

# High Strength Geopolymers from Fractionated and Pulverized Fly Ash

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## ABSTRACT

Coal combustion residues are ideal precursors for the production of geopolymer cements. Activated in alkaline solutions, fly ash provides the necessary Si and Al for the polymer chains that form the matrix of the hardened product. Potassium silicate and blast furnace slag are added to enhance the strength developed. Compressive strength values of over 100 MPa are obtained in these matrices, much higher than observed with normal Ordinary Portland Cement binders.

Besides the chemistry, also the physical characteristics of the fly ash are of importance for the development of high strength. The fine particle size and the high sphericity of the particles, both favor good and dense packing of the material into the matrix.

In order to further benefit from the physical characteristics of fly ash, size fractions were separated and geopolymers produced from them. However, the relation between size and strength was not clear, mainly due to the fact that, when separating, the chemistry of the different fractions turned out to be different as well. This was clearly reflected by the difference in pH for the fractions (varying from 10.2 to 12.5). When size fractions were obtained by grinding, the chemistry was much less affected as shown by a much smaller pH variation of the ground fractions (11.1 to 11.6). Furthermore, a relation between geopolymer compressive strength and fly ash particle size becomes apparent. Workability seems to be influenced by free lime content of the ash. The addition of  $K_2HPO_4$  helps to extend the working time for the paste.

## INTRODUCTION

Geopolymers are inorganic polymeric materials with a chemical composition similar to zeolites but possessing an amorphous structure. Geopolymers may be seen as man-made rocks. They can be produced by reacting solid aluminosilicates with a highly concentrated aqueous alkali hydroxide or silicate solution. The chemistry and terminology of inorganic polymers was first discussed in detail by Davidovits.<sup>1</sup> Since the first mention of the term 'geopolymer' by Davidovits,<sup>2</sup> extensive research in this field has been carried out, also by authors using different wordings for the same kind of

materials. 'Low-temperature aluminosilicate glass',<sup>3</sup> 'alkali-activated cement',<sup>4</sup> 'alkali-bonded ceramic',<sup>5</sup> 'inorganic polymer concrete',<sup>6</sup> and 'hydroceramic',<sup>7</sup> are some of the frequently occurring designations.

Geopolymers form three-dimensional disordered frameworks of the tecto-aluminosilicate type with the general empirical formula  $M_n[-(\text{SiO}_2)_z-\text{AlO}_2]_n \cdot w\text{H}_2\text{O}$ , in which  $n$  is the degree of polycondensation, and  $M$  is predominantly a monovalent cation ( $\text{K}^+$ ,  $\text{Na}^+$ ), although  $\text{Ca}^{2+}$  may replace two monovalent cations in the structure.<sup>1</sup> In the same paper, Davidovits states that although the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio  $z$  is 1, 2 or 3 for the poly(sialate)-, poly(sialate-siloxo)- and poly(sialate-disiloxo)-chains,  $z$  can also be larger than 3 (up to 32), which can be explained by cross linking of polysilicate chains, sheets or networks with a sialate link (-Si-O-Al-O-).

Different types of materials such as resins, foams and fibers were developed on the basis of geopolymers.<sup>1</sup> Due to their low porosity highly-packed microstructure, high-temperature resistance, water resistance, acid resistance, low thermal expansion and fire-proofness, geopolymers can be used in many applications, among which binders in certain specialty cements and for immobilization, stabilization and solidification of a large number of materials, are best known.

Geopolymers with a Si:Al ratio of 1 or 2 will present a rigid 3D network and may be used for bricks, ceramics and cements and concretes, but as well for fire protection and the immobilization of nuclear and toxic waste. These are products and applications normally seen in connection with cement and ash. The interjection of the geopolymerization reaction in the traditionally used processes for such products may pay off by the enormous product improvement this brings about. Such products are bulky and this is one reason more why fly ash should be thought of as an option for a geopolymer precursor. One of the most promising fields is the replacement of ordinary cements by geopolymers.

Usually, geopolymers are synthesized at relatively low temperatures from meta-kaolinite, whereby the geopolymerization reaction is favored by its amorphous state. The smaller the particle size of the starting material the higher the reactivity and the geopolymerization rate will be. Duxson and co-workers gave an overview of geopolymer technology.<sup>8</sup> Further information is available in the first book on geopolymers by Davidovits.<sup>9</sup>

Successful attempts of using fly ash for the synthesis of geopolymers were reported at the international conferences on geopolymers.<sup>10,11,12</sup> The first commercial geopolymer from fly ash was produced in the USA in 1997 by a company named ZeoTech Corp under the name ZeoTech Concrete 100<sup>13</sup> after the research work at the Drexel University in Philadelphia.<sup>14</sup> This acid resistant concrete was made of a blend of sodium silicate solution, alkaline activator, Class F fly ash, silica-bearing aggregates and water. Research in the field of immobilization of heavy metals and toxic waste was reported from Australian and South-African research groups.<sup>15,16,17</sup> The idea of developing low  $\text{CO}_2$  cement was first stated by Davidovits.<sup>18,19,20</sup> An overview of geopolymer chemistry, synthesis and applications was presented at earlier WOCA conferences.<sup>21,22</sup>

Apart from the high strength, fast hardening is often mentioned as an advantage of geopolymers over ordinary cement. However, if hardening reactions are very fast, this may become a problem if it affects the workability. In extreme cases, paste may harden instantaneously upon mixing and one may speak about 'flash set'. This behavior is

believed to be influenced by the natural pH of the fly ash used as well as the particle size. This means that the available Ca and the reactive surface may be the key factors. In mortars made with OPC a number of additives are used to delay the hardening reactions. Since the chemistry of geopolymers is different it is expected that different retarders have to be developed for geopolymer pastes. According to Lee and van Deventer,<sup>23</sup> a number of potassium salts have the effect of retarding geopolymer reactions, among which  $K_2HPO_4$  had the largest effect.

The present work is carried out in the framework of a project (GEOASH), sponsored by the European Coal and Steel Community. The project aims to produce geopolymeric matrices, stronger and denser than obtained by using Portland Cement binders, for the long term stabilization of inorganic toxic waste. The particular work presented in this paper deals with the influence of particle size on strength development and workability. Fine fractions were separated from fly ash by wind sifting as well as produced by grinding. Further, the effect of certain additives was studied on the same properties.

## MATERIALS AND METHODS

From a selection of 17 European coal (co-)combustion ashes, an alkaline fly ash from a major Dutch power station was selected and used for this study. The fly ash was produced from the combustion of a blend of Indonesian and South-African coals with 14% co-combustion of biomass, consisting of wood pellets and palm pit scales. The slag is a blast furnace slag originating from a steel plant in Belgium. The chemical composition of the ash and slag are shown in Table 1.

Table 1. Chemical composition of fly ash and slag

	Fly ash TUD-1	Slag
SiO <sub>2</sub>	48.94	37.17
Al <sub>2</sub> O <sub>3</sub>	27.76	11.83
TiO <sub>2</sub>	2.44	0.58
Fe <sub>2</sub> O <sub>3</sub>	7.90	0.34
MnO	0.04	
CaO	6.03	42.04
MgO	1.77	7.48
K <sub>2</sub> O	0.84	
Na <sub>2</sub> O	0.58	0.24
P <sub>2</sub> O <sub>5</sub>	1.11	
LOI	2.39	
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	1.76	

Size fractions of the fly ash were obtained by particle size separation as well as by grinding. The particle separation of the fly ashes is done with an Alpine centrifugal zigzag classifier of the type 100 MZR. Varying gear speed, air flow and ash throughput, four fine size fractions were obtained and one coarse fraction was retained for further use. Grinding was performed with a Laboratory Attritor (Union Process, type 01-HD) using ceramic grinding medium. Four ground fractions were obtained corresponding to

grinding times of 15, 30, 60 and 120 minutes. All particle size distributions were measured with a Malvern Mastersizer S laser diffraction instrument dispersing the samples in ethanol and using sonication until a stable response was obtained. The pH of the samples was measured after 10 minutes stirring of a mixture of 5 grams of ash and 50 ml demi-water.

Geopolymers were produced from mixes consisting of fly ash, blast furnace slag, potassium silicate solution (0.8 mole  $K_2O$  for 1 mole  $SiO_2$ , which was obtained by adding KOH to a commercial potassium silicate solution) and water. Mix compositions were prepared such that the pastes were just workable for the time required to mould 8 cylinders of 29 mm diameter to a height of about 25 mm. This resulted in geopolymer rod samples of approximately 30 g each. The mix proportions K-silicate:Water:Slag (10:10:15 on a weight basis) were kept constant, whereas the fly ash content was varied and optimized to give the best results. Mixing was done in a simple mixer (Philips Cucina HR1351), while water and K-silicate solution is poured slowly onto the solids. The mix is hold thixotropic by performing mixing and pouring in the moulds, while keeping it on a shaker (Retsch KG 19805). Preferably, four moulds were filled with the same paste. The closed Teflon containers with the mixes were cured for 28 days at room temperature, before compression tests were performed.

The cylinders were flattened and compression tests were performed on a Zwick Z100 tensiometer, stress controlled compression instrument (crosshead SN 149992), using testXpert software. The compression tests were performed in batches of 4 cylinders. The lowest result was discarded and the remaining three results averaged to obtain the value for the sample. The highest result was also retained and recorded in the graphs. Davya 30, a commercial metakaolinite-based geopolymer form Cordi-Géopolymère, was used as a reference material.

For studying the workability and setting time, commercial superplasticizers and retarders (from CUGLA BV) and analar grade reagents  $CaO$ ,  $KCl$ ,  $K_2CO_3$ ,  $K_2HPO_4$  and  $K_2C_2O_4$  were used.

## RESULTS AND DISCUSSION

### *Characterization of size fractions*

The size characteristics of the samples produced are given in Table 2. Size distributions curves for the size separation were published earlier by the authors.<sup>24</sup> The yield, the amount produced from the feed (in wt%), is inevitably decreasing when separating finer fractions. As can be seen from the table, for the finest fractions this can even be less than 10%, since the original ash only contains small amounts of such fine particles. It was further calculated that in general from the fine particles present in the feed, between 20 and 70% were recovered in the separated fractions. For the grinding the full sample after grinding was taken without further separation. It must be noted that the finest fractions as were produced by separation could not be obtained and that the size distribution is significantly broader than for the separated samples.

Table 2. Size characterization of the used fly ash and the samples thereof.

Sample	Yield (% of feed)	Particle size characteristics			Cut Point
		d <sub>10</sub>	d <sub>50</sub>	d <sub>90</sub>	d <sub>97</sub>
Original Ash		3.4	24	86	
<i>By sifting:</i>					
Coarse		23	55	115	
Fine	41	1.9	9.3	25	36
Finer	19	1.2	4.3	10	14
Finest	6	0.9	2.2	4.6	6.5
Ultra-fine	4	0.9	1.7	3.2	4.5
<i>By grinding:</i>					
15 minutes		2.1	11.1	35	53
30 minutes		1.7	8.1	25	39
60 minutes		1.2	6.4	22	34
120 minutes		1.0	4.6	16	25
Slag		1.8	13.6	44	

As discussed earlier, the pH of the size fractions obtained by separation decreases from 12.2 for the original sample down to 10.2 for the finest fraction due to free lime particles present in the coarser fractions. The coarse fraction recorded a pH of 12.5.<sup>22,24</sup> Bulk chemical and mineralogical analysis of these fractions shows that the chemistry and mineralogy change with particle size as well. This phenomenon was also found in other ashes used in the project.

To the contrary, as expected, the samples obtained by grinding did not show marked variations in pH and chemistry and mineralogy (pH varying between 11.1 and 11.6).

#### *Geopolymerisation and strength development*

The final compressive strength depends on the mix used, that is the amount of fly ash that is added to the fixed amount of slag, K-silicate solution and water. For the original TUD-1 ash, the highest strength is found for the highest workable mix at 43 (K-silicate:Water:Slag:Fly ash 10:10:15:43 on a weight basis). Further increase of the amount of fly ash makes the paste unworkable. The operational window is found to be somewhere between 28 and 43, with the highest strength at the extremes (84 and 97 MPa) and the lowest strength in the middle of the window (76 MPa).<sup>24</sup> It was found that for the different fractions of the same fly ash TUD1, the operational windows were different and also the mix at which highest compressive strength was obtained was different. Therefore, in a number of preliminary tests, for each size fraction the optimum mix had to be determined.

Figure 1 shows the results of compressive strength obtained for the different size fractions obtained by separation. For each size fraction, the average compressive strength and the maximum value obtained were plotted for the highest workable mix and for a lower mix that gave a much more watery and easier workable paste. For the fine and the original samples results from duplicate tests were plotted as well. There is no clear trend of increasing compressive strength with decreasing particle size.

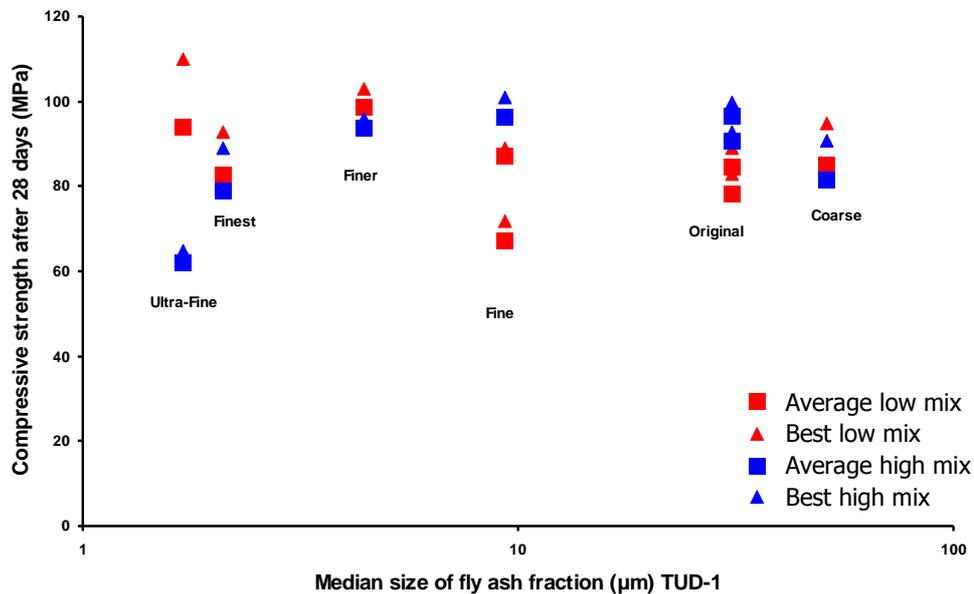


Figure 1. Compressive strength for geopolymers produced from different size fractions from fly ash TUD1 obtained by separation. Blue symbols represent the values for the maximum workable mix, whereas red symbols are for lower mixes.

Remarkable is that the 'coarse' fraction performs similar to the 'finest' fraction. A possible explanation for the lack of clear relation between strength and particle size may be that the conditions and mixing proportions do not allow full benefit of the available fly ash surface area. As can be seen from Figure 1, for the fine fractions the highest strengths are found when less fly ash is used in the mix (low mix). The fresh paste is easier to handle and there is more time for dissolution of the fly ash before the mix starts to set. For the coarse fractions, it appears that a maximum amount of fly ash in the mix (high mix) is favorable for getting high geopolymer strength. The liquid:solid ratio may be of influence on the amount of free lime dissolved during mixing. The dissolution of free lime is known to influence the geopolymeric reaction in a negative way. A high mix will probably limit the dissolution of free lime, predominantly present in the coarser size fractions, and therefore be in favor of high strength.

For the samples prepared by grinding, there was an initial increase of compressive strength with decreasing particle size, but for the two finest fractions the strength decreased, as can be seen in Figure 2. This decrease was accompanied by a marked difficulty of preparing a workable paste. The amount of fly ash had to decrease, that is the lower mixes had to be used, to avoid immediate hardening upon mixing (flash set). As for those samples the pH is equal, the higher liquid:solid combined with a higher surface area will probably result in increased dissolution of lime, resulting in decreased compressive strength.

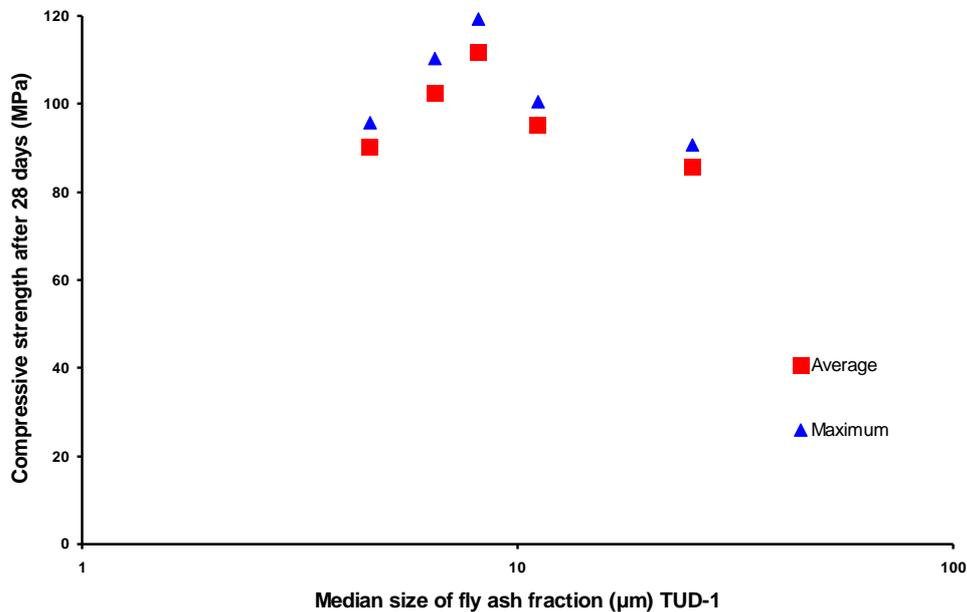


Figure 2. Compressive strength for geopolymers produced from different size fractions from fly ash TUD1 obtained by grinding.

### *Workability and working time*

By adding more and more fly ash, there seems to be a subtle turn-over point from where the mix changes from thixotropic to dry and inconsistent. This determines the upper limit of the operation window. The lower limit of the window is less well defined. By putting less fly ash in the mix, the paste becomes more fluid until it reaches a point that no good hardening can be expected. The workability is thus determined by the amount of ash added. Another difficulty is the limited working time, the time that is available from the mixing until hardening occurs to the point that the paste becomes unworkable. In the most extreme case hardening occurs directly upon mixing. The natural pH of the fly ash has an influence on the working time. To test that, a different fly ash was used (CSIC-1 from Spain) with a natural pH of 7. To this fly ash different amounts of CaO were added in order to produce ashes with increasing pH (from 7 to 12.5). By keeping the mix proportions constant, at pH around 10.5 the paste became difficult to work with and the hardening time decreased markedly. For the highest pH a flash set was found. For the samples for which still containers could be filled, the compressive strength after 28 days decreased with increasing pH of the fly ash. This supports the observation made for the geopolymers produced from the ground samples. In an attempt to influence workability and working time of the pastes, two superplasticizers and two retarders commonly in concrete were added to the original ash TUD-1. This had no influence on the paste properties. From the potassium salts used by Lee and van Deventer,<sup>23</sup> only  $K_2HPO_4$  had significant influence on the workability. The addition of 1.2 g to the standard mix (1.2 g per 10 g of K-Silicate solution), extended the working time from 15 minutes to more than 5 hours. However, the compressive strength of the geopolymers produced decreased from 84 MPa to 67 MPa, probably due to the weakness of the apatite formed.

## CONCLUSIONS

High strength geopolymers, up to compressive strength values of over 100 MPa, were produced from mixtures of coal fly ash, blast furnace slag, a potassium silicate solution and water, in which the fly ash is the majority component. Compressive strength for size fractions prepared by separation did not show a significant relation to size. Mix proportions, chemistry and pH are different for the different size fractions produced and could have had an impact on the performance. For the geopolymers produced with ground fly ash, there seems to be an increase in strength for the finer fractions, but this was reversed by workability difficulties for the finest fractions. Workability seems to be influenced by free lime content of the ash. The addition of  $K_2HPO_4$  helps to extend the working time for the paste.

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