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A DETAILED PROCEDURE OF MIX DESIGN FOR FLY ASH BASED GEOPOLYMER CONCRETE

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ABSTRACT

The engineering properties of fly ash-based geopolymer concrete have been studied previously but very little work has been conducted on mix design procedures that may be suitable for this new type of concrete. This study proposes a method for selecting the mix proportions of geopolymer concrete which may be suitable for concrete containing fly ash to be used as a cementitious material. Using a flow chart, the paper first describes the procedure in general and then illustrates it using an example. A range of mixes were made to test the method varying water-to-geopolymer solid ratio. It was found that certain basic principles established for conventional concrete still apply for geopolymer concrete mix designs. A simple graphical relationship between 28-day and 7-day compressive strengths of geopolymer concrete is also presented.

KEYWORDS

Fly ash, geopolymer concrete, mix design.

INTRODUCTION

In 1978, Davidovits (Davidovits 1999) proposed that a binder could be produced by a polymerisation process involving a reaction between alkaline liquids and compounds containing aluminium and silicon. The binders created were termed "geopolymers". Unlike ordinary portland/pozzolanic cements, geopolymers do not form calcium-silicate-hydrates (CSHs) for matrix formation and strength, but silica and alumina reacting with an alkaline solution produce an aluminosilicate gel that binds the aggregates and provides the strength of concrete. Source materials and alkaline liquids are the two main constituents of geopolymers, the strengths of which depend on the nature of the materials and the types of liquids.

Materials containing silicon (Si) and aluminium (Al) in amorphous form, which come from natural minerals or by-product materials, could be used as source materials for geopolymers. Kaolinite, clays, etc., are included in the natural minerals group whereas fly ash, silica fume, slag, rice-husk ash, red mud, etc., are by-product materials. For the manufacture of geopolymers, the choice of source materials depends mainly on their availability and cost, the type of application and the specific demand of the users (Lloyd and Rangan 2010). Fly ash-based geopolymer concretes provide excellent engineering properties that make them suitable materials for structural applications (Rangan *et al.* 2005; Fernández-Jiménez *et al.* 2006).

The type of alkaline liquid used plays an important role in the polymerisation process (Palomo *et al.* 1999). Sodium hydroxide (NaOH) with sodium silicate (Na_2SiO_3) and potassium hydroxide (KOH) with potassium silicate (K_2SiO_3) are the most common alkaline liquids used in geopolymerisation (Hardjito and Rangan 2005). Both sodium hydroxides and potassium hydroxide have a strong base and, at room temperature, exhibit almost identical solubilities in water. In 2005, Fernández-Jiménez and Palomo studied the effect of an alkaline liquid on the mechanical strength of fly ash-based mortar (Fernández-Jiménez and Palomo 2005). They stated that the mechanical strength of mortar increases when waterglass (Na_2SiO_3) is added to NaOH, compared with using only NaOH. The addition of waterglass increases the Si/Al and Na/Al ratios, resulting in increased formation of N-A-S-H (sodium aluminosilicate gel) which indicates greater strength. Hardjito and Rangan (Hardjito and Rangan 2005) showed that the compressive strength of fly ash-based geopolymer concrete can be improved by either increasing the concentration (in molar terms) of the sodium hydroxide solution or increasing the mass ratio of the sodium silicate to sodium hydroxide solutions. Since many reports on the destructive effect of cement production on the environment have been published (IEA 2007; Worrell *et al.* 2001) and, currently, fly ash-based geopolymer concrete has proven to be a suitable replacement for cement concrete due to their excellent engineering properties (Palomo *et al.* 1999; García-Lodeiro *et al.* 2007).

MATERIALS

Aggregates: Three different sizes of coarse aggregates (14 mm, 10 mm and 7 mm) obtained in crushed rock form and fine aggregate in uncrushed form were used to prepare concrete in the laboratory. The specific gravity of aggregate was measured according to relevant ASTM standard.

Cement: Cement was used to prepare normal concrete for the comparison with fly ash based geopolymer concrete. ASTM C188 was followed to measure the specific gravity.

Fly Ash: Fly ash was obtained from the Boral Company, Australia, and used in this research as the main constituent of the binding materials in geopolymer concrete. Its specific gravity was measured using the same procedure described in ASTM C188 for cement. The XRF analysis showed that the percentage sum of SiO_2, Al_2O_3 and Fe_2O_3 in the fly ash was around 93% which ensured that the fly ash used was a Class F type. Chemical compositions of cement and fly ash are given in Table 1.

Table 1. Chemical composition of fly ash and cement

Oxide (%)	SiO_2	CaO	Al_2O_3	MgO	Fe_2O_3	SO_3	TiO_2	Na_2O	K_2O	L.O.I
Fly ash	62.19	1.97	27.15	0.40	3.23	0.07	1.06	0.30	0.89	1.75
Cement	20.18	65.94	4.14	1.77	3.65	2.61	0.19	0.06	0.62	0.56

Alkaline Liquid: In the present experimental work, a combination of sodium silicate (Na_2SiO_3) and sodium hydroxide (NaOH) solutions with molarity 16M was chosen as the alkaline liquid. The sodium silicate solution was obtained from IMCD Australia Limited and the sodium hydroxide solution was prepared in the laboratory by dissolving sodium hydroxide pellets in water.

Super-plasticiser: A super-plasticiser was used to improve the workability of fresh geopolymer concrete. A carboxylic ether polymer-based super-plasticiser under the brand name ADVA 142 was applied in the mix.

PROPOSED MIX DESIGN PROCEDURE WITH AN EXAMPLE

To date, there has been very limited research on the mix design of geopolymer concrete, let alone directives on a practical and systematic procedure that takes into consideration the strength and durability of the final product. In 2008, Lloyd and Rangan (Lloyd and Rangan 2010; Rangan 2008a; Rangan 2008b) proposed a method for a mix design of fly ash-based geopolymer concrete but it did not discuss how to deal with the effects of the ingredients' specific gravities or the air content volume on the mix design. A constant concrete density of 2400 kg/m^3 was assumed by Lloyd and Rangan which is not realistic because the density of concrete varies from one mix to another depending on the amount of ingredients in the mix. Sometimes, extra water or a super-plasticiser is needed to improve the workability of fresh geopolymer concrete which has an effect on the total volume of the concrete. Their method did not explore the design for workability which in geopolymer concrete seems to assume a yet more important effect than other types of concrete. Now, it is believed necessary that a rigorous, but still easy, method for geopolymer concrete mix design be established. The following sections present such a method. Firstly, its procedure described in general using a flowchart and then a detailed example is presented.

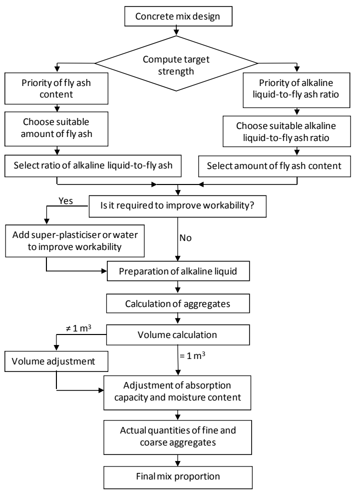

Figure 1. Flow chart for mix design procedure

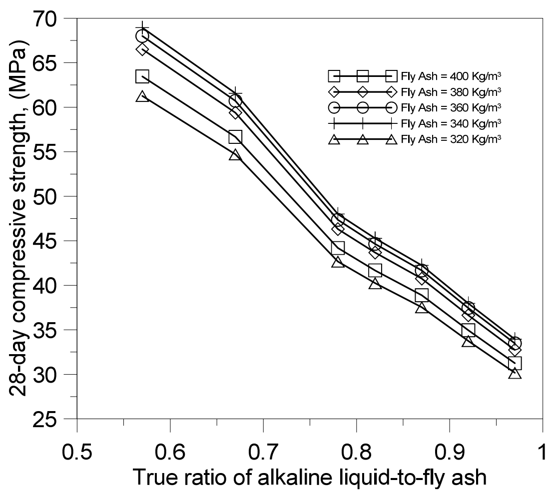

Figure 2. Strength vs alkaline liquid-to-fly ash ratio

A design graph with respect to the two major variables that have a significant effect on the water-to-geopolymer solids ratios (W/GS) was prepared. These two variables are the alkaline liquid-to-fly ash ratio and the amount of fly ash in the mixture. The addition of extra water to improve the workability of the mix had an influence on the alkaline liquid-to-fly ash ratio obtained at the end of the mix design which was different from the initial ratio and is called the true ratio. It can be seen in Figure 2 that the optimum compressive strength was obtained when the volume of the fly ash content was 340 kg/m^3 compared with other volumes with the same alkaline liquid-to-fly ash ratio. This indicates that more fly ash content in the mix did not lead to the concrete having more strength.

Let, the mean compressive strength at 28 days is targeted as 45 MPa. The necessary data for the design is given in Table 2.

Table 2. Material properties of concrete ingredients

Materials	Specific gravity	Absorption capacity (% of Oven Dry, OD)	Moisture content (% of Oven Dry, OD)	Remarks
14 mm aggregates	2.65 (OD)	0.675	0.254	-
10 mm aggregates	2.63 (OD)	0.772	0.316	-
7 mm aggregates	2.59 (OD)	1.382	0.445	-
Fine aggregate	2.57 (OD)	1.174	0.202	-
Fly ash	2.06	-	-	-
Na_2SiO_3 solution	1.52			Na_2O =14.7%, SiO_2 = 29.4%, H_2O=55.9%
Superplasticiser	1.082			400-1200ml/100 kgs of cementitious materials
Entrapped air				Average value after several trial mixes = 3.29 %

Step 1: Requirements for Weight of Fly Ash and Alkaline Liquid

In this design, the first main factor is the amount of fly ash content. As the most costly ingredient in a geopolymer concrete mix is alkaline liquid, for an economic design of concrete, designers should try to use minimum amounts of it in their mixes. Figure 2 shows that, for a 45 MPa concrete, the alkaline liquid requirements are lower when the fly ash content is 320 kg/m^3 and the corresponding alkaline liquid-to-fly ash ratio is 0.76. To increase the workability of the mixture (based on previous trials), a super-plasticiser and water, each in the amount of 1% of the total amount of fly ash weight, are added. Although the alkaline liquid-to-fly ash ratio does not depend on the addition of a super-plasticiser, it can increase with the addition of water for workability. The design starts by taking an alkaline liquid-to-fly ash ratio 0.74 which could be increased to 0.76 and is termed the true ratio at the end of the mix design. Therefore, for 320 kg/m^3 of fly ash, the required alkaline liquid will be 237 kg/m^3.

Step 2: Addition of Chemical Admixture or Water for Workability (If Needed)

The dosage of a super-plasticiser is taking 1% of the fly ash weight which amounts 3.2 kg/m^3. Then the approximate rate of addition of a super-plasticiser comes 924 ml/100kg fly ash which is in the range 400 to 1200 ml/100kg recommended by the manufacturer. To improve the workability, if the extra water is added 1% of the fly ash weight then the amount of extra water required 3.2 kg/m^3.

Step 3: Calculation and Preparation of Alkaline Liquids

Taking, 2.5 as the ratios of Na_2SiO_3 solution-to-NaOH solution (from experience Lloyd and Rangan 2010), Therefore, NaOH solution and Na_2SiO_3 solution required 68 kg/m^3 and 169 kg/m^3 respectively. Taking 16 Molar of the NaOH solution, this can be prepared by mixing 44.4% of a NaOH solid with 55.6% of water. The specific gravity (Sp.G) of the 16M NaOH solution comes 1.44. Therefore, NaOH solid and water required 30 kg/m^3 and 38 kg/m^3 respectively. In this design, as 3.2 kg of extra water is required to improve workability, the total amount of water in solution goes 41 kg/m^3. To keep the concentration (16M) of the NaOH solution constant, the required NaOH solid is now recalculated as 33 kg/m^3.

Step 4: Required Weight or Volume of Coarse and Fine Aggregates

The volume occupied by fly ash, NaOH solution, Na_2SiO_3 solution and entrapped air is 0.1553, 0.0510, 0.1113 and 0.0329 m^3 respectively. The total volumes occupied by these constituents are 0.3505 m^3 which indicates 0.6495 m^3 of aggregates is needed to get the desired strength. To fulfil the grading requirements of the aggregates, it is necessary to mix the oven dry 14 mm, 10mm, 7mm and fine aggregates by 15%, 35%, 20% and

30%, respectively. Then the combined Sp.G of coarse aggregate obtained 2.62. Now considering the specific gravity of aggregates, the volume factor of the coarse and fine aggregates comes 0.02669 (% volume/Sp.G/1000) and 0.01167 respectively. Therefore, the actual oven dry (OD) volume of the coarse and fine aggregates is 69.57% and 30.43% respectively instead of 70% and 30%. Now, the actual volumes of coarse and fine aggregates are 0.4519 m^3 and 0.1976 m^3 which calculate the weight 1185 kg/m^3 and 508 kg/m^3 correspondingly. Broadly, the oven dry coarse aggregates of size 14 mm, 10 mm, 7 mm and fine aggregates required 254, 593, 339 and 508 kg/m^3 respectively.

Step 5: Adjustment of Absorption Capacities and Moisture Contents of Aggregates

The absorption and moisture of aggregates cannot be avoided as it has an effect on the liquids of the mixture. The amounts of water required for the absorption of the oven-dry aggregate is calculated as 17 kg per cubic meter of concrete.

Table 3. Total volume of ingredients per cubic meter of concrete

Ingredients	Amount (kg/m^3)	Sp.G	Volume (m^3)	Remarks
Coarse aggregates	1185	2.62	0.4519	Oven-dry aggregates
Fine aggregate	508	2.57	0.1976	Oven-dry aggregate
Fly ash	320	2.06	0.1553	
Na_2SiO_3 solution	169	1.52	0.1113	
NaOH solution	74	1.44	0.0510	
Super-plasticiser	3.2	1.082	0.0030	
Entrapped air (%)	3.29	-	0.0329	
Absorption water	17	1	0.0000	Volume already accounted
		Total volume =	1.0030	Total volume $\neq$1 m^3

The total volumes of ingredient are calculated in Table 3. As the total resultant volume 0.3% more than 1 m^3 due to the use of a super-plasticiser, it is required to adjust the volume.

Step 6: Volume Adjustment (Only When Using Super-plasticiser)

The volume could be adjusted by dividing the amount of each ingredient by 1.0030, as shown in Table 4.

Table 4. Adjusted volume of concrete ingredients

Ingredients	Amount (kg/m^3)	Sp.G	Volume (m^3)	Remarks
Coarse aggregates	1182	2.62	0.4505	Oven-dry aggregates
Fine aggregate	506	2.57	0.1971	Oven-dry aggregate
Fly ash	319	2.06	0.1549	
Na_2SiO_3 solution	169	1.52	0.1110	
NaOH solution	73	1.44	0.0508	
Super-plasticiser	3.19	1.082	0.0029	
Entrapped air (%)	3.28	-	0.0328	
Absorption water	17	1	0.0000	Volume already accounted
		Total volume =	1.0000	Total volume = 1 m^3

Step 7: Details of Mixing for Oven-Dry Aggregates (1 m^3 of Concrete)

Therefore, the adjusted required amount of 14 mm, 10 mm and 7 mm coarse aggregates are 253, 591 and 338 kg respectively as shown in Table 5. As it is difficult to obtain oven-dry aggregates at the time of mixing, a better procedure is to prepare the chart of mix details considering aggregates as they are found in field ‘as is’ conditions.

Table 5. Mix proportions of ingredients

Ingredients		Oven dry aggregates, (kg/m^3)	Aggregates in ‘as is’condition, (kg/m^3)
Coarse aggregates	14 mm	253	254
	10 mm	591	593
	7 mm	338	339
Fine aggregate		506	507
Fly ash		319	319
Na_2SiO_3 solution		169	169
NaOH solution		73	73
Superplasticiser		3.19	3.19
Water required for absorption		17	12

Step 8: Details of Mixing for Aggregates in Field Conditions (1 m^3 of Concrete)

Considering the moisture content in this example, the required amount for the 14 mm 10 mm, 7 mm and fine aggregates are 254, 593, 339 and 507 kg respectively. Therefore, for the field conditions in this example, the amount of water required for the absorption of aggregates reduced to 12 kg from 17 kg. The mix proportions of ingredients in the field conditions are also given in Table 5.
Now the true ratio of alkaline liquid-to-fly ash comes 0.76 (as mentioned earlier) and that of the Na_2SiO_3-to-NaOH solutions 2.3. The density of concrete is then 2269 kg/m^3. The relative ratios of Fly ash: Fine aggregate: Coarse aggregate are 1: 1.59: 3.71 where the aggregates are considered in oven dry conditions.

Step 9: Water-To-Geopolymer Solids Ratio Calculation

The total geopolymer solids in this mix can be obtained from Na_2SiO_3 solution (44.1%), NaOH solution (44.4%) and Fly ash. On the other hand, water provides Na_2SiO_3 (55.9%) and NaOH (55.6%) solutions only. These percentages are obtained from the properties of alkaline liquids. Therefore, the water-to-geopolymer solids ratio of this mix obtained 0.32.

RESULTS AND DISCUSSION

Water-To-Geopolymer Solids Ratio (W/GS) of Mixture

Like, the water-cement ratio and compressive strength of ordinary Portland cement (OPC) concrete, geopolymer concrete has an inverse relationship between the water-to-geopolymer solids ratio and compressive strength, as shown in Figure 3. It has been observed that the water-to-geopolymer solids ratio linearly increases with increases in the alkaline liquid-to-fly ash ratio if the molarity of the NaOH solution and the ratio of the sodium silicate-to-sodium hydroxide solutions remain the same in all mixes. Variations in the water-to-geopolymer solids ratio with the alkaline liquid-to-fly ash ratio are depicted in Figure 4. This information is useful at the start of mix design when the water-to-geopolymer solids ratio has still not been clearly determined by the designer.

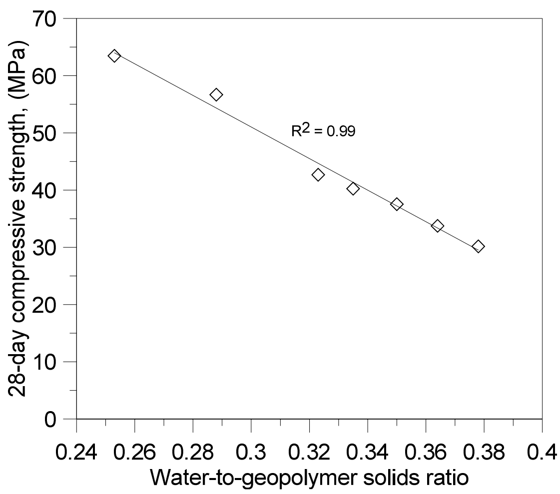

Figure 3. Compressive strength vs W/GS

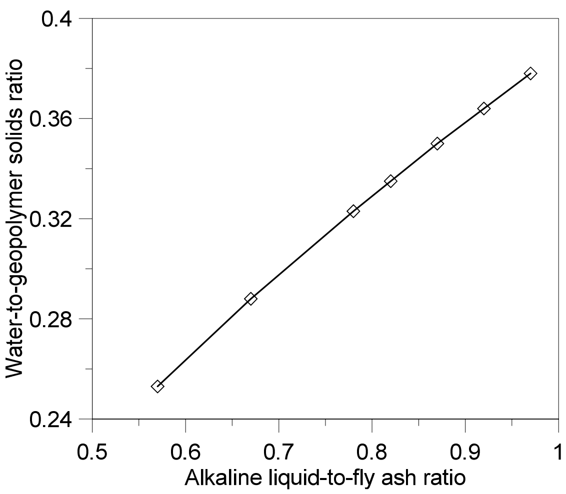

Figure 4. (W/GS) vs alkaline liquid-to-fly ash ratio

Relationship between 28-Day and 7-Day Compressive Strengths

Figure 5 compares the relationships between 28-day and 7-day compressive strengths of OPC concrete and geopolymer concrete. The data required to plot the relationship for geopolymer concrete were obtained from laboratory experiments in which the geopolymer cylinders were heated at 60^{0}C for 3 days in the oven. A range of mixes were also made in the laboratory for OPC concrete to select the suitable mix for normal concrete composite beam.

The most valuable aspect noted in Figure 5 is that the compressive strength of OPC concrete at 28 days is around 1.5 times that at 7 days whereas, for geopolymer concrete this relationship is only 1.15 times on average. This indicates that geopolymer concrete gained strength rapidly at an earlier stage than OPC concrete. In other words, geopolymer concrete achieved 87% of its 28-day strength in 7 days while OPC concrete achieved only 67%.

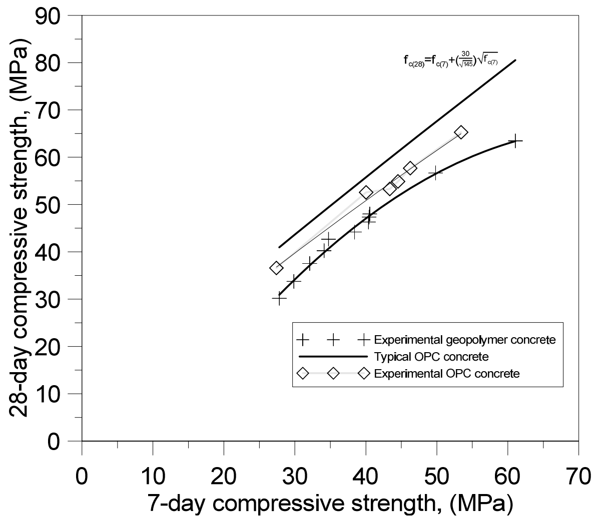

Figure 5. Correlation between 28-day and 7-day compressive strength

CONCLUSIONS

A mix design method for fly ash-based geopolymer concrete has been proposed in a different approach. Variable concrete densities, the effects of the ingredients' specific gravities, contributions of air volume, flexibility to improve the workability of fresh concrete and the opportunity to use aggregates in their 'as is' condition were considered importantly for overcoming the main limitations of current design methods. Experimental results showed that the compressive strength of the fly ash-based geopolymer concrete decreased linearly with increases in the water-to-geopolymer solids ratio. This observation was in agreement with the basic principles of ordinary portland cement concrete, the strength of which decreases with increases in the water-cement ratio.

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