Geo-polymerization mechanism and factors affecting it in Metakaolin-slag-fly ash blended concrete

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Abstract. This paper presents the mechanism and chemistry behind the geo-polymerization and its application in development of Geo-polymer concrete. In this paper, guidelines to develop a geo-polymer concrete is discussed along with the factors affecting the geopolymerization process in concrete. It is concluded that curing temperature, ratio of alkaline liquids, chemical ratio of silicate and sodium in sodium silicate, alkaline liquids / Si-Al source materials ratio, sodium silicate/ hydroxyl ions ratio, presence of calcium, presence of excess water and Si/Al ratio in source materials have significant effect on the development of geopolymer concrete and its performance.

1 Introduction

Production of cement emits high amount of carbon dioxide so always efforts are made to control or reduce or use zero emissions methods to produce cement. Similarly another by-product called fly ash is also produced abundantly in thermal plants so always researchers are evolving new methods to reuse this fly ash in various applications of civil engineering. So 'Davidovits' suggested a method to use fly ash in concrete instead of cement but cement plays the role of binding all the materials in concrete whereas fly ash is not a cementitious material. Then he came up with a process where fly ash is activated and in such way that Si and Al ions present in fly ash will react in the presence of alkaline solutions such as sodium silicate and sodium hydroxide or potassium silicate and potassium hydroxide to synthesize into binding material. This process is called geopolymerization because a inorganic polymer type substance is produced with materials of geological origin. The mechanism of polymerization comprises few chemical reactions in the presence of alkaline environment on Si and Al minerals present in fly ash resulting in a polymeric chain and ring type inorganic structure. There are various forms of geopolymers such as Phosphate-based geopolymer, Fly ash based Geopolymer, Silico-phosphate based geopolymer and Organic-mineral geopolymer

2 Geopolymer mechanism

Fig. 1. Geopolymer matrix, coarse aggregate and rebar interface

Alkaline liquids such sodium silicate and sodium hydroxide or potassium silicate and potassium hydroxide dissolve the Si and Al atoms present in the fly ash. On application of heat, a gel type structure is formed binding the aggregates

and any other unreacted constituents of the concrete together to produce a new generation material called ‘Geopolymer Concrete’. The chemical process in the geopolymerization activity is essentially Si and Al atoms in fly ash, GGBFS, metakaolin etc. will get dissolved in the OH⁻ solution from sodium hydroxide and reorients itself and sets as inorganic polymer under the process of poly-condensation.

3 Constituents of geopolymer concrete

Any supplementary cementitious material that has mostly Silicon (Si) and Aluminum (Al) mineral ions in fluid form is a potential base material for replacing cement in the geopolymer concrete manufacturing.

3.1 Fly ash

Fly ash consists of silicon dioxide (SiO₂), aluminum oxide (Al₂O₃), iron oxide (Fe₂O₃), and calcium oxide (CaO) in the decreasing order of amount present. Low-calcium fly ash or Class F fly ashes per ASTM classification is used as a base material for preparation of geopolymer and is obtained from the Thermal Power Station at Vijayawada, Andhra Pradesh, India.

3.2 GGBS

GGBS is added to reduce the setting times of concrete. It has calcium source which will impart setting to the concrete.

3.3 Metakaolin

Metakaolin is the source for Al atoms and also has Si ions abundantly.

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Sodium silicate (Na₂SiO₃) and 8 Molar Sodium hydroxide (NaOH) are used as alkaline binders. Sodium silicate is obtained in liquid form from the factory based on the chemical requirement of (Na₂O=13%, SiO₂=26%, H₂O=61% by weight; SiO₂/Na₂O=2.0 by weight) (Rs. 22 per litre). Sodium hydroxide is available in the form of solids or in flaky form of purity 98% (Rs. 200 per 500 g) so to make NaOH solution, NaOH solids are dissolved in deionized water for required molarity.

3.5 Water

The water content in the geopolymer concrete mixtures was stated by a factor called “water to geopolymer solids ratio” by weight. In this factor, the total weight of water is the sum of water present in the sodium silicate liquid, the water required to make sodium hydroxide solution, and the additional water used to regulate the workability of the geopolymer mixture. Generally the ‘water to geopolymer solids’ ratio adopted was a constant value of 0.26.

4 Mix design

Assuming the unit-weight of geopolymer concrete as 2400 kg/m³. The amount of combined aggregates is generally 75% of the total quantity of concrete.

1. Quantity of combined aggregates = $0.75 \times 2400 = 1800$ kg/m³ (75%)

2. Quantity of fly ash and alkaline liquid (Na₂SiO₃ + NaOH) = $2400 - 1800 = 600$ kg/m³

3. Ratio of alkaline liquid / fly ash by weight = 0.35 (say)

4. Quantity of fly ash = $600 / (1 + 0.35) = 444$ kg/m³

5. Quantity of alkaline liquids (Na₂SiO₃ + NaOH) = $600 - 444 = 156$ kg/m³

Take the ratio of sodium silicate / sodium hydroxide solution by weight is adopted as 2.5

6. Quantity of NaOH solution = $156 / (1 + 2.5) = 45$ kg/m³

7. Quantity of Na₂SiO₃ = $(156 - 45) = 111$ kg/m³

Water / geopolymer solids ratio (equivalent to w/c ratio) by weight is computed as shown below:

(a) In Na₂SiO₃ solution (Na₂O=13%, SiO₂=26%, H₂O=61% by weight),

Water present is = $0.61 \times 111 = 62$ kg and Solids are $111 - 62 = 49$ kg

(b) In NaOH solution, Solids present are $0.262 \times 45 = 12$ kg and the water present is $45 - 12 = 33$ kg (262 g of NaOH pellets are added in 738 ml of water to make one litre of NaOH solution)

(c) Therefore total weight of water present in alkaline solution = $62 + 33 = 95$ kg

(d) Weight of geopolymer solids = $444 + 49 + 12 = 505$ kg

Hence Water / Geopolymer solids ratio by weight = $95 / 505 = 0.19$

Fig. 2. Freshly mixed Geopolymer Concrete

Which indicates that the workability of fresh geopolymer concrete is moderate. If desirable, add super plasticizer to the mix to make more workable.

4.1 Fresh Properties

The fresh geopolymer concrete will stay workable up to 2 hrs. without any setting and loss of the compressive strength.

Fig. 3. Casted Geo-polymer concrete specimens

Fig. 4. Sodium hydroxide (NaOH)

Fig. 5. Sodium Silicate (Na_2SiO_3)

5 Guidelines to develop Geo-polymer Concrete

1. Low calcium fly ash is obtained for replacement of cement. In GPC, no hydraulic binder such as cement or lime are used or required.
2. Alkaline activators used are (1) 98% purity NaOH in pellet form and (2) Na_2SiO_3 having $\text{Na}_2\text{O} = 13\%$, $\text{SiO}_2 = 26\%$ and water = 61% by weight
3. NaOH solution is prepared from NaOH solids (Calculations are given below)
4. NaOH solution was prepared one day before and Na_2SiO_3 is added to NaOH just 30 minutes before use in making concrete.
5. Coarse aggregates of size viz., 20 mm, 10 mm (60%:40% ratio) and river sand as fine aggregate in saturated surface dry condition are used
6. The dry quantities of coarse, fine aggregates along with the fly ash, GGBS and metakaolin were pan mixed for 3 minutes
7. The alkaline liquids are added then and mixed for 3 to 5 minutes more until stiff consistency with glossy appearance is obtained.
8. Cubes are casted and are covered with sheet to prevent water vaporization and were kept at room temperature of 28 degrees Celsius (Ambient temperature) for air dry curing for 28 days and some specimens are oven cures at a temperature of 60°C for a period of 24 hours.
9. If specimens are kept in oven immediately (rest period zero) always seal the specimens otherwise if the rest period of 1- 3 days can be given and then keep in oven without seal.

5.1 Calculation of Alkaline liquids Quantities (example for 8M NaOH)

Alkaline binders to fly ash ratio is usually assumed as 0.5 based on previous research i.e. $\text{Na}_2\text{SiO}_3 + \text{NaOH} / \text{Fly ash ratio} = 0.5$

Cement is replaced with fly ash in Geo-polymer concrete so cement quantity is assumed for fly ash quantity. Let us assume cement quantity for M20 grade concrete is 320 kg. So fly ash quantity is 320 kg ----- (1)
 Then Alkaline binders ($\text{Na}_2\text{SiO}_3 + \text{NaOH}$) quantity = Fly ash $\times 0.5 = 320 \times 0.5 = 160$ kg ----- (2)
 The ratio of alkaline liquids are assumed as $\text{Na}_2\text{SiO}_3/\text{NaOH} = 2.5$ for optimum binding.
 So to prepare 8 Molar NaOH solution, $8 \times 40 = 240$ g of NaOH pellets or flakes are required to mix in one litre of water. 40 is the molecular weight of the NaOH.
 So add 240 grams of NaOH to 1000 ml of water so the weight of NaOH solution becomes $1000 + 240 = 1240$ g in total.
 So in 1240 g of NaOH solution, 240 g is NaOH and the remaining 1000 ml or g is water.
 To prepare 1240 ml of NaOH solution, NaOH pellets required are 240 g so for 1000 ml of NaOH solution, the required NaOH computed as 193.5 g. So 193.5 g of NaOH is required to dissolve in 806.5 ml or g of water to prepare 1L solution of eight molar NaOH.
 So, 1 litre of 8 molar NaOH solution contains 193.5 g of NaOH flakes or pellets ----- (3)
 The Na_2SiO_3 solution taken as 2.5 litres (Available in market as liquid)
 For each 1m^3 of geopolymer concrete, the material calculated is-
 Mass of NaOH = $(320 \times 0.5) / (1 + 2.5) = 45.71$ kg ----- (4)
 Mass of 8M NaOH = $(45.71 \times 193.5) / 806.5 = 10.96$ kg of NaOH flakes are added to 34.74 litres of water to make 45.71 kg of NaOH.
 Mass/volume of $\text{Na}_2\text{SiO}_3 = 160 - 45.71 = 114.29$ kg or 114.29 litres
 $\text{Na}_2\text{SiO}_3 = 114.29$ kg ----- (5)

6 Factors effecting the polymerization in Concrete (GPC)

1. Curing Temperature
 Generally, optimum temperature for curing is adopted as 60°C and period of curing is 24 hrs. Studies showed that beyond 24 hrs. period, heat curing is not required. Many researchers opined that longer curing times would increase compressive strength (generally 4 to 96 hrs.).
 As curing temperature increases compressive strength increases. There is insignificant increase in compressive strength beyond 60°C optimum curing temperature 60°C . Compressive strength increases as temperature of oven curing increases from 30°C to 90°C
2. Molarity of Alkaline liquids
 As concentration of sodium hydroxide (NaOH) varies from 8M to 16M compressive strength of concrete increases. Since NaOH is expensive, it is always that 8M NaOH is chosen for study and quantities are arrived at based on 8M NaOH.

16 Molar or 18 Molar NaOH gives maximum compressive strength but quantity of NaOH pellets required will be more to prepare high molar solution. Since NaOH is expensive ingredient in GPC, so always prefer to develop GPC with 8M NaOH and accordingly design the GPC mix.

3. $\text{Na}_2\text{SiO}_3/\text{NaOH}$ Ratio
 Higher $\text{Na}_2\text{SiO}_3/\text{NaOH}$ (2.0 to 3.5) higher compressive strength but research shows that $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio of 2.5 is optimum. Maintain $\text{SiO}_2/\text{Na}_2\text{O}$ in the preparation of Sodium silicate = 2.00 (Research shows that $\text{SiO}_2/\text{Na}_2\text{O}$ in sodium silicate can be between 2.00-2.40)
4. Aggregates
 It can be understood that only the binder (which usually occupies around 20 to 25% of total mass) is different in geopolymer concrete when compared to OPC concrete. Therefore, the effects of properties and grading of aggregates were not investigated in this study.
5. Preparation of Alkaline binders solution
 Generally alkaline liquids are prepared by mixing of the sodium hydroxide solution and sodium silicate solution at the room temperature. When the solution mixed together the both solution start to react that is polymerization takes place. It liberates large amount of heat so Alkaline chemicals are mixed before 30 minutes of concrete making. Many researchers opined that it should be mixed 1 day before using in concrete. Sodium silicate should be added before 30 min of concrete making to Sodium hydroxide. But Sodium hydroxide should be prepared one day before. It is strictly suggested that the NaOH solution must be ready 24 hours prior to use and also beyond 36 hours NaOH becomes into semi-solid liquid. So the prepared solution should be used within this time.
6. Setting times
 Initial setting of geopolymer is very high, so GGBS should be added to reduce setting time. Only with fly ash, addition will not set for even 2 days. Adding metakaolin will improve the process of polymerization because in metakaolin, aluminates are abundantly available. Silicate and Aluminates are essential requirements for polymerization.
7. Rest Period
 Rest period is the period before keeping in oven for curing. Always seal and keep it in oven or allow rest period of 1- 3 days and keep in oven without seal.
8. Alkaline liquids type
 NaOH /or KOH and Na_2SiO_3 /or K_2SiO_3 are the alkaline liquids used. Potassium silicate and hydroxide are very expensive compared to Sodium silicate and hydroxide.
9. Si/Al Ratio

Si-Al source (fly ash, GGBS and metakaolin + silicates+ water+ alkaline liquid forms Geopolymer precursor. Microstructure of geopolymer depends on the ratio of Si/Al. For geopolymer concrete it is assumed Si/Al ratio to be 2.0, for use of geo-polymers for making bricks or ceramics or fire refractory tiles Si/Al ratio should be maintained to 1, to prepare geopolymer sealants Si/Al ratio should be greater than 3.0.

10. Water

Water will be freed from the geopolymer matrix throughout chemical reactions. This water unbound from the geopolymer matrix makes discontinuous nano level pores in the matrix which are helpful to the performance of geo-polymers.

11. pH value

In ordinary Portland cement concrete has high alkalinity i.e. high pH, this feature is advantageous to concrete embedded with rebars because high

alkaline environment will create a passive layer on the surface of the steel reinforcement preventing them from corrosion where as in in Geopolymer concrete, high alkalinity is deleterious to its performance .

12. Fly ash Class

Fly ash must be finer to enhance its reactivity. Sub-bituminous coal on burning produces fly ash with calcium content more than 20% and less percentage of iron whereas bituminous coal and anthracite coal produces fly ash with less than 10% calcium and more percentage of iron. Existence of high percentage of calcium effects the polymerization process and consequently its microstructure.

Fig. 6. Effect of curing temperature and alkali/fly ash ratio on the compressive strength

7 Conclusions

This study summarizes the factors effecting the geopolymerization and mechanism behind it as follows-

1. Generally, optimum temperature for curing is adopted as 60°C and period of curing is 24 hrs.
2. Always prefer to develop GPC with 8M NaOH and accordingly design the GPC mix.
3. Maintain $\text{SiO}_2/\text{Na}_2\text{O}$ in the preparation of Sodium silicate =2.00
4. It is strictly suggested that the NaOH solution must be ready 24 hours prior to use and also beyond 36 hours NaOH becomes into semi-solid liquid. So the prepared solution should be used within this time.

5. Initial setting of geopolymer is very high, so GGBS should be added to reduce setting time. Only with fly ash, addition will not set for even 2 days. Adding metakaolin will improve the process of polymerization because in metakaolin, aluminates are abundantly available. Silicate and Aluminates are essential requirements for polymerization.
6. Always seal and keep it in oven or allow rest period of 1- 3 days and keep in oven without seal.
7. Si-Al source (fly ash, GGBS and metakaolin + silicates+ water+ alkaline liquid forms Geopolymer precursor. For geopolymer concrete it is assumed Si/Al ratio to be 2.0.

8. Fly ash with less than 10% calcium and more percentage of iron is best to use because the existence of high percentage of calcium effects the polymerization process and consequently its microstructure.

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