

## Flyash Geopolymer Concrete as Future Concrete

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### Abstract

Demand for concrete as construction material is on the increase so as the production of cement. It is estimated that ~6-8% of total CO<sub>2</sub> is generated from construction industry. To reduce the concrete industry's carbon footprint, blended cements are in use in the market. The research trend is directed towards more eco-friendly concrete such as geopolymer. Recently the focus of research has been shifted on use of fly ash for geopolymerisation. This is based on the alumino-silicate composition of fly ash, its easy availability, better flow ability and improved durability.

The chemical composition of geopolymer is similar to that of zeolite, but amorphous in microstructure. Flyash-based geopolymer concrete show excellent short and long-term properties. The properties and uses of geopolymers are being explored in many scientific and industrial disciplines like modern inorganic chemistry, physical chemistry, colloid chemistry, mineralogy, geology, and in all types of engineering process technologies. The current paper presents scope of flyash based geopolymer concrete as future concrete, summarizes and critically analyses the most important research findings.

**Keywords:** *Geopolymers; Zeolites; Microstructure; Compressive strength*

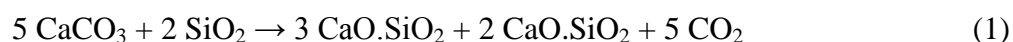
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## **1.Introduction**

Many concrete structures, especially those built in corrosive environments, start to deteriorate after 20 to 30 years, even though they have been designed for more than 50 years of service life (Mehta.P.K,2001)<sup>1</sup>.

The search for environment friendly construction materials is imperative, as the world is facing serious problems due to environmental degradation. There is a significant expectation on the industry to reduce carbon dioxide (CO<sub>2</sub>) emissions to the atmosphere. In view of this, one of the efforts to produce environmentally friendly concrete is to reduce the use of Portland cement by using by-product materials, such as fly ash. It is known that production of one ton of Portland cement accounts for about one ton of carbon dioxide released to the atmosphere, as the result of de-carbonation of limestone in the kiln during manufacturing of cement, i.e.:



Alkali Activated systems was first introduced by Victor Glukhovsky and subsequently Pavel Krivenko developed in the 1950s in Ukraine. The alkaline alumino-silicate cementitious systems were first called “soil silicates” (Glukhovsky,1959<sup>2</sup>,1965<sup>3</sup>,1989<sup>4</sup>; Krivenko and Kovalchuk, 2007<sup>5</sup>). The term “geopolymers” was first introduced to the chemical world by Davidovits in the mid 1970’s (Davidovits, 1993<sup>6</sup>). The main barrier that geopolymerisation has to overcome and become accepted by the industry is mainly related with the entrenched position of OPC.

## **2. Raw materials for future concrete**

The production of consistent geopolymer concrete from heterogeneous industrial waste sources is a challenging issue for the minerals industry, since raw material suitability cannot be fully guaranteed by elemental composition analysis (Fernández-Jiménez and Palomo, 2003<sup>7</sup>). As far as flyash based geopolymer concrete are concerned, the mechanical strength increases due to the formation of an Al-rich alumino-silicate gel during the first stage of alkaline activation of ash particles, and may further increase as a result of the Si enrichment of the material (Fernández-Jiménez et al.,2006<sup>8</sup>). Therefore, it is critical to manipulate Al and Si dissolution from the raw materials, through pre-processing and/or use of combinations of raw materials with different reactivity (Duxson et al., 2007c<sup>9</sup>).

The manufacture of lightweight geopolymer based building materials (pre-formed blocks) can be effectively manufactured at 25<sup>0</sup>C starting from fly ash (S. Andini et. Al.).

properties of the final products depend on a number of variables such as composition of the starting mixture, nature of the alkali metal silicate and polycondensation conditions (temperature and time). The original quantitative method for the determination of reacted water and alkali metal silicate previously developed for a metakaolinite-based system has been successfully applied to the systems investigated for flyash based systems. The results have shown that the kinetics of the polycondensation reaction is less favoured at 40 and 60°C in respect to 25°C and that a strong enhancement occurs at 85°C.

Another important issue that has to be considered during geopolymerisation is the assessment of the effect of contaminants present in the raw materials that add reaction pathways and affect the properties of the final product as a result of changes in setting times, slump, strength and shrinkage. This issue is very well covered for flyash geopolymers in a recent publication (Duxson et al., 2007c<sup>9</sup>).

### **3. Focus for use of flyash as principal ingredient**

According to the American Concrete Institute (ACI) Committee 116R, fly ash is defined as “the finely divided residue that results from the combustion of ground or powdered

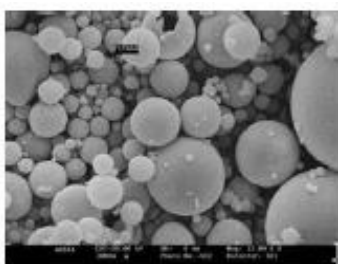


Figure 1 Ungraded fly-ash

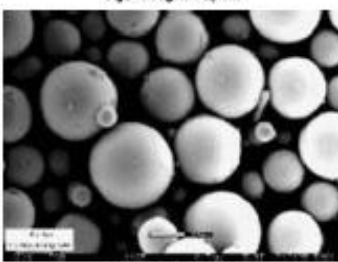


Figure 2 Graded fly-ash

coal and that is transported by flue gases from the combustion zone to the particle removal system”. Fly ash particles are typically spherical, finer than Portland cement and lime, ranging in diameter from less than 1 µm to no more than 150 µm. The chemical composition is mainly composed of the oxides of silicon (SiO<sub>2</sub>), aluminium (Al<sub>2</sub>O<sub>3</sub>), iron (Fe<sub>2</sub>O<sub>3</sub>), and calcium (CaO), whereas magnesium, potassium, sodium, titanium, and sulphur are also present in a lesser amount. The characteristics of fly ash that generally considered are loss on ignition (LOI), fineness and uniformity. LOI is a measurement of un-burnt carbon

remaining in the ash. Fineness of fly ash mostly depends on the operating conditions of coal crushers and the grinding process of the coal itself. Finer gradation generally results in a more reactive ash and contains less carbon.

A series of tests were performed on geopolymer concrete made using fly ash as the source material (D. Hardjito, et al, 2004<sup>10</sup>). Based on the results of his tests the following conclusions are drawn:



results in amorphous to semi-crystalline matrices compared with the highly crystalline and regular zeolitic structures. The electron diffraction analysis conducted by (Van Jaarsveld et al. 1999<sup>14</sup>) showed that the structure of geopolymers is amorphous to semi-amorphous. In aluminosilicate structures silicon is always 4 co-ordinated, while aluminium ions can be 4 or 6 co-ordinated. It is possible that the coordination number of aluminium in the starting materials will have an effect on its eventual bonding in the matrix.

### 5. Characterization and other analytical techniques

A number of relatively simple or advanced techniques may be used to obtain maximum information and elucidate geopolymerisation mechanisms. The ability of Al-Si minerals to undergo geopolymerisation may be predicted by specific surface area measurements, which provide an indication of how much surface area participates in heterogeneous reactions within a solid-fluid system (Van Jaarsveld, 2000<sup>15</sup>).

The XRD patterns (E. Alvarez-Ayuso a, X. Querol, et al., 2008<sup>16</sup>) of flyash samples as well as those of geopolymers synthesised from them. The XRD patterns of flyashes displayed

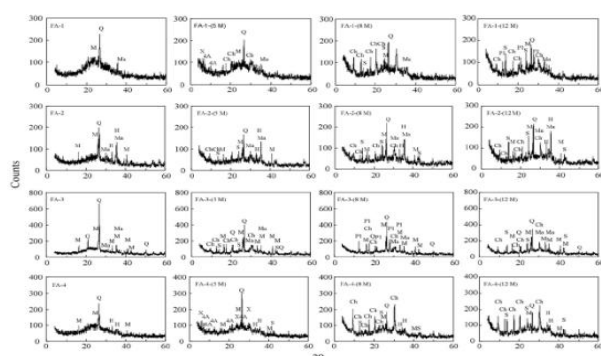


Fig. 3. XRD diffraction patterns of original fly ashes and geopolymer samples arising from them after the activation process (curing time, 48 h; curing temperature, 80 °C) at different NaOH concentrations (Q, quartz; M, mullite; Ma, magnetite; H, hematite; Ch, chabazite; S, sodalite; X, zeolite X; 4A, zeolite 4A; P1, zeolite NaP1).

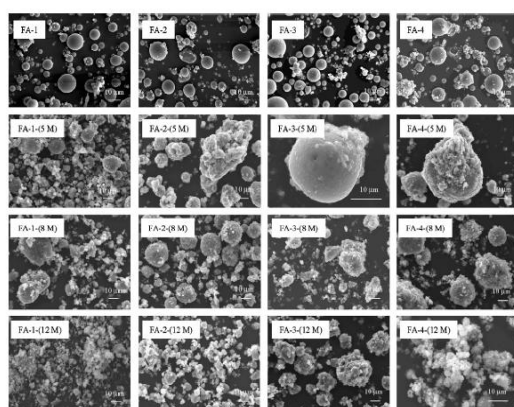


Fig. 4. SEM images of original fly ash and finely ground geopolymer samples arising from them after the activation process (curing time, 48 h; curing temperature, 80 °C) at different NaOH concentrations.

of flyashes.

peaks in Fig.3 due to quartz, mullite and iron oxides either magnetite or hematite or both, also other crystalline phases such as anhydrite, calcite, anorthite-albite, illite and microcline were also detected in some samples, but always at trace level. In addition to these crystalline components, a broad peak in the region 20–32°2θ arising from the glassy phase of flyashes could be observed in all the patterns. For all the studied flyashes the intensity of this peak was progressively decreased after the geopolymerisation processes with the activation medium concentration increase. This decrease is related to the high glassy phase content

The morphological features (E. ´Alvarez-Ayuso a, X. Querol,et.al.,2008<sup>16</sup>) of the original fly ashes and derived geopolymers in Fig.4 shows different degree of reaction was observed at the different concentrations of activation medium for the different fly ashes is subject of study. When the least concentrated alkaline solution (5M NaOH) was employed in the activation process this always yielded the lowest degree of reaction, although great differences between fly ashes were apparent, with the FA-1 and FA-3 samples being the most extreme examples.

Fourier transform infrared spectroscopy (FTIR) analysis in Fig. 5 shows the infrared spectra of the original fly ashes and geopolymer samples synthesised from them. Original fly ash samples (E. ´Alvarez-Ayuso a, X. Querol,et.al.,2008<sup>16</sup>) showed two main spectral peaks at about 480 and 1110 cm<sup>-1</sup>, the former has been assigned to Si–O–Si and O–Si–O bending,

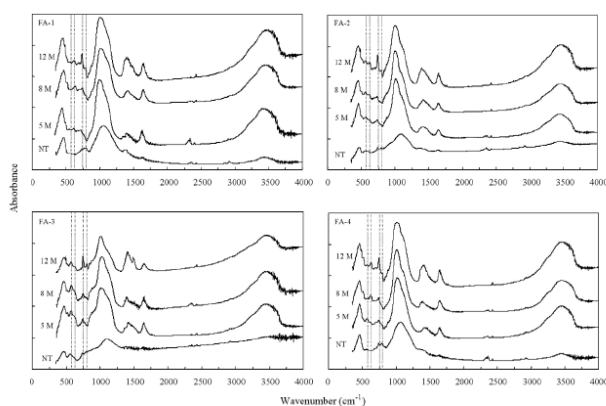


Fig. 5. FTIR spectra of original fly ashes (NT) and geopolymer samples arising from them after the activation process (curing time, 48 h; curing temperature, 80 °C at different NaOH concentrations (dashed lines indicate positions at 590, 635, 750 and 810 cm<sup>-1</sup>).

and the latter to Si–O–Si and Al–O–Si asymmetric stretching. In addition to these two bands, the spectra of untreated fly ashes showed three other peaks associated with their Al–Si framework, generally of much lesser intensity, at about 810, 750 and 590 cm<sup>-1</sup>, being attributed to Si–O–Si and Al–O–Si symmetric stretching [Farmer.V.C,1974<sup>17</sup>

and J.A. Gadsden,1975<sup>18</sup>] was generally manifested. After the fly ash activation, besides spectral changes related to the Si–Al framework, also broad bands at about 3485 and 1655 cm<sup>-1</sup> were present in the spectra of geopolymer samples, these bands are associated to –OH stretching and H–O–H bending, respectively, being characteristic of weakly bound molecules of water either surface adsorbed or trapped in large cavities.

## **6. Factors affecting compressive strength**

Compressive strength development is a primary measure of the utility of materials used in different applications of the construction industry (Hardjito,2004<sup>19</sup>).

### *Compressive Strength at Different Ages*



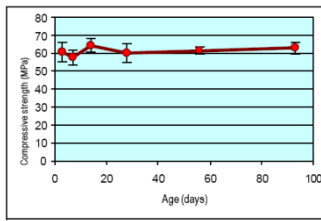


Fig. 6 Compressive Strength of Different Ages.

strength over the time.

### Effect of Curing Time

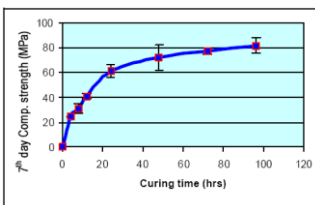


Fig. 7 Influence of Curing time on Compressive Strength.

The effect of age of concrete on the compressive strength is shown below in Fig. 6. The chemical reaction of the geopolymer gel is due to substantially fast polymerisation process, the compressive strength does not vary with the age of concrete. This observation is in contrast to the well-known behaviour of OPC concrete, which undergoes hydration process and hence gains

The influence of curing time on the compressive strength is shown in Fig. 7. Longer curing time improves the polymerisation process resulting in higher compressive strength. The results shown indicate that longer curing time does not produce weaker material as claimed by van Jaarsveld<sup>18</sup> et al. However, the increase in strength after curing for 48 hours is not significant.

### Effect of Superplasticizer

In the fresh state, the geopolymer concrete has a stiff consistency. Although adequate

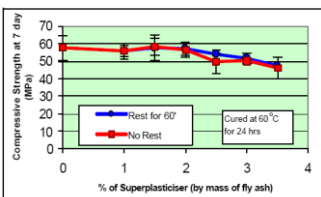


Fig. 8 Effect of Superplasticizer on the Compressive Strength

compaction was achievable, an improvement in the workability was considered as desirable. Tests were therefore performed to study the effect of adding commercially available naphthalene-based superplasticizer. The results of these tests are shown in Figure 8. The addition of superplasticizer improved the workability of the fresh concrete but had very little effect on the

compressive strength up to about two percent of this admixture to the mass of fly ash. Beyond this value, there is some degradation of the compressive strength.

### Effect of Water Content in the Mix

Previous research by Barbosa et.al,2000<sup>20</sup> on geopolymer pastes showed that the water

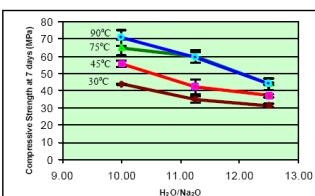


Fig. 9 Effect of the molar H<sub>2</sub>O to Na<sub>2</sub>O on Compressive Strength

content in the mix played an important role on the properties of geopolymer binders. The addition of water improved the workability of the mixtures. The results shown in Figure 9 clearly demonstrate the effect of the molar ratio of H<sub>2</sub>O-to-Na<sub>2</sub>O on the compressive strength of geopolymer concrete. The trends of these test results by Hardjito,2004<sup>18</sup> are similar to those observed

by Barbosa et. al,2000<sup>19</sup> for their tests on geopolymer pastes.

The test data shown in Figure 10 demonstrate that the compressive strength of geopolymer concrete decreases as the ratio of water-to-geopolymer solids by mass increases. The test trends shown in Figure 10 are somewhat analogous to the well-known effect of water-to-cement ratio on the compressive strength of OPC concrete, although the chemical processes involved in the formation of the binders of both these types of concretes are entirely different.

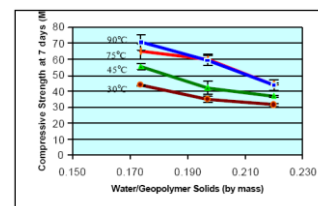


Fig. 10 Effect of water-to-geopolymer solids ratio on Compressive Strength

## 7. Long term performance

The long term behaviour of geopolymer concrete by D. Hardjito et.al. 2004<sup>21</sup> were being showed by the test results that the drying shrinkage strains of fly ash-based geopolymer concretes were found to be insignificant. The ratio of creep strain to-elastic strain (called creep factor) reached a value of 0.30 in approximately 6 weeks after loading on the 7th day with a sustained stress of 40% of the compressive strength. Beyond this time, the creep factor increased only marginally (Hardjito.D et.al. 2003<sup>22</sup>).

A series of tests were performed on the resistance of fly ash-based geopolymer concrete to sulfate attack. After soaking the specimens in a 5% sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) solution for 12 weeks, there were no significant changes in the compressive strength, the mass, and the length of the test specimens (Wallah, S.E. et.al. 2003<sup>23</sup>). These series of tests on the long-term behaviour of the fly ash based geopolymer concrete are continuing for a period of one year. Davidovits,1999<sup>24</sup> has reported earlier that geopolymer cement is acid resistant. He also reported that geopolymer materials do not generate any dangerous alkali-aggregate reaction, even in the presence of high alkali content.

Phair et al. (2003<sup>25</sup>) investigated alumino-silicate geopolymer and hydrogel microstructure by differential scanning calorimetry (DSC). This technique was used to determine the glass transition temperature of precursor sodium silicate and sodium aluminate solutions. The use of DSC is also very useful for optimisation purposes, due to its ability to assess the reactivity of the products obtained under different calcination conditions (Cioffi et al., 2003<sup>26</sup>).

Leaching tests are a very powerful tool to determine the degree of ion immobilisation within a geopolymeric system. Yunsheng et al.(2007<sup>27</sup>) conducted leaching tests which



revealed that geopolymers can effectively immobilise Cu and Pb. Zaharaki et al. (2006<sup>28</sup>) conducted durability and structural integrity studies for geopolymers made of slag and kaolinite. The specimens were almost unaffected when immersed in distilled- and seawater over a period of one year, whereas noticeable loss of strength was seen when immersed in 1N HCl or simulated acid rain solutions.

Alkali-activated fly ash cement exhibited good durability when exposed to sulphates and seawater. However, in highly acidic media loss of mass due to dealumination and poorer mechanical strength was seen (Fernández-Jimeñez et al., 2007<sup>29</sup>). Geopolymers derived from various combinations of granulated blast-furnace slag, Class C fly ash, clay, sand, and basalt were tested for resistance to solid particle erosion. The geopolymer that did not contain fly ash eroded most rapidly. Fly ash promoted dissolution of slag and sand aggregates, but the mechanism involved in improved erosion resistance has yet to be identified (Goretta et al., 2007<sup>30</sup>).

## **8. Conclusions**

Geopolymer concrete shows significant potential to be a material for the future, because it is not only environmentally friendly but also possesses excellent mechanical properties, both in short term and long term, and durability. Significant information is already available in the literature to utilise geopolymer concrete technology in practical applications such as precast concrete products and waste encapsulation.

Due to the involvement of very strong research groups considerable progress has been made in this field over the last years and it is believed that relatively soon the geopolymerisation potential for large scale applications in the construction and minerals industry will be well established. The knowledge gained will enable broad exploitation of the technological potential of these materials and the production of tailored geopolymers.

Future study in the field of the application of geopolymer is required for its commercial uses. Establishment of geopolymerisation as a feasible technology for the management of industrial wastes will contribute to considerable savings in disposal costs, recycling of wastes, and substantial reduction of greenhouse gas emissions and enhanced social acceptance of the industry.

## **9. Acknowledgement**

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