PORTLAND CEMENT ACTIVATED GEOPOLYMER PASTE AND MORTAR

Ashis Kumar Panda[1], B Bhattacharjee[1]

1. Indian Institute of Technology, New Delhi, India

ABSTRACT. Results of an investigation on geopolymer paste and mortar cured at ambient temperature are reported in this paper. The geopolymer is activated with small percentage of OPC cement, sodium silicate and sodium hydroxide. The cement activated geopolymer paste and mortar is prepared and cured at ambient temperature using different curing methods through curing agents such SAP, PEG and also applied were dry and wet curing regimes etc. Results on setting time, strength, water absorption and porosity etc. for paste and mortar is reported. Potential of such material is then described in terms of their sustainability and cost implications.

Keywords: Geopolymer, Cement activated, Curing methods, Strength, Moisture absorption

Ashis Kumar Panda has been M. Tech Student at IIT Delhi from 2016 to 2018**.** This work is part of the project work carried out for M. Tech dissertation at IIT Delhi.Telephone with Country Code. +91- 9040709265. Email Id: ashiskumarp7@gmail.com

Dr Bishwajit Bhattacharjee is a Professor of Civil Engineering at Indian Institute of Technology Delhi, India. His research interests relate to science and technology of concrete material in general and building engineering. Telephone with Country Code: +91-11-26591193. Email Id: bishwa@civil.iitd.ac.in

INTRODUCTION

Cement based concrete is one of the most widely used materials in the construction industry. However, cement industry is often linked with hazardous effects like direct and indirect emission of greenhouse gases through heating of limestone or burning of fossil fuels to heat the kiln thus necessitating the need to search for alternatives to replace cement in concrete production [1]. Fly ash, a viable option for partial replacement of cement, has been increasingly used in concrete production, owing to its availability in huge quantities and problems relating to its disposal [2]. Geopolymer (GP) is one such construction material that could utilise fly ash to address the sustainability issues posed by cement production. Geopolymers consist of cross-linked network aluminates and silicates which are formed due to alkali activation of minerals rich in alumina-silica (such as fly ash, slag, etc.) [3]. It has emerged as one of the alternatives to Portland cement concrete due to its superior mechanical, thermal and chemical properties.

In the current paper, fly ash and OPC have been used along with alkali activators (namely, sodium silicate and sodium hydroxide) to produce ambient-cured geopolymer. Fly ash based geopolymer require curing temperature of around 40° to 90° C to gain considerable amount of strength thus constraining its use in in-situ conditions [4]. Addition of OPC in the range of 5% to 15% in fly ash based geopolymer systems not only improves the mechanical properties and microstructure of GP at ambient curing conditions but also accelerates the geopolymerisation process eventually increasing 28-day compressive strength (up to 60 N/mm^2) of GP mortar [5]. Suwan et al. used higher amount of OPC (up to 30%) and reported a 3-day compressive strength of 21.91 N/mm^2 at ambient curing conditions. Initial setting times of the geopolymer system, however, were found to be as low as 30 minutes [6].

This paper also attempts to explore the applications of superabsorbent polymers (SAP), polyethylene glycol (PEG) and membrane curing compounds (wax and resin-based) as curing agents to alleviate the huge water demand created by conventional method of curing [7]. SAP, available in the form of finely divided particulate materials, consists of cross-linked networks of hydrophilic polymers [8]. They absorb water depending upon their shape, size and molecular structure and with respect to the ionic concentration of water, and release this absorbed water to dry capillary pores in later stages thus increasing the degree of hydration and help in averting the propagation of micro-cracks due to the formation of a denser paste phase [9]. PEG, on the other hand, is usually used in self-curing regime because of its high solubility in water at room temperature. It forms hydrogen bonds with the water molecules and reduces their partial vapour pressure and eventually evaporation of water decreases and the retained water helps in further hydration of cement [10]. Use of PEG has also been studied on the properties of geopolymer mortar based on metakaolin and sodium silicate [11]. Recent works have shown that internal curing and self-curing regimes achieve similar results in concrete as compared to conventional methods of curing [9]. In case of ordinary cementitious systems, both SAP and PEG prolong the setting times of cement. Higher dosage of SAP improves the degree of hydration, water retention and compressive strength but reduces the capillary porosity. Similar results were obtained for PEG, although, at a lower dosage [9]. The effect of wax and resin based membrane curing compounds on the properties of concrete was compared by K. Sarkar et al. and results showed that the use of membrane curing compounds gave 78-87% of the strength with respect to plain water curing at 28 days and 67-76% at 90 days. Resin based curing compounds performed better than wax based compounds in terms of strength development and surface imperviousness [12].

Effectiveness of application of SAP, PEG and membrane curing compounds in fly ash based geopolymer is an unexplored area and hence, is adopted in this paper and the properties of fly ash based GP paste and mortar like compressive strength (7 and 28-day) and water absorption are compared. The composition of the OPC and fly ash based ambient-cured geopolymer is kept constant (optimal content) [13], and dosage of SAP and PEG is varied. Further, the suitability of resin and wax based membrane curing compounds is also studied.

EXPERIMENTAL PROGRAMME

The research was planned to study the effect of different ambient curing methods on the properties of geopolymer such as setting times (initial setting times and final setting times), compressive strength (7 days and 28 days) and water absorption (7 days and 28 days). Three curing regimes were studied: internal curing method by using SAP, self-curing regime by using PEG and membrane curing regime by using resin and wax based membrane curing compounds.

Materials

Ordinary Portland Cement of 43 grade was used for the experimental works. The fly ash belonged to class F, as per ASTM Standards [14]. Specific Gravity of fly ash and cement were found to be 2.06 and 3.11, respectively. Natural sand, with a specific gravity of 2.62 and belonging to zone 2, was used in the experimental works.

Sodium Hydroxide (NH) and Sodium Silicate (NS) solutions were used as alkaline activators. Sodium Hydroxide solution were prepared by dissolving desirable amount of sodium hydroxide pellets in appropriate amount of water. After stirring, the solution was kept undisturbed for 15 minutes, to bring down its temperature, so as to avoid rapid setting of cement. However, the solution was used in warm state for efficient dissolution of fly ash. Laboratory grade Sodium Silicate solution of specific gravity 1.4 was used in the experimental works. SAP was used as internal curing agent and PEG was used a self-curing agent. Average molecular mass of PEG was 400.

Preparation of samples

Optimum composition of the OPC-FA mix was taken to prepare the samples, on the basis of earlier works done by P. Wadhwa [13]. The optimum composition of GP paste was: Cement Quantity: 10% of the total amount of cement and fly ash, NS/NH: 2, Molarity of NH: 12M and Alkali content: 45% of the mass of fly ash.

The GP-OPC paste samples were prepared by using Hobart mixer. Desired amount of FA and OPC were dry mixed for 90 seconds. NH solution of desired molarity and volume was prepared, and was allowed to cool for 15 minutes. Then the NH solution was mixed thoroughly with weighted quantity of NS solution and water. This solution was added to the dry mix of OPC and FA and they were mixed for 90 seconds to obtain a homogeneous mixture. The mix was then filled in cubical moulds of sides measuring 50 mm each and compacted by using a mechanical vibrating table. The samples were demoulded after 24 hours.

Five dosages of SAP, 0.25, 0.35, 0.50, 0.70 and 1%, and four dosages of PEG, 0.5, 1.0, 1.5, 2% with respect to mass of OPC and FA mix were adopted. These curing agents were added during mixing procedure. The samples were air-cured in a temperature controlled room at 27°C and 65% relative humidity. In addition to these, samples were also prepared for dry curing and wet curing, which were devoid of curing agents. The dry cured samples were also air-cured in the temperature controlled room. The wet cured samples were immersed in water at for 28 days (or up to testing date).

Membrane cured compounds were prepared by applying a coat of resin and wax based membrane curing compounds on the exposed surface of the specimen in moulds soon after the bleed water had dried. The remaining surfaces were treated after demoulding. The curing compounds were applied on the samples with the help of a brush. The layer formed by the curing compounds was removed prior to water absorption tests.

The mix proportioning of the GP mortar was done according to packing density method [15]. The bulk density of sand was found to be 1536.67 kg/m^3 in accordance with relevant Indian standard code [16]. Packing density of sand, which is the ratio of bulk density to specific gravity, was calculated as 0.586. Mortar samples with 58% paste content (40% excess of voids) were prepared and placed at different curing conditions. The mix proportioning details of Geopolymer paste and mortar are shown in table 1 and 2 respectively.

Initially, problem was encountered during the mixing of ingredients of geopolymer mortar due to difference between specific gravities of OPC and fly ash. OPC, being heavier, settled at the bottom of the mixer. The problem was resolved by modifying the mixing procedure and mixing time of the dry ingredients. Firstly, sand, OPC and fly ash were added in pan mixer and mixed for 5 minutes till a homogeneous mixture was obtained. NH solution was prepared and was allowed to cool for 15 minutes. Then, NS and NH solutions were added to the dry mixture and the resultant mixture was mixed. The mixture thus obtained was filled in moulds of side 7.06 cm each and compacted with the help of a vibrating table to expel the air bubbles.

Table 1 Mix proportioning details of geopolymer paste for 1 kg of OPC and fly ash mixture

OPC, gm	FLY ASH, gm	WATER, gm	SODIUM SILICATE, gm	SODIUM HYDROXIDE, gm
100	900	23	270	135

Table 2 Mix proportioning details for 1 m^3 of geopolymer mortar

MIX	SAND, kg	OPC, kg	FLY ASH, kg	WATER, kg	SODIUM SILICATE, kg	SODIUM HYDROXIDE, kg
S58	1101.45	73.24	659.16	16.84	197.75	98.87

Test procedures

Initial setting times and final setting times for GP paste were found out as per IS 4031 (Part 5) [17] by using vicat apparatus. Compressive strength testing of the samples was carried out at the age of 7 and 28 days. Compressive strength of GP specimens was found out by using Automatic Compression Testing Machine (CTM) at a loading rate of 2.4 kN/second. An average of three specimens were taken to calculate the compressive strength. Water Absorption test was performed in accordance with the guidelines of ASTM C-642 [18]. The test was performed on the specimens on 7 day and 28 day samples. An average of three replicates were taken to calculate the average value of water absorption and volume of permeable voids.

RESULTS AND DISCUSSIONS

The effect of different ambient curing methods on the compressive strength and water absorption of Geopolymer paste and mortar could be seen from figure 1 to 8.

Geopolymer paste

Setting Times

Figure 1 describes the variation of setting times (IST and FST) with the dosage of SAP and PEG. Both, IST and FST, are found to increase with increase in dosage of SAP. Since SAP absorbs water at the time of mixing, the amount of water available for hydration of cement and alkali activation of fly ash decreases delaying the setting of GP paste.

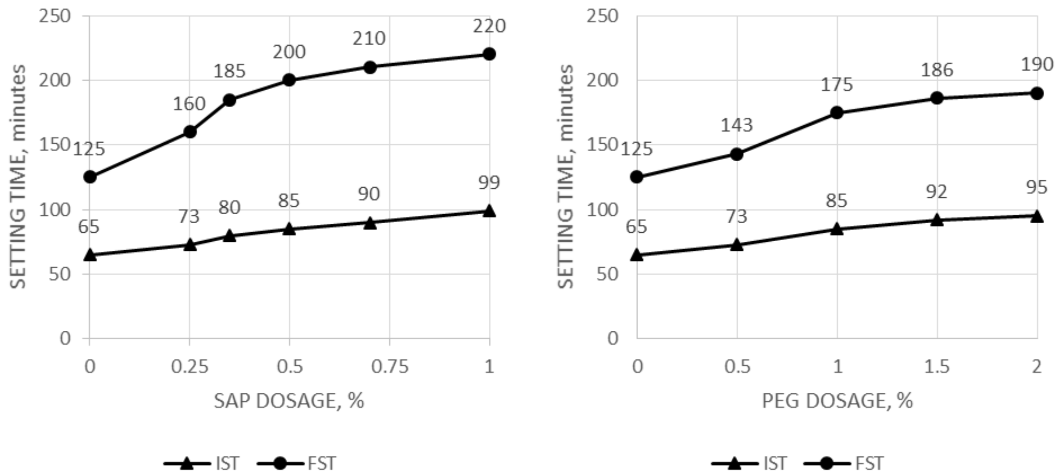


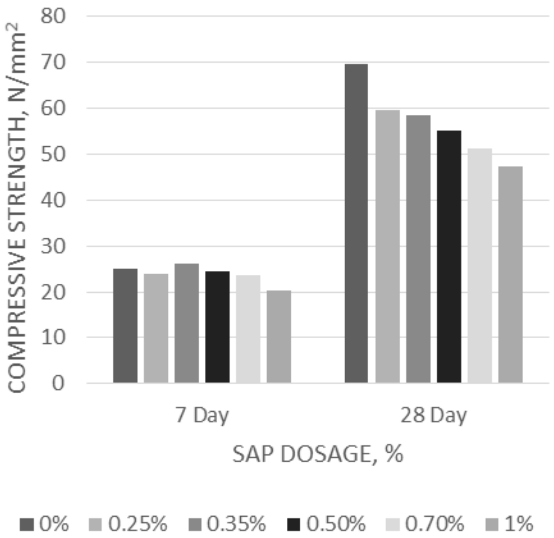
Figure 1 Variation of setting times of geopolymer paste with SAP and PEG doses

Variation of setting times in case of PEG is similar to that of SAP. Precipitated polymer complexes of PEG are deposited on the surfaces of the hydrating cement particles decreasing the rate of geopolymerisation reaction and consequently delaying the setting of GP paste with PEG dosage [10].

Compressive strength

The variation of compressive strength with dosage of SAP and PEG is shown in Fig. 2. Compressive strength of the geopolymer paste decreases with increase in SAP content achieving a value up to 59.68 N/mm^2 which is lower than that of dry cured samples (69.59

N/mm^2). With increase in SAP dosage, new voids are created due to the collapsed SAP particles leading to increase in porosity and decrease in strength. This is in contrast to the results obtained from SAP cured conventional concrete samples in which compressive strength increases till a certain dosage and thereafter decreases [9].



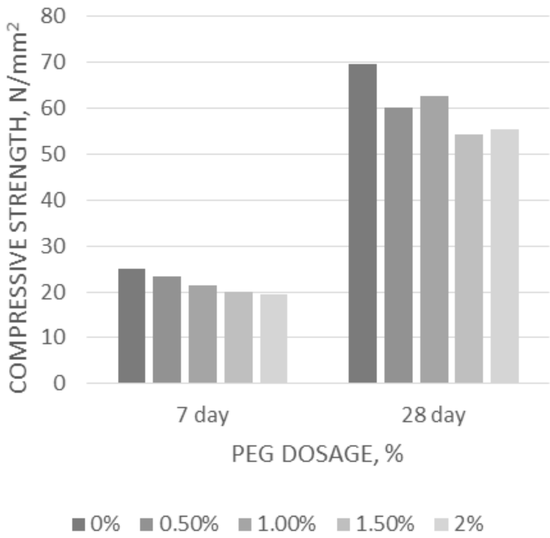


Figure 2 Variation of compressive strength of geopolymer paste with SAP and PEG doses at 7 and 28 days

For higher doses of PEG, compressive strength reduces. Compressive strength of 62.81 N/mm^2 was achieved at a PEG dosage of 1%. The decrease in strength with higher dosage might be due to deposition of PEG polymers on the hydrating cement particles, which leads to lower degree of hydration and hence lower rate of alkali activation of fly ash.

The compressive strength of wet cured samples was found to be higher than that of dry cured samples for the initial period. Better hydration of cement particles in wet curing leading to evolution of heat is a possible reason for the increased strength. This evolved heat further facilitates efficient action of alkali activators on fly ash. However, 28-day compressive strength of dry cured samples was found to be 30.39% higher than that of the wet cured ones. This might have happened due to faster geopolymerisation reaction in the later stages of dry curing regime. Water is itself released at the end of geopolymerisation reaction [19]. This released water is sufficient enough to drive the strength gain process forward in case of dry cured samples. In case of wet curing, the water molecules released from the geopolymerisation process in addition to the water from the wet curing regime leads to higher porosity which consequentially decreases the compressive strength.

Compressive strength of RB cured membrane and WB cured membrane was found to be 41.38% and 57.52% lower than that of dry cured compounds. The interference of these curing compounds with the geopolymerisation process acts as a hindrance in the process of development of strength. Since these compounds restrict the escape of water from the system, the excess water present in the system leads to increase in porosity of the system causing detrimental effects on the compressive strength. Compressive strength of RB cured compounds was found to be higher than that of WB cured compounds.

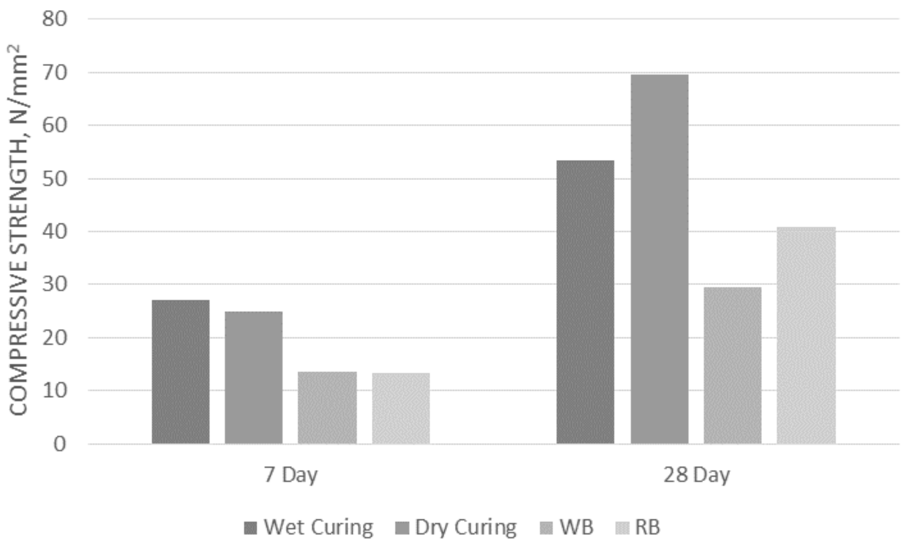


Figure 3 Variation of compressive strength of geopolymer paste with different methods of curing at 7 and 28 days

Water Absorption

Effect of variation of SAP and PEG doses on water absorption of geopolymer paste is shown in figure 4 and 5 respectively. Water absorption decreases with increase in SAP dosage till 0.7% and increases thereafter. This abrupt increase in water absorption (after 0.7%) can be attributed to rehydration of the SAP particles (which are present in high quantity) upon coming in contact with water.

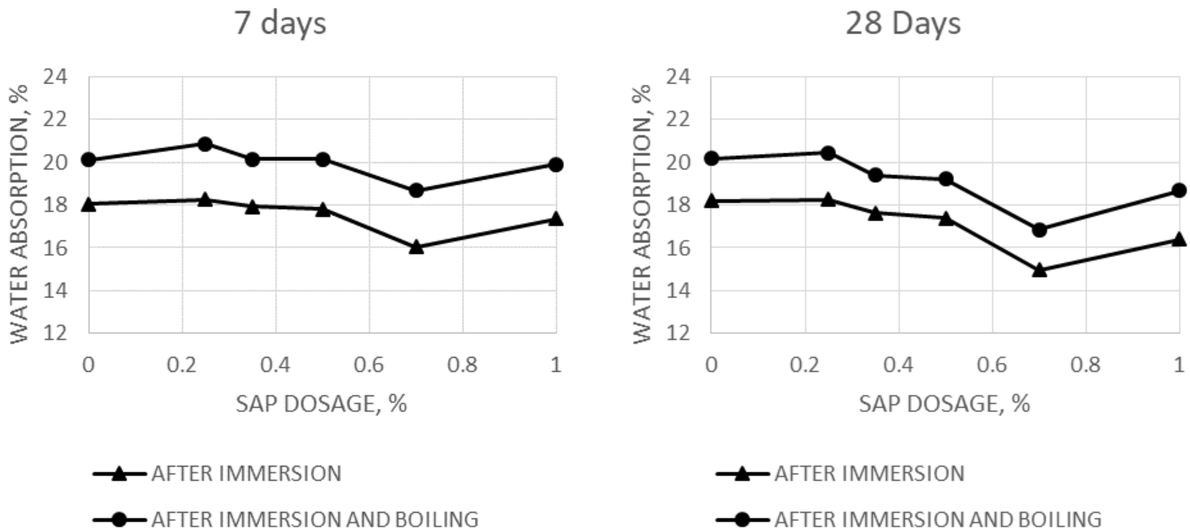


Figure 4 Variation of water absorption in geopolymer paste with SAP doses

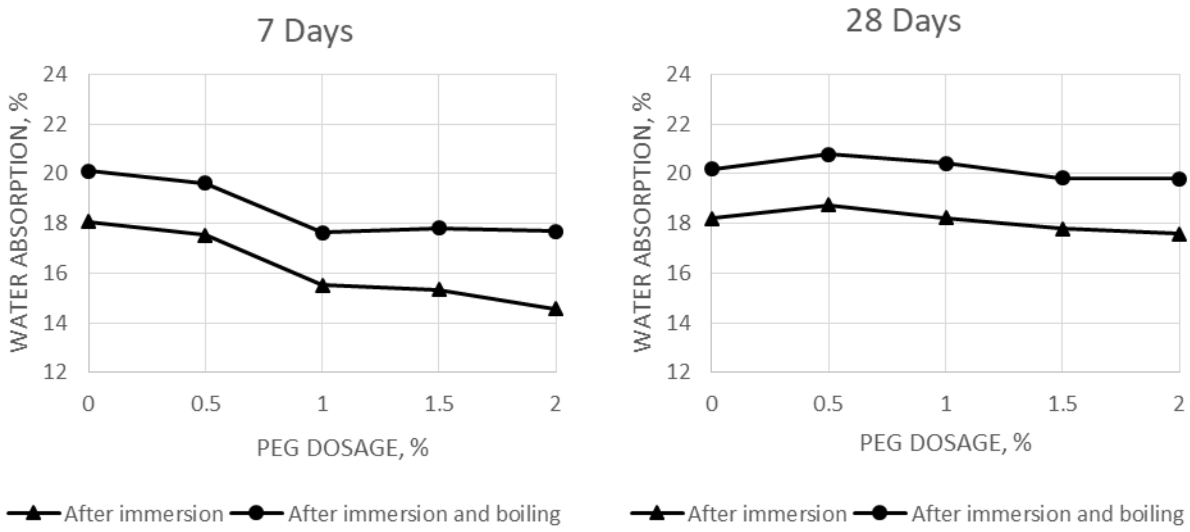


Figure 5 Variation of water absorption in geopolymer paste with SAP doses at 7 and 28 days

Water absorption decreases with increase in PEG dosage. Since PEG helps in retaining water in the specimen, the amount of free voids decrease.

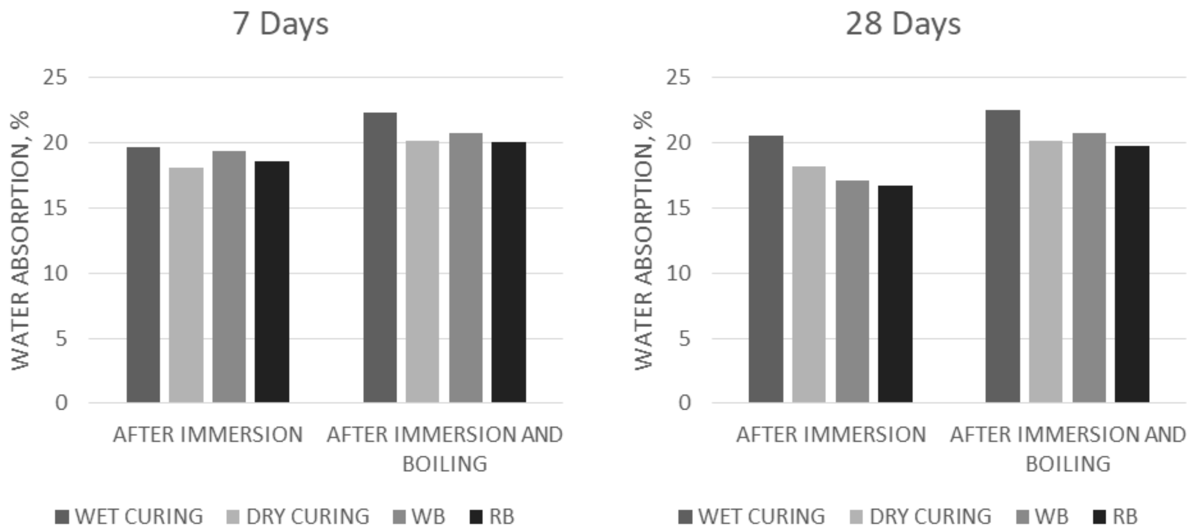


Figure 6 Variation of water absorption in geopolymer paste with different methods of curing

Water absorption in wet cured samples is more than those in dry cured samples. It can inferred that dry cured samples have better pore structure than the wet cured specimens. This explains the higher compressive strength of dry cured samples. Since the compressive strength of the membrane cured samples was much lower with respect to other methods of curing, use of membrane curing method was discontinued in the study.

Geopolymer Mortar

On the basis of the results of the compressive strength and water absorption tests of geopolymer paste, the mixes that were considered for further study were: dry curing, wet curing, PEG 0.5%, PEG 1.5%, SAP 0.25% and SAP 0.75%.

Compressive Strength

Compressive strength up to 40.91 N/mm^2 was obtained in case of GP Mortar. This is lower than the strength obtained in case of GP paste (up to 69.59 N/mm^2). Strength of dry cured samples was found to be the highest. Although the compressive strength of dry cured mortar and PEG cured (0.5%) mortar (40.73 N/mm^2) was almost same, dry cured samples are economical and hence better. The variation of compressive strength with change in method of curing is consistent with the results obtained in the case of GP paste samples.

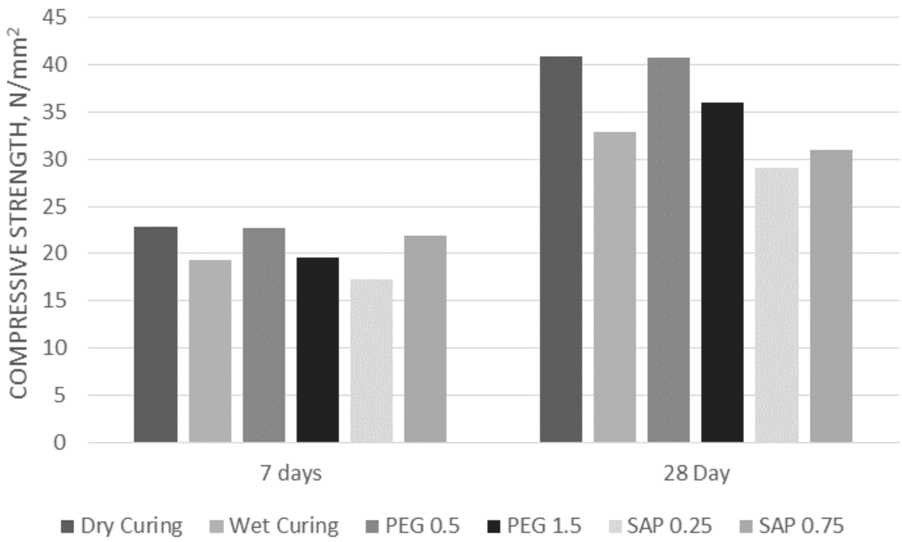


Figure 7 Variation of compressive strength of geopolymer mortar with different methods of curing at 7 and 28 days

Water Absorption

The water absorption of SAP 0.25 and SAP 0.75 are on the higher side due to rehydration of the SAP particles when they comes into contact with water. This should not considered as an indication of worsening pore structure. Porosity of PEG 0.5 cured samples and dry cured samples are almost and hence, their compressive strengths are also same.

Cost Analysis

Cost analysis of the GP paste and mortar has been done as per the rates shown in Table 3. All the geopolymer paste and mortar samples were prepared by using laboratory grade chemicals. Cost of GP paste (dry cured) is Rs. 39.44 per kg and S58 mix of GP mortar (dry cured) is Rs. 42358 (considering laboratory grade chemicals). However, if we consider commercial grade

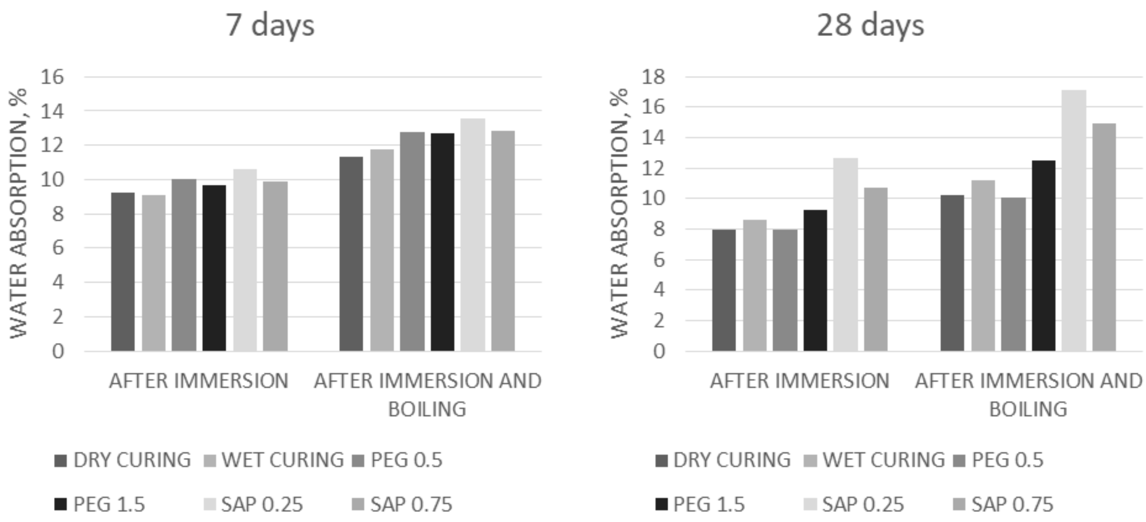


Figure 8 Variation of water absorption in geopolymer mortar with different methods of curing at 7 and 28 days

chemicals, cost of 1 m^3 of dry cured S58 mix of geopolymer mortar is Rs. 8217. Efficiency of commercial grade chemicals is assumed to be same as that of laboratory grade chemicals in this analysis.

Table 3 Cost of raw materials

SL. NO.	MATERIAL	COST, Rs. per kg
1.	Cement (OPC 43 grade)	6
2.	Fly ash	2
3.	Sodium silicate	
	Laboratory grade	108.94
	Commercial grade	11
4.	Sodium hydroxide	
	Laboratory grade	480
	Commercial grade	85
5.	Natural sand	1

CONCLUSIONS

The study investigated the effect of different ambient curing methods on the performance of OPC and fly ash based geopolymer paste and mortar. Based on the experimental results, the following major conclusions may be drawn:

1. It is clear that dry curing is the most suitable method of curing for geopolymer paste. Dry cured specimens had better compressive strength (up to 69.59 MPa) and pore structure as compared to other methods of curing.

2. Considerable decrease was observed in the compressive strength with increase in dosage of SAP. Water absorption of GP of the GP paste decreases till 0.7% dosage of SAP and increases, thereafter.

3. Similar trend was observed for compressive strength in case of PEG curing as was observed in SAP curing. Porosity, however, decreased with increased dosage of PEG.

4. Membrane cured compounds showed the least compressive strength among all the methods of curing that were employed in the research work.

5. Compressive strength of up to 40.91 MPa was achieved in dry cured GP mortar. GP Mortar samples cured with 0.5% dosage of PEG had similar compressive strength and water absorption. Decrease in compressive strength was observed for other methods of curing.

This study confirms that use of small quantity of OPC in fly ash based geopolymer gave favourable results. Further, by adopting dry curing method, tremendous amount of water could be saved.

REFERENCES

1. CENTRAL ELECTRICITY AUTHORITY. Report on fly ash generation at coal/lignite based thermal power stations and its utilization in the country for the 1st half of the year 2014-15. CEA New Delhi, February 2015, 25p.
2. WILES CC. Standard handbook of hazardous waste treatment and disposal, McGraw Hills New York, 1988, p 7.85.
3. DAMILOLA O M, Syntheses, Characterization and Binding Strength of Geopolymers: A Review. International Journal of Materials Science and Applications, Vol 2, No 6, 2013, pp 185-193.
4. HADDAD R H AND ALSHBUOL O, Production of geopolymer concrete using natural pozzolan : A parametric study. Construction and Building Materials, Vol 114, 2016, pp 699–707.
5. NATH P AND SARKER P K, Use of OPC to improve setting and early strength properties of low calcium fly ash geopolymer concrete cured at room temperature. Cement and Concrete Composites, Vol 55, 2015, pp 205–214.
6. SUWAN T AND FAN M, Influence of OPC replacement and manufacturing procedures on the properties of self-cured geopolymer. Construction and Building Materials, Vol 73, 2014, pp 551–561.
7. RIJSBERMAN F R, Water scarcity: Fact or fiction?. Agricultural Water Management, Vol 80, No 1–3 SPEC. ISS., 2006, pp 5–22.
8. LURA P, FRIEDEMANN K, STALLMACH F, MÖNNIG S, WYRZYKOWSKI M AND ESTEVES L P, Kinetics of Water Migration in Cement-Based Systems Containing Superabsobent Polymers. Application of Super Absorbent Polymers (SAP) in Concrete Construction, Springer Netherlands, 2012, pp 21–37.
9. SARBAPALLI D, DHABALIA Y, SARKAR K AND BHATTACHARJEE B, Application of SAP and PEG as curing agents for ordinary cement-based systems: impact on the early age properties of paste and mortar with water-to-cement ratio of 0.4 and above. European Journal of Environmental and Civil Engineering, Vol 21, No 10, 2017, pp 1237–1252.
10. DHIR R K, HEWLETT P C AND DYER T D, Influence of Microstructure on the

Physical Properties of Self-Curing Concrete. ACI Materials Journal, Vol 93, No 5, September 1996, pp 465–471.

11. MIKHAILOVA O AND ROVNANÍK P, Effect of Polyethylene Glycol Addition on metakaolin-based geopolymer. Procedia Engineering, Vol 151, 2016, pp 222–228.
12. SARKAR K, MIRETU T M AND BHATTACHARJEE B, Curing of concrete with wastewater and curing compounds: Effect on strength ond water absorption. Indian Concrete Journal, Vol 88, No 10, October 2014, pp 87-93.
13. WADHWA P AND BHATTACHARJEE B, Geopolymer paste cured at ambient temperature through OPC addition. Indian Concrete Journal, Vol 92, No 9, September 2018, pp 11-24.
14. ASTM INTERNATIONAL. ASTM C618 - 12a. Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete. ASTM International Pennsylvania, 2010, pp. 3–6.
15. RAJ N, PATIL S G AND BHATTACHARJEE B, Concrete Mix Design By Packing Density Method. IOSR Journal of Mechanical and Civil Engineering, Vol 11, No 2, 2014, pp 34–46.
16. BUREAU OF INDIAN STANDARDS. IS: 2386 (Part lll) - 1963. Methods of Test for aggregates for concrete. BIS New Delhi, March 1997.
17. BUREAU OF INDIAN STANDARDS. IS: 4031 (Part 5) - 1988. Methods of physical tests for hydraulic cement - determination of initial and final setting times. BIS New Delhi, 1988.
18. ASTM INTERNATIONAL. ASTM C 642 - 06. Standard Test Method for Density, Absorption, and Voids in Hardened Concrete. ASTM International Pennsylvania, March 1997, pp 1–3.
19. KHALE D AND CHAUDHARY R, Mechanism of geopolymerization and factors influencing its development: A review. Journal of Materials Science, Vol 42, No 3, 2007, pp 729–746.