Chapter 2
Precursors and Additives for Geopolymer Synthesis

Abstract The raw materials typically used in geopolymer manufacturing are described. The use of metakaolin, coal derived fly ash and slag as aluminosilicate sources is presented. The use of readily available coal fly ash in geopolymer products offers sustainability and technical benefits, especially in niche applications such as fire resistant products. There are national standards for the use of fly ash in concrete and these have some applicability to geopolymer production. For instance, beneficiation of fly ash by screening and milling can significantly improve physical properties of resultant geopolymer products. Activation of high calcium ground blast furnace slag and other slags result in more complex microstructures and are not as suitable for fire resistant products. Metakaolin is a purer source of aluminosilicate than fly ash. It is capable of ambient cures but has the penalty of high water demand which influences property development. The investigation of volcanic ashes as aluminosilicate sources has grown in importance recently. Alkaline hydroxides and silicates are used to activate the aluminosilicate sources and the sodium and potassium derivatives are commercially available. The speciation of alkali metal silicates is briefly outlined together with the influence of the alkali metal cation on this speciation. The use of sodium aluminate derivatives is examined, in particular the use of Bayer liquor, a by-product of alumina extraction from bauxite. The structure of sodium aluminate solutions is also reviewed. A final section describes the admixtures, typically superplasticisers and fibres, and fillers employed to modify the plastic and cured properties of geopolymers with emphasis on optimisation of fire resistant properties.

Keywords Fly ash · Fly ash beneficiation · Metakaolin · Sodium silicates · Sodium aluminates · Admixtures and fillers

The precursors and additives required for the synthesis of geopolymer systems are:

- Alkali soluble aluminosilicates
- Alkaline dissolution media
- Admixtures to develop specific properties
- Aggregates and fillers.

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2.1 Alkali Soluble Aluminosilicate Sources

Alkali soluble aluminosilicate sources include granulated blast furnace slag (GBFS), fly ash, and volcanic ashes. Metakaolin, calcined clay, has an amorphous structure with a silicon to aluminium ratio of 1. It is used to manufacture geopolymers and can increase the aluminium content of geopolymers when used with fly ash and GBFS. Materials such as silica fume from smelting operations and from rice husk ashes do not contain aluminium, but are alkali soluble and are used to adjust silicon content of geopolymers for property control. All the above materials have utility as Supplementary Cementitious Materials (SCM) in conjunction with Portland cement.

Sources of aluminium are limited to waste anodising solutions (Nugteren et al. 2011), sodium aluminates including Bayer liquor (Jamieson et al. 2012) and aluminium smelting slag although the latter is toxic and requires additional processing prior to use. These aluminium based materials may be used to adjust aluminium levels in geopolymer synthesis. A potential source of aluminium is waste water treatment sludge which has been evaluated in brick and cement manufacture (Babatunde and Zhao 2007).

GBFS does not form geopolymers based on aluminium and silicon tetrahedral structures, but rather a calcium silicate hydrate which is also present in OPC. GBFS's calcium levels tend to be in excess of 40 wt%. GBFS can be used in blends with fly ash to give hybrid structures (Buchwald 2009; Sofi et al. 2007; Puertas et al. 2000). Alkali activated binders based on GBFS yield products with higher compressive strengths and durability compared to OPC (Fernández-Jiménez et al. 1999). The reactions of slags are dominated by small particles. Particles greater than 20 μm in size react only slowly, whilst particles less than 2 μm react completely within 24 h. To achieve these small particle sizes grinding of the granulated slag is required (Wan et al. 2004).

Fly ash is the by-product formed during power generation by the combustion of coal. It comprises fine particles which rise with the flue gases (ash that does not rise is termed bottom ash) and is collected by electrostatic precipitators or other filtration equipment prior to the flue gases reaching the exhaust chimneys.

The source and chemical composition of coal and the operating conditions of the combustion process have a major impact on the resulting fly ash chemical composition and physical properties. The main components of fly ash are silica, alumina, ferrous oxide and calcium oxide with variable amounts of carbon as shown by LOI (loss on ignition) results (Blissett and Rowson 2012). They also observed that fly ashes derived from sub-bituminous and lignite coals are characterised by higher calcium oxide and lower silica and alumina contents compared to high grade bituminous and lignite coals (see Table 2.1). Fly ash from coals containing less than 10 wt% calcium oxide consists mainly of aluminosilicate glasses and do not usually contain crystalline calcium compounds. Fly ash with greater than 15 wt% calcium oxide contained calcium aluminosilicate glasses and crystalline calcium compounds.

Table 2.1 Bulk composition of fly ash by coal type—modified from Blissett and Rowson (2012)

Component (wt%)	Bituminous	Sub-bituminous	Lignite
SiO_2	20–60	40–60	15–45
Al_2O_3	5–35	20–30	20–25
Fe_2O_3	10–40	4–10	4–15
CaO	1–12	5–30	15–40
LOI	0–15	0–3	0–5

The Ash Development Association of Australia has published The Coal Combustion Products Handbook (Gurba et al. 2007). This handbook is a useful reference source for Australian fly ashes and their current and potential applications.

The morphology of fly ash particles is controlled in the main by combustion temperature and subsequent cooling rate. SEM imaging showed a mix of solid spheres, hollow spheres (cenospheres), irregular unburnt carbon, and mineral aggregates with quartz, corundum and magnetite. Mullite and quartz are the predominant crystalline constituents of Australian fly ashes (Rickard et al. 2011; French and Smitham 2007).

Kutchko (2006) studied 12 class F fly ashes from the United States using SEM-EDS. She found mainly amorphous aluminosilicate spheres with some iron rich spheres, the latter consisting of iron oxide and amorphous aluminosilicate. The morphology of the particles was used to determine the relative amorphous and crystalline compositions. Cross sections showed the iron oxide and aluminosilicate were mixed throughout the fly ash particles. The calcium was not associated with the aluminium or silicon. In addition to the particles reported above she also found agglomerated and amorphous material, the formation being attributed to inter-particle contacts.

The amount of alkali soluble (amorphous) fly ash material is the critical quantity for geopolymer synthesis calculations (Fernandez-Jimenez 2003). Allowance must also be made for the fact that not all the amorphous material is accessible by the activating alkali solutions.

The total bulk elemental composition (as oxides) can be determined by X-ray fluorescence (XRF) and the phase abundance by quantitative X-ray diffraction (QXRD). If the composition of the crystalline component is subtracted from the total elemental composition what is left is the composition of the amorphous content some of which can react with alkaline activators to form geopolymer products. Chen-Tan et al. (2009) carried out this type of analysis on Collie fly ash. Rickard and Williams extended this work to several other Australian fly ashes with a view to determining thermal properties of the synthesised geopolymers (2010, 2011, 2012).

Font et al. designed a simplified XRD based method for determination of the glass content and mineralogy of coal based fly ashes. A glass standard based on a >99 % aluminosilicate glass was added to fly ash in known proportions and the mixtures evaluated by XRD (Font et al. 2010).

Van Jaarsveld et al. (2003) carried out XRF to get the total elemental composition, but used FTIR to determine the aluminium co-ordination. Bands

at 550 and 557 cm^{-1} had previously been assigned to aluminium in octahedral co-ordination. This latter co-ordination form will not form geopolymers. He attributed differences between two Port Augusta fly ash batches to slight differences in the silica amorphous phases. It was proposed that these differences could be due to variations in the coal feed stock composition or the variation in furnace temperatures.

Recent work using dilatometry by Provis et al. (2012) claims that mechanical properties of fly ash based geopolymers can be predicted from the temperature at which the high temperature expansion peak attributed to release of strongly chemically bound water is observed. High strength samples generally display this expansion at a higher temperature than low strength samples. Samples made either with poorly reactive fly ash or with an excessive amount of silica in the activating solution also expand by up to 10–15 % below 200 °C. This was attributed to a combination of low extent of crosslinking by aluminium entities and vaporisation of added water to produce an expanded material. Additional water was added to the geopolymer synthesis mixture to give sufficient workability to fill the 4 mm diameter moulds for dilatometer test pieces. This will also reduce strength properties of these samples. This work was based on potassium silicate activating solutions for six different fly ashes. This method may have potential to screen the suitability of fly ash for geopolymer manufacture. The key outcome of this work is the influence of available (for geopolymerisation) aluminium from the fly ash on strength development.

There are national standards for fly ash for use in concrete and these also have relevance to geopolymer synthesis (ASTM Committee C09 2012a). Table 2.2 outlines the basic requirements of fly ash in ASTM C618-2 and EN450-1. EN 450-1 uses 3 LOI categories and 2 fineness categories for the initial classification of fly ash grades.

Class F fly ash is regarded as a pozzolanic material. A pozzolan has no intrinsic cementitious properties. It will react with calcium hydroxide at ambient temperatures and in the presence of water to form compounds exhibiting cementitious properties. The high calcium content of Class C fly ash will result in the formation of cementitious properties in the absence of calcium hydroxide and hence are not true pozzolans (Blissett and Rowson 2012).

Table 2.2 ASTM and EN fly ash requirements adapted from Blissett and Rowson (2012)

ASTM C618-12	$SiO_2 + Al_2O_3 + Fe_2O_3$	SO_3	Moisture	LOI	Max retained on 45 μm sieve
Class C	>50 %	<5 %	<3 %	<6 %	34 wt%
Class F	>70 %	<5 %	<3 %	<6 %	34 wt%
EN450-1	$SiO_2 + Al_2O_3 + Fe_2O_3$	SO_3	Reactive silica	LOI	Max retained on 45 μm sieve
Category A	>70 %	<3 %	>25 %	<5 %	Category N < 40 wt%
Category B	>70 %	<3 %	>25 %	2–7 %	Category S < 10 %
Category C	>70 %	<3 %	>25 %	4–9 %	

Not all of the amorphous material in fly ash reacts during alkaline dissolution. Amorphous material can be encased inside spheres and the deposit of alkali-fly ash reaction product on the spheres can act as a barrier to further dissolution. Mechanical activation of fly ash has been evaluated to increase the amount of fly ash material reacting with the alkaline solutions (van Riessen and Chen Tan 2013).

The simplest procedure is to screen the fly ash to remove particles retained on a 45 μm screen. This effectively increases the surface area of the material which has passed through the screen. Also larger sized non aluminosilicate materials such as quartz and carbon are removed. The removal of the latter is important as it has a high water demand which can result in a drop in compressive strength (Silverstrim et al. 1997).

Nugteren (2009) separated raw fly ash into six different size fractions by air classification. Geopolymers were made from these fractions in combination with GBFS using potassium silicate solution as the alkaline activator. The window of workability varied with each fly ash fraction. He found that there was no clear trend for increases in compressive strength with finer fractions. However, mix proportions were varied for each fraction and this may have impacted on the results.

Several authors have investigated mechanical activation of fly ash (Chindaprasirt and Rattanasak 2010; He et al. 2005; Kumar and Kumar 2010; Temuujin et al. 2009c; Kumar et al. 2007).

Kumar (2007) compared raw fly ash (RFA) with mechanically activated material from vibratory milling (VMFA), attrition milled (AMFA) and jet milled classified (CFA). The median particle size of the RFA of 36 μm was reduced to 5 μm (VMFA), 4.3 μm (AMFA) and 2.8 μm (CFA). FTIR showed changes in peak intensity which was attributed to the structural rearrangements occurring during milling. Geopolymers made from mechanically activated fly ashes developed compressive strengths up to 120 MPa, with VMFA giving the highest rate of strength development.

Further work by Kumar (2010) investigated the effects of extended vibratory milling times. Particle size decreased and heat flow measured during the geopolymer synthesis increased with milling time. SEM and EDS results showed a more compact microstructure and no unreacted fly ash spheres for fly ash milled for 30 min compared to unmilled fly ash. EDS results for geopolymer based on raw fly ash gave silicon to aluminium ratios in the range 2.2–2.9 and a silicon to sodium ratio in the range 0.9–1.2. Corresponding values for geopolymer based on fly ash milled for 30 min were silicon to aluminium of 2.9–3.2 and silicon to sodium of 3.5–4.2. Extended milling time also reduced setting time and increased compressive strength.

Temuujin (2009c) treated raw Collie fly ash in a vibratory mill for 60 min. SEM of the fly ash showed that the spherical morphology was substantially removed by milling. Particle size was reduced from 14.4 to 6.8 μm by the milling procedure. Initially, fast setting of the geopolymer based on milled fly ash was experienced. This was overcome by the addition of extra water which also gave suitable workability. Compressive strength, after an ambient temperature cure regime, was increased from 16 to 45 MPa by virtue of using milled fly ash. This

increase in compressive strength is claimed to be due to higher rates of geopolymerisation in samples based on milled fly ash. The ability of geopolymer systems, without added calcium compounds, to cure at ambient temperatures is imparted by the use of milled fly ash.

Temuujin (2009) investigated preliminary calcination of Collie fly ash at 500 and 800 °C as a potential activation method prior to synthesising geopolymer. This preliminary calcination caused crystallisation of mullite and hematite on the fly ash surface, lowering the reactivity of the fly ash as shown by the drop in compressive strength from 55.7 MPa (uncalcined) to 44.3 MPa (calcined at 800 °C).

Metakaolin is produced by dehydroxylation of kaolin between 650 and 800 °C. At temperatures beyond this metakaolin converts to spinel, which in turn converts to mullite (McCormick 2007). Gastuche (1962) investigated the transformation of kaolin to metakaolin and concluded that (a) the reaction proceeded by stepwise removal of constitutional water from successive octahedral sheets, (b) water removal was accompanied by a gradual transformation of Al(VI) to Al(IV), (c)cohesion between individual layers is reduced and the internal surface becomes progressively more susceptible to acid attack, whereas the silica sheets still organised as a "ring structure" remain and dissolve at a somewhat slower rate.

Metakaolin is used as an SCM with OPC where it functions by reacting with calcium hydroxide to form hydrated calcium aluminates and silicoaluminates and thus improving the durability of the resultant binders. Metakaolin has a much greater surface area than cement (12,000 m^2/g vs. 333 m^2/g). This high surface area contributes to an increase in the water demand to maintain workability. The addition of superplasticisers can help to reduce this water demand (McCormick 2007).

Metakaolin was the material used by Davidovits (2008b) for the early geopolymer development and commercialisation. Since then several research groups have used metakaolin to elucidate the kinetics, mechanisms and microstructure formation of geopolymer systems (Granizo et al. 2007; Barbosa et al. 2000a; Duxon et al. 2005, 2006, 2007a, b; Duxson et al. 2006a, b, c; Fletcher et al. 2005; Rahier et al. 1997, 2007; Weng and Sagoe-Cretsil 2007; Zuhua et al. 2009b; Zhang et al. 2010; Barbosa and MacKenzie 2003a; Kamseu et al. 2010; Subaer and van Riessen 2007).

The relative purity of metakaolin compared to fly ash and GBFS makes it eminently suitable for basic research into the many aspects of geopolymers. From a practical perspective metakaolin has a high water demand which can limit strength development and the relatively high aluminium content makes it suitable as a blending component with fly ash and GBFS to reduce the silicon:aluminium ratio of geopolymer systems where required (Phair et al. 2004).

The investigation of volcanic ash for the production of geopolymers has become more common in recent years. Volcanic ash (44 wt% SiO_2, 14 wt% Al_2O_3, 10 wt% CaO and 13 wt% Fe_2O_3) from Cameroon was activated with caustic soda to synthesis geopolymer paste with a maximum compressive strength of 55 MPa after curing at 90 °C. Mortar with 40 wt% sand gave a compressive strength of 30 MPa. This level of compressive strength exceeds the requirements of ASTM C216-12, Grade SW (severe weathering). ASTM C216 specifies the requirements

for face brick (solid masonry units from clay or shale). The development of building products from readily accessible volcanic ash with suitable conversion techniques could have genuine economic benefits (Lemougna et al. 2011). The second piece of work (Tchakoute Kouamoa et al. 2012) uses volcanic ash activated by alkali fusion at 550 °C. Metakaolin is used to consume the excess alkali from the fusion process and to adjust aluminium levels in the geopolymer produced by activating with sodium silicate solutions. The Romans used volcanic ash (harena fossica) from the Naples area mixed with lime to produce concrete and mortar (Davidovits and Davidovits 1999).

Other naturally occurring pozzolanic materials are suitable for geopolymer synthesis (Bondar et al. 2010). Xu and van Deventer (2000) investigated the geopolymerisation of 16 naturally occurring minerals using sodium and potassium hydroxides as activating materials and concluded that all 16 could be suitable geopolymer precursors.

2.2 Alkaline Dissolution Media

Alkaline dissolution media come from the family of alkali and alkali earth metal hydroxides, carbonates, aluminates and silicates in aqueous solution. Sodium hydroxide is the predominant material (due to cost considerations) with the other members of the Group I family used for specific applications. Calcium (Group II), as the hydroxide, is the only alkali earth used.

In general alkali hydroxides and silicates at pH values of greater than 13 are required to activate aluminosilicates for geopolymer synthesis (Khale 2007). Alkali metal carbonates as the sole activating agent are insufficiently alkaline for geopolymerisation reactions. However, sodium carbonate can react with calcium hydroxide to form sodium hydroxide in solution. Provis (2009) gives a comprehensive overview of alkali hydroxide solutions. There is a significant increase in solution viscosity of all alkali metal hydroxides at concentrations greater than 10 M. Efflorescence (formation of white crystalline sodium carbonates) is a known issue in geopolymers activated with an excess of sodium hydroxide. Atmospheric carbon dioxide reacts with the excess alkali to give white crystalline surface deposits which are mainly cosmetic in effect. Temuujin (2009b) found efflorescence containing phosphorus on ambient cured geopolymers. XRD showed this to be sodium phosphate hydrate and was assumed to derive from the 1.3 wt% P_2O_5 in the Collie fly ash.

Potassium hydroxide activation imparts onset of densification at higher temperature than in sodium activated geopolymers (Barbosa and MacKenzie 2003a; Duxon et al. 2007b). Blends of sodium and potassium hydroxides have been evaluated (Duxson et al. 2006b) with respect to thermal shrinkage of metakaolin based geopolymers with the blended cation geopolymer laying between the pure cation systems.

Alkali metal silicates, based on sodium and potassium are commercially available (PQ Europe 2004). Production can be via the hydrothermal or furnace route.

Generally silicates are identified by the SiO_2:M_2O ratio, known as the modulus. Commercially this ratio is normally specified in terms of weight. To convert to a molar ratio the following multiplier factors are used, sodium 1.033 and potassium 1.567. The viscosity of sodium silicate solutions is a function of concentration, modulus and temperature. Potassium silicate solutions show similar behaviour, but are more viscous than corresponding sodium silicate solutions at equal concentration. The pH of commercial silicate solutions is in the range of 10–13. Sodium silicate solutions will polymerise to form silica gel when the pH drops below 10. Solutions of sodium silicates react with dissolved polyvalent cations such as Ca^{2+} or Al^{3+} to form insoluble forms of silicates.

Potassium silicate resembles its sodium counterpart in physical properties but also shows several advantages: it does not develop efflorescence, displays higher solubility and compatibility with other additives and imparts higher refractoriness, flowing at higher temperatures than the sodium analogues.

Sodium and potassium silicate solutions consist of a range of silicate anions (PQ Corporation 2005). The basic building block is the tetrahedral silicate anion, the monomer unit. These monomer units can link in a variety of ways to form linear, planar cyclic and three dimensional silicate anion structures. There are two main factors which influence the distribution of silicate anion types, the ratio of silica to alkali and the concentration. Figure 2.1 shows the distribution of silicate anion species as the modulus increases at constant concentration. Moving from left to right (reducing alkali content) shows a shift from high monomer ("monosilicate") to more complex structures and polymers via a series of growing chains and rings.

The distribution of anionic species can be altered by the addition of alkali or dilution with water, known as respeciation. This causes the solution to change to the species distribution appropriate to the new modulus. A full strength solution

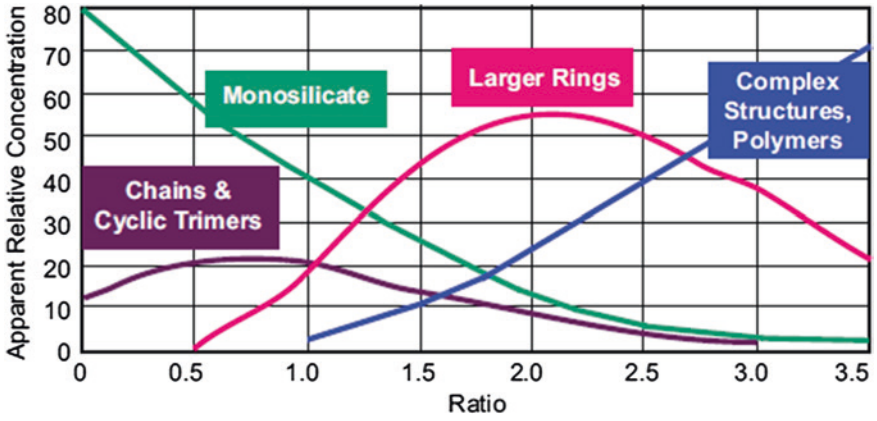


Fig. 2.1 Silicate anion structure equilibria (1 M solution) (PQ Corporation 2005) (The ratio is the modulus of the sodium silicate solution)

can take up to 48 h to respeciate at room temperature. In very dilute solutions it can occur in a matter of minutes.

The above confirms the work of Applin (1987) who thought that at pH values in excess of 13 the predominant species was $SiO_2(OH)_2^{2-}$.

Kinrade and Pole (1992) working on zeolites thought that three main structural directing roles could be attributed to M^+. Firstly it stabilises oligmeric "mineral precursor" species in aqueous alumina-silicate systems. Secondly, hydrated M^+ have a templating effect whereby silicate and aluminate species replace water of hydration for a sufficient time to enable them to join together in a structural configuration. A third hypothesis was that the extent of condensation in alkali metal-silicate solutions increases slightly as the molecular weight of M^+ increases and M^+ forms ion-pairs with silicate anions. Higher silicate oligomers are favoured due to preferred ion-pairing with heavier cations.

They concluded that there are three means for alkali metal ions to influence aqueous silicate equilibria:

1. Electrostructive water structuring by small cations increases overall level of polymerisation. They thought that this was only relevant to lithium.
2. Ion pairing of silicate anions and M^+ increased polymerisation. Cations promote encounters between dissolved silicate anions by overcoming their electrostatic repulsion. Strongly paired cations will resist subsequent formation of a siloxane bond, thus the extent of polymerisation increases in the order $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ (i.e. as the ion pair formation constants decrease).
3. Ion paired cations stabilise several specific oligomers by immobilising labile appendages and large ring structures.

Phair and van Deventer (2001) used ^{29}Si NMR to analyse the degree of polycondensation during geopolymerisation and confirmed that the basicity and hydration sphere of the alkali metal as well as it's concentration had a controlling effect on the degree of polycondensation and rate of dissolution from aluminosilicate minerals.

Sodium Aluminate (SA) is prepared by the action of sodium hydroxide solution on aluminium metal or by dissolving alumina in sodium hydroxide solution. Industrially aluminium hydroxide is dissolved in 20–25 % sodium hydroxide. Higher concentrations of sodium hydroxide give a semi solid product. In the production of solid SA aluminium hydroxide is added to boiling 50 % sodium hydroxide until a pulp forms. This pulp is cooled to give a 70 % solids SA product which is crushed and dehydrated to give a solid product (Kirk-Othmer 1991).

SA solutions tend to precipitate out alumina on standing unless stabilised with an excess of sodium hydroxide. Unstabilised SA solutions have a $Na_2O{:}Al_2O_3$ molar ratio of 1.51:1. Stabilised solutions have an excess of 11–13 % NaOH and a molar ratio in the range 1.75–1.95 (Orica Chemicals 2011). Total solids should also be considered with 38 wt% being usual (Southern Ionics 2006). However, the Coogee Chemicals (2012) stabilised product is a nominal 44.5 wt% solids with alumina content of 19 and 25.5 wt% NaOH.

SA may be obtained from the following waste product streams:

1. Aluminium industry as salt cake and spent potliner. Spent potliner is hazardous due to the presence of cyanides and fluorides and therefore requires pre-treatment to obtain SA. Salt cake is a by-product of aluminium dross formation in the recycling of aluminium metal. Processes to obtain SA from the salt cake recycling process are available (Rayzman et al. 1998).
2. Anodising bath spent solutions (Nugteren et al. 2011).
3. Bayer liquor from alumina refineries (Sipos 2009).

Aluminium does not appear to form products analogous to sodium and potassium water glass solutions even though it is present in the same tetrahedron configuration as silicon. This may be as a consequence of Lowenstein's rule. Catlow (1996) investigated the energies of formation and hydration of small clusters and rings containing silicon and aluminium. The results provided a rationalisation of Lowensteins rule in terms of the energetics of species containing Al–O–Al bridges. Whilst the formation of dimers is calculated to be energetically unfavourable in the unhydrated state, when the effects of solvation energies are added the reaction is now exothermic and possible. The formation of small rings involving Al–O–Al bridges is energetically unfavourable and hence further condensation of dimers is considered unlikely.

Moolenaar (1970) obtained vibrational spectra of sodium and potassium aluminates at a range of concentrations in sodium hydroxide solutions. Single crystal X-ray diffraction was used to determine the structure of potassium aluminate and demonstrated the presence of the dimer ion, $(OH)_3AlOAl(OH)_3^{-2}$, built up from two AlO_4^- tetrahedral which share an oxygen. At less than 1.5 M (aluminium) $Al(OH)_4^-$ was the main component. At 6 M an equilibrium between $Al(OH)_4^-$ and $Na_2Al_2O_4^{-2}$ (dimer) co-existed. Also in this work stable solutions containing appreciable amounts of aluminium could not be prepared at pH values less than 13.

Chen (1992) prepared SA solutions of equal concentrations by two different methods. Method 1 involved dissolving aluminium metal into highly concentrated NaOH solution. Method 2 involved dissolving aluminium metal in dilute NaOH solution, leaving it to stand for 15 days and solid NaOH added to bring the solution composition to that of Method 1.

Raman spectra of potassium and barium aluminate dimers show peaks at 540 and 550 cm^{-1}, respectively. The spectra from material prepared by method 1 showed a higher peak in this region than did method 2 material. The authors believe that this is indicative of higher sodium aluminate dimer content and this is supported by higher solution viscosity and lower electroconductivity in material from method 1 compared to material from method 2.

Nianyi and Honglin (1994) studied the aluminate ion using quantum chemical methods. The Al–O bonds (of the Al–O–Al bridge) in aluminate ions have significant covalent character so reactions involving the formation or cleavage of the Al–O bond may be a slow process. In UV spectra a broad absorption band near 2,700 Å was assigned to the aluminate dimer ion. Excitation energy calculations

gave a value of 2,666 Å close to the experimental value. Excitation energy calculations for $Al(OH)_4^-$ and $Al(OH)_6^{3-}$ gave wavelengths of 2,300 and 2,645 Å, respectively.

Concentrated sodium aluminate solutions with high Na_2O:Al_2O_3 ratio contain small amounts of Al(VI) as $Al(OH)_6^{3-}$. Ma et al. (2007) attributed a UV peak at 3,700 Å to this Al(VI) co-ordinated species. They claim that this peak only appears when solutions are made by dissolving aluminium trihydroxide. This peak disappeared when the solution was heated to 135 °C.

Bands observed at 725 cm^{-1} (infrared) and 621 cm^{-1} (Raman) are attributed to asymmetric and symmetric Al–O stretching vibrations of the aluminate ion, $Al(OH)_4^-$ in solution. Other low intensity bands at 890 and 630 cm^{-1} (infrared) and 540 cm^{-1} (Raman) indicate the formation of a second aluminate ion species, the dimer.

Sipos (2009) reviewed the structure of aluminium in strongly alkaline aluminate solutions. Apart from $Al(OH)_4^-$ only one further Raman distinguishable aluminate species appears to exist in significant concentrations, the dimer.

One possible explanation of unusually high viscosity values of SA solutions is that aluminate ions in aqueous solutions form an extended network of ions (both same and opposite charge) which is held together by bridging counter ions and possibly hydrogen bonds. Such extended networks could explain the variations observed in transport properties of these solutions. This network cannot be described as a polymer, but as a diffuse network of hydrated closely packed ions.

Solutions of SA appear to contain monomer, dimer and some aluminium in VI co-ordinate form. Therefore care must be taken in identifying the composition of SA solutions prior to use in geopolymer synthesis.

Brew and MacKenzie (2007) produced a geopolymer by reacting sodium aluminate solution with a slurry of silica fume in sodium hydroxide. By keeping the H_2O:Na_2O ratio <10 an X-ray amorphous material was obtained. Higher ratios gave rise to crystalline zeolites.

^{27}Al MAS NMR of the sodium aluminate solution gave a sharp resonance at 78.3 ppm indicative of crystalline material containing aluminium in tetrahedral co-ordination. There is evidence of a very small aluminium resonance at 13 ppm indicative of octahedral aluminium. This latter peak remained in the geopolymer made from the sodium aluminate. Curing for 48 h at 40 °C gave a compressive strength of 26 MPa.

Nugteren et al. (2011) investigated waste etching solutions as an alkaline source to activate fly ash and slag to manufacture geopolymers. Potassium silicate/potassium hydroxide/sodium aluminate blends were evaluated and compared to waste etch bath solution. Potassium silicate/potassium hydroxide activation gave a compressive strength of 94 MPa. Gradually replacing potassium hydroxide with sodium aluminate gave a dramatic drop in compressive strength to 3 MPa. This was attributed to preferential reaction of the potassium silicate and sodium aluminate with little waste activation occurring. Additional water was added to improve workability which would also have inhibited strength development. Using sodium aluminate as the sole activator saw compressive strength increase to 31 MPa, whilst the addition of the etch bath activator (polyalcohol/thiosulphate) at 0.4 wt% saw a further increase to 38 MPa.

The use of the waste solution in combination with potassium hydroxide gave a range of compressive strengths between 43 and 59 MPa. Replacing potassium hydroxide with sodium hydroxide gave a drop in compressive strength from 59 to 49 MPa. Increasing the fly ash to slag ratio (reduced calcium) saw the compressive strength drop from 59 to 43 MPa.

The presence of calcium containing slags leads to the formation of calcium aluminate hydrates in which aluminium is present in VI co-ordinate state.

The authors commented that when excess silica (from potassium silicate) is available in solution, liberation of alumina may quickly result in the formation of sialate chains to form geopolymer precursors. These pastes will thicken and the setting point will be quickly reached. However, when aluminate is present instead of silica, it will take time before sufficient silica is liberated from the fly ash to give a suitable silicon to aluminium ratio to form geopolymer gels. It will take longer to thicken and set.

Phair and van Deventer (2002) investigated alkali activation of various materials with several combinations of alkali activating solutions. In the case where SA ^{27}Al NMR and FTIR were performed on the sodium aluminate solution, they found that the sodium aluminate solution they used to be predominantly IV co-ordinate with a small amount of VI co-ordinate material. (Note: the SA specification was Al_2O_3:$Na_2O = 0.89$ and 26.5 wt% Al_2O_3. This is an excess of around 12 wt% alkali). FTIR of the geopolymer samples revealed a peak at 730 cm^{-1} indicating VI co-ordinate aluminium for 5.1 M aluminium. Peaks for IV co-ordinate aluminium were less prominent. Increasing the NaOH content has a minimal effect on reducing the VI co-ordinate aluminium or promoting the presence of IV co-ordinate material.

Bayer liquor is a by-product from alumina refineries. A typical composition is shown in Table 2.3 (Marciano et al. 2006).

Bayer liquor (Jamieson et al. 2012) has been used to replace sodium silicate as an activator for fly ash based geopolymers. Compressive strengths in excess of 40 MPa were obtained for geopolymer pastes cured at ambient temperature.

Verdolotti (2008) compared NaOH and sodium aluminate slurry in NaOH to consolidate pozzolanic soils. They claim that the IV co-ordinate aluminium atoms present

Table 2.3 Typical Bayer Liquor Composition based on Marciano et al. (2006)

Component	Concentration
Al_2O_3	96 g/l
Na_2O caustic	160 g/l
Na_2O carbonate	28 g/l
Organic carbon	10 g/l
Cl^-	3 g/l
SiO_2	1 g/l
SO_3^-	0.7 g/l
pH	~14
TDS	30 wt%
Viscosity at 50 °C	3,300 Pa.s

in the pozzolana and sodium aluminate change their co-ordination state splitting between IV and VI co-ordinate, modifying the traditional polysialate chemistry.

The pozzolana had silicon to aluminium compositional ratio of 3:1; this ratio in the geopolymer was 2.71:1 for 10 M NaOH and 2.28 for the sodium aluminate slurry in NaOH. This would indicate that the aluminium from the sodium aluminate is affecting the final composition.

The sample treated with 10 M NaOH showed the highest concentration of Q^4 (1Al). The presence of sodium aluminate promotes the co-ordination of four aluminium atoms to SiO_4 tetrahedra. SEM micrographs showed amorphous morphology from 10 M NaOH activated samples. The sample activated by sodium aluminate showed a less homogeneous structure plus needle like crystals spreading over the sample surface.

XRD patterns (Cu kα radiation) showed new crystalline peaks at 42° (2θ) in both geopolymer samples and a peak at 27.5° (2θ) in the sodium aluminate activated sample. Neither NaOH nor sodium aluminate have reflections at these positions. The peak at 42° (2θ) can possibly be attributed to zeolite formation. The intensity of the peak at 27.5° (2θ) reduced during the curing period. The authors, supported by FTIR and NMR data, concluded that sodium aluminate activation was capable of generating VI co-ordinate aluminium at least during short term curing.

The presence of Al (VI) co-ordinated aluminium species, for short curing times, might affect the polysialate formation in terms of aluminium type and quantity available.

"This result represents further evidence that the polysialate chemistry based on IV co-ordinate aluminium is not capable of describing all the phases of geopolymers".

The best compressive strengths, 20 MPa (10 M NaOH) and 45 MPa (10 M NaOH/sodium aluminate), were obtained after 300 days curing time.

Hajimohammadi et al. (2008) described the development of a "just add water" geopolymer cement based on sodium aluminate (solid) and geothermal silica. He observed that high early aluminium concentration inhibits geopolymerisation whilst high early silicon concentration enhances the reaction. To match these requirements the silica source must have a fast dissolution rate so that solutions will rapidly become rich in silicon entities similar to sodium silicate solutions. High early concentrations of aluminate are adsorbed onto the silica surface inhibiting dissolution and high early silicon forms silicate oligomers which can react with aluminate promoting geopolymerisation.

2.3 Admixtures and Fillers for Geopolymer Systems

2.3.1 Admixtures

Additives to geopolymer systems can be used to enhance specific properties of the system. The term admixture (ASTM Committee C09 2012b) is used to cover the wide range of materials added to OPC.

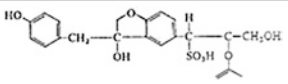
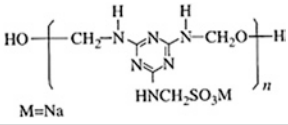
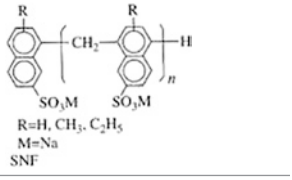
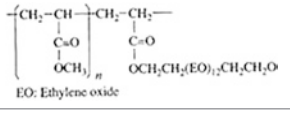
Improvements in workability and setting, reduction in final density, improvements in physical properties, particularly toughness and thermal performance can all be enhanced by the judicious choice of additive(s). The economics of geopolymer systems can be influenced by the addition of a wide range of fillers (aggregates) of varying compositions and size. Materials such as fly ash, fumed silica, metakaolin and slag are considered as admixtures in OPC (ASTM Committee C09 2012a), but in geopolymers they are considered to be part of the binder system.

Test methods for workability have been reviewed (Koehler 2009; Koehler and Fowler 2003). Kantro (1980) developed the mini cone slump test which is suitable for evaluation of the addition of admixtures to cementitious pastes.

In OPC processing superplasticisers are used to improve workability (and reduce water demand) and there are several classes available commercially (Table 2.4) (Rixom and Mailvaganam 1999).

Superplasticisers are polymeric molecules with several anionic segments. When anionic superplasticisers are added to cement the negative charged segments adsorb on to the surface of the cement particles increasing the overall negative charge. This causes mutual repulsion of the cement particles, breaking up the flocculation and releasing trapped water. This released water reduces the plastic viscosity, improving workability and hence the water-cement ratio can be reduced. In addition to electrostatic repulsion, superplasticisers containing non-polar polymer segments also function by steric hindrance. Segments of the polymer protrude out from the polymer surface into the aqueous phase preventing cement particles from agglomerating (BASF 2008).

Table 2.4 Superplasticiser structures adapted from Rixom and Mailvaganam (1999)

Class	Origin	Structure (typical repeat unit)
Lignosulphonates	Derived from neutralization, precipitation, and fermentation processes of the waste liquor obtained during production of paper-making pulp from wood	
Sulphonated melamine formaldehyde (SMF)	Manufactured by normal resinification of melamine-formaldehyde	
Sulphonated naphthalene formaldehyde (SNF)	Produced from naphthalene by oleum or SO_3 sulphonation; subsequent reaction with formaldehyde leads to polymerization and the sulphonic acid is neutralized with sodium hydroxide or lime	
Polycarboxylic ether (PCE)	Free radical mechanism using peroxide initiators is used for polymerization process in these systems	

There are many references to the use of superplasticisers in OPC (Liu et al. 2008; Xiao et al. 2011; Bassioni 2010; Wild et al. 1996a, b; Yilmaz et al. 1993; Jiang et al. 1999; Gołaszewski and Szwabowski 2004; Fernàndez-Altable and Casanova 2006a, b; Yllmaz et al. 1993; Agullo et al. 1999).

References to the use of superplasticisers in geopolymer are more limited and are generally based on slag based systems. Bakharev (2000) investigated a range of admixtures in alkali activated slag concrete and found that the air entraining agent improved workability. She suggested that admixtures with nonpolar molecules are better suited to work in a media of strongly charged particles of alkali activated slag and activator. Palacios (2005) found that only a naphthalene based product retained paste fluidity in a sodium hydroxide activated paste. This was attributed to the good sodium hydroxide resistance of this admixture. The use of calcium hydroxide solution in the chemical resistance test did not affect any of the tested admixtures and confirmed their suitability for use in OPC.

Yilmaz et al. (1993) treated SMF and SNF superplasticisers in 1 M KOH solution. The SMF precipitated out of solution, whilst the SNF was substantially unaffected.

Work by Hardjito (2005) on fly ash based geopolymer concrete used a naphthalene sulphonate type super plasticiser at up to 4 wt% and achieved increased slump (Fig. 2.2). Above 2 wt% super plasticiser addition compressive strength began to decline.

Ghosh and Ghosh (2012) evaluated the workability of fly ash based geopolymer mortar using a mini slump cone. The effect of alkali content, silicon to aluminium ratio, water content and plasticiser dosage where evaluated. He considered that 150 mm flow diameter was the minimum value suitable for mortar that could be readily placed in a mould. Table 2.5 shows their suggested workability criteria for geopolymer mortars.

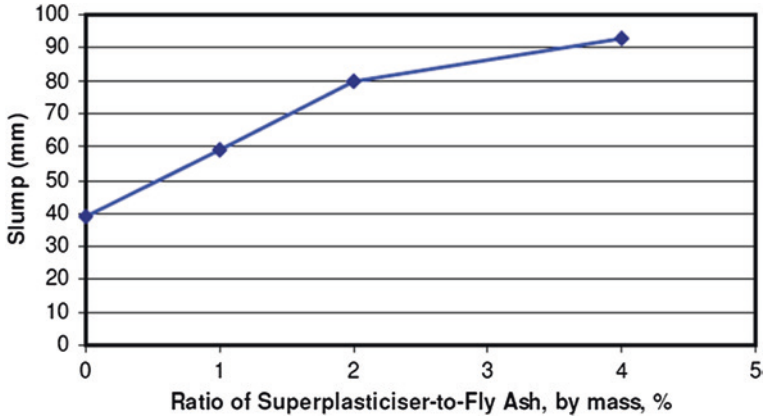


Fig. 2.2 Geopolymer concrete slump versus superplasticiser content (Hardjito and Rangan 2005)

Table 2.5 Workability criteria for geopolymer mortar (Ghosh and Ghosh 2012)

Flow diameter, mm	Workability
Above 250	Very high
180–250	High
150–180	Moderate
120–150	Stiff
Below 120	Very stiff

Increasing alkali content and silica content reduced workability. Dosages of naphthalene super plasticiser above 1 wt% gave marked improvements in workability.

Memon (2012) reported on the production of self-compacting geopolymer concrete. This type of concrete must be able to flow into position without the use of external vibration. They found that the addition of superplasticiser up to 7 wt% not only improved flowability but increased compressive strength.

Moura (2011) investigated the formulation of metakaolin geopolymer repair mortars. He found that the use of 3 wt% superplasticiser with 10 wt% calcium hydroxide and using 10 M sodium hydroxide gave 80 % increase in flow. Compressive strengths over 40 MPa were obtained.

Setting times can be adjusted by the use of accelerators and retarders. Calcium oxide and hydroxide have been reported to accelerate geopolymer setting (Jamieson et al. 2012; Temuujin et al. 2009b).

In US patent 7794537 (Barlet-Gaudedard et al. 2010) the use of lithium chloride, up to 7 %, acts as an accelerator, whilst 0.65 wt% sodium pentaborate extended setting time from 1.5 to 3 h at 110 °C. Nicholson (2005) claimed the use of inorganic boron compounds for retarding the setting time of high calcium fly ash based geopolymers.

The introduction of gas cells into geopolymers gives rise to materials with good sound and thermal insulation properties. Air can be entrained in the system during the mixing process and the air bubbles are stabilised by the addition of air entraining admixtures, which reduce the surface tension at the air-water interface. Alternatively gas bubbles can be generated in situ by chemical reaction. Blowing agents can be hydrogen peroxide, sodium perborates and the reaction of aluminium metal with the activating alkali solution (Liefke 1999; Reid 2011; Vaou et al. 2010). Bell and Kriven (2009) compared hydrogen peroxide and spherical aluminium powder as blowing agents in metakaolin based geopolymers. The hydrogen peroxide gave a non-percolating foam structure which cracked on firing. The aluminium powder gave irregular shaped pores with a wide pore size distribution which was crack free after firing.

Cementitious materials, typically concrete, are the most widely used materials for infrastructure construction. They are typically characterised by low tensile strength and low strain capacity and are sensitive to micro cracking. Fibres and steel and FRP rebar may be incorporated into cementitious matrices to overcome these deficiencies giving materials with increased tensile strength, ductility, toughness and increased durability (Chanh 2004; Hameed et al. 2009).

Steel bars are the materials of choice for structural applications, but the addition of "short fibres" now plays an important role in the processing and the development of early stage properties such as plastic and drying shrinkage. The addition of non-metallic structural fibres in geopolymers is opening up new applications. Table 2.6 compares the three main classifications of discontinuous fibres. Additionally microfibers can reduce spalling in fire situations. The cement and concrete Association of New Zealand has published a bulletin on fibre reinforced concrete (CCANZ 2009).

Natural fibres are also finding utility in concrete (Buckeye Building Fibres 2009; Hercules Fibres 2011b). Both the natural cellulose fibres listed here are shorter than typical polypropylene fibres of the same diameter. This will lead to more fibre per unit volume of fibre and hence the possibility of better crack control. These shorter fibres should have less influence on workability.

Table 2.6 Comparison of steel and synthetic fibres (Wimpenny et al. 2009)

	Steel fibres	Synthetic micro-fibres	Synthetic macro-fibres
Property	Characteristic property of fibres		
Shape/texture	Cold drawn hooked ends	Straight smooth	Continuously embossed
Collation	Glued bundles	Fibrillated	Uncollated
Typical length (mm)	60	12	48
Typical diameter (mm)	0.75	0.02–0.03	0.5–1
Tensile strength (MPa)	1050	30	550
Elastic modulus (GPa)	>200	2	10
Dosage (kg m^{-3})	25–35	1–2	6–10
Service temperature (°C)	300	60	60
Melting point (°C)	>800	150	150
Base material	Carbon steel	Polypropylene	Polyolefin (polypropylene, polyethylene)
Comparison with conventional concrete (unreinforced except for *)			
Workability	Reduced	Slightly reduced	Slightly reduced
Plastic shrinkage cracking	Unaffected	Reduced	Slightly reduced
Early-age thermal cracking	Reduced	Unaffected	Reduced
Long-term shrinkage cracking	Reduced	Unaffected	No data
Stray current corrosion	Reduced	Unaffected*	Eliminated

(continued)

Table 2.6 (continued)

	Steel fibres	Synthetic micro-fibres	Synthetic macro-fibres
Durability in chloride exposure*	Increased	Unaffected*	Greatly increased
Fire spalling resistance	Slightly increased	Greatly increased	Increased
Compressive strength	Unaffected	Unaffected	Unaffected
Residual flexural strength	Increased	Unaffected	Increased
Impact strength	Greatly increased	Unaffected	Increased
Flexural toughness	Increased	Unaffected	Increased
Abrasion resistance	Increased	Slightly increased	Slightly increased
Freeze-thaw resistance	Slightly increased	Increased	Increased
Flexural energy absorption	Greatly increased	Unaffected	Greatly increased
Concrete permeability	Slightly increased	Slightly increased	Slightly increased
Pump wear	Increased	Reduced	Reduced
Safety*	Hazard from handling and protruding fibres	Increased	Increased
Finishing	Extra care during floating	Exposed fibres soon abrade	Fibres may float and protrude in poorly designed mixes

For high temperature applications a range of fibres with increased thermal stability is available. These include, but are not limited to, alkali resistant glass fibre, basalt fibre, carbon fibre, ceramic fibres (alumina and silicon carbide) and wollastonite (Thang et al. 2010; Fibres Unlimited 2007; Morrison 2008; Silva and Thaumaturgo 2003; Chen and Chung 1993).

Fibre blends have been introduced to overcome short comings in the use of single type/size fibres. A blend of long and short fibres, where the long fibre imparts structural improvements and the short fibre imparts shrinkage improvements is typical. These blends can be all steel fibres, all organic fibres or mixtures of the two (CCANZ 2009).

Figure 2.3 and Table 2.6 show the types and properties of the two most commonly used fibre types i.e. steel and polypropylene.

2.3.2 Fillers

Fine aggregates (<53 μm) can be used as fillers to improve specific properties. Wollastonite, chamotte, and α-alumina are all stable beyond 1,000 °C and help to control shrinkage in high temperature applications (Kamseu et al. 2010; Buchwald et al. 2009).

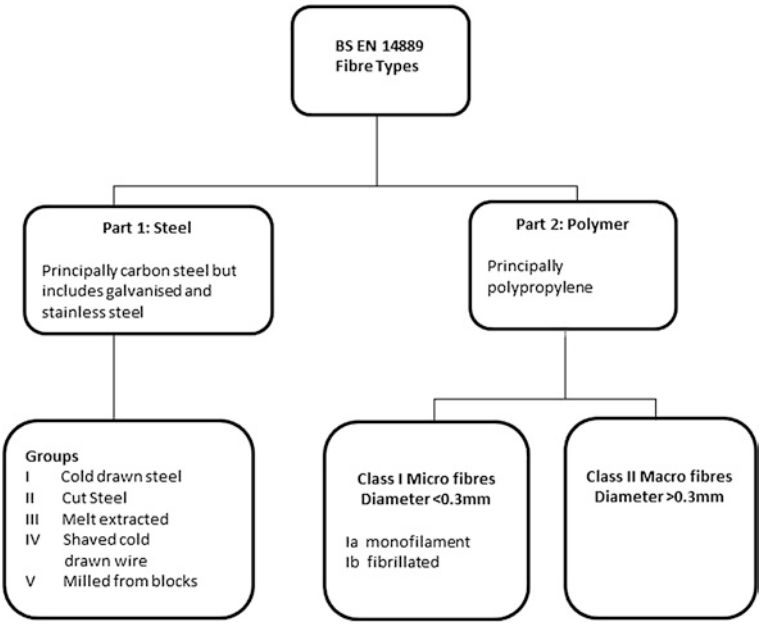


Fig. 2.3 Fibre types according to BS EN 14889 (Wimpenny et al. 2009)

Davidovits (2008a) compared cordierite (magnesium aluminosilicate) and mica in K-polysialate geopolymer and in a (Na, K) polysialate and measured thermal behaviour after an initial post cure of two hours at 650 °C. In the second heating cycle the cordierite filled (Na, K) polysialate showed an expansion of 0.1 % up to 600 °C before undergoing strong shrinkage above this. The mica filled system showed 0.5 % expansion up to 600 °C before shrinking. Davidovits attributed this shrinkage to the collapse of the sodalite cage. A Na polysialate filled with cordierite and post cured for 3 h at 500 °C gave an average coefficient of thermal expansion (COTE) between 20 and 700 °C of 1.9×10^{-6} K^{-1}.

Barbosa and MacKenzie (2003b) added various inorganic fillers to a metakaolin based geopolymer activated with sodium silicate and measured physical properties and thermal shrinkage of the composites. The fillers included crushed building brick, powdered granite, kaolinite, iron sand (black titanomagnetite with 7 % TiO_2), α-alumina and β-Sialon. All the filled geopolymer composites showed reductions in strength which was attributed to the lack of reaction between the fillers and the geopolymer binder.

Lin et al. (2009b) investigated the use of alumina as a filler in a metakaolin based geopolymer and found marked reductions in shrinkage after elevated temperature exposure.

Siva and Thaumaturgo (2003) used wollastonite to improve fracture toughness of metakaolin based geopolymers. The addition of 2 vol.% of wollastonite gave the optimum toughening effect.

Temuujin et al. (2012) added ground vermiculite to a fly ash based geopolymer to improve the thermal properties of a sprayed coating. Vermiculite expands when heated above 300 °C showing low thermal conductivity. The ground sizes used were −63 and −250 μm. The presence of vermiculite modified the water release mechanism on heating. The early water loss shown by unfilled geopolymers up to 400 °C is replaced by a more continuous loss up to 1,000 °C. This latter effect has a more beneficial influence on fire resistance.

Mullite is usually present in coal fly ash and remains reasonable stable through the geopolymerisation process and any elevated temperature exposures up to 1,000 °C (Williams and van Riessen 2010; Rickard et al. 2012). This probably contributes to the thermal stability of fly ash based geopolymers. Mullite is available commercially (Washington Mills 2008) and is used commercially in the manufacture of refractory products where resistance to spalling and low thermal conductivity are important. Mullite also possesses a low (5.62×10^{-6} K^{-1}) COTE between 25 and 1,500 °C without any phase changes occurring in this range.

Medri et al. (2011) used a potassium activated metakaolin as a binder for recrystallised silicon carbide to produce refractory coatings for silicon nitride-titanium nitride substrates. After curing at 80 °C and subsequent water removal a coating with 90 wt% silicon carbide was obtained. Long term oxidative testing of the silicon carbide grains and the filled geopolymer coating was carried out for 100 h at 1,200 °C. The weight gain of the silicon carbide coating in this test was 7 % and is around 50 % lower than for the grains. Shrinkage of these coatings after 1 h at 1,300 °C in argon was 0.1 %. Adhesion of the coating is good as shown by the absence of exfoliation detachment when cutting or polishing the cross sections prior to and after high temperature exposure.

Wang et al. (2011) added hollow cenospheres sourced from coal fly ash to geopolymers to reduce density and reduce thermal conductivity in the composites. The geopolymer was a potassium activated metakaolin and the cenospheres were claimed to have good alkali resistance. The addition of 40 vol.% of cenospheres reduced compressive strength from 105 to 40 MPa, the thermal conductivity from 0.361 to 0.173 W m^{-1} K^{-1} and density from 1.37 to 0.82 g cm^{-3}.

Chen et al. (2011a) developed a sodium activated metakaolin geopolymer suitable for coating concrete where good thermal insulation properties were required. The addition of mica (15 %) and wollastonite (10 %) together with 5 % of a silane gave a product with good compressive strength (27.4 MPa) and adhesion (5.14 MPa). To reduce the thermal conductivity hollow glass spheres (20–50 μm diameter) were added to the filled geopolymer. A 4:1 by volume of glass spheres to geopolymer mix gave the optimum results with respect to compressive strength (18.9 MPa), adhesion (4.78 MPa) and thermal conductivity (0.21 W m^{-1} K^{-1}).

Concrete is a cement-water paste in which aggregate is embedded. Aggregate is granular material such as sand, gravel, crushed stone, and other speciality materials that occupy 60–75 % of the concrete volume. Aggregate properties affect the plastic concrete (workability and drying shrinkage) and hardened properties such as durability, strength, thermal properties and density.

Aggregates are classified as natural, synthetic and recycled. Grading is by particle size and size distribution, particle shape and water content. Crushed aggregate obtained by quarrying and crushing of rock can contain substantial amounts of flat or elongated particles, whereas natural gravel has a rounded shape and smooth surface texture (Cement Concrete and Aggregates Australia 2008). The ACI committee E-701 produced a bulletin on “Aggregates for Concrete” (ACI E-107 2007).



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