASTM standards (Philadelphia).
 - [10] ASTM C642-97, Standard test method for density, absorption, and voids in hardened concrete. West Conshohocken (PA): ASTM International, 1997.
 - [11] Baker, A.L.L. "The Ultimate-Load Theory applied to the design of Reinforced and prestressed Concrete frames", Concrete Publications Limited, London, 1956.
 - [12] Bakharev, T. "Durability of geopolymer materials in sodium and magnesium sulphate solutions", Cement and Concrete Research, Vol.35, pp.1233-1246, 2005.
 - [13] Bakharev, T. "Resistance of geopolymer materials to acid attack", Vol.35, pp. 658-670, 2005a.
 - [14] Bakharev, T. "Geopolymeric materials prepared using Class F fly ash and elevated temperature curing", Cement and Concrete Research, Vol.35, No.6, pp. 1224-1232, 2005b.
 - [15] Bhanumathidas, N. and Kalidas, N. "Flyash for Sustainable Development", Ark communications, Chennai, 2004.
 - [16] BIS-Bureau of Indian Standards.
 - [17] Chang and Ee Hui, "Shear and bond behaviour of reinforced fly ash- based geopolymer concrete beams", Ph.D Thesis, Curtin University, Perth, Australia, 2009.
 - [18] Chindaprasirt, P., Chareerat, T. and Srivivatnanon, V. "Workability and strength of coarse high calcium fly ash geopolymer", Cement and Concrete Composites, Vol.29, pp.224-229, 2007.