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Relationships between composition, structure and strength of inorganic polymers

Part 2 *Fly ash-derived inorganic polymers*

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This article is the second in a two-part series and discusses inorganic polymers derived from fly ash. Part 1 [1] concerns inorganic polymers derived from a metakaolin precursor. For this study, 15 fly ash-derived inorganic polymers were produced with various compositions. The effect of the concentration of each of the four component oxides (Na_2O, SiO_2, Al_2O_3 and H_2O) and two alkali cations (Na and K) on the microstructure and compressive strengths were assessed. Similar to metakaolin-derived inorganic polymers, it was observed that high-strength fly ash inorganic polymers were related to low porosity and a dense, fine-grained microstructure. Such structures were characteristic of formulations with high silica mole fractions ($SiO_2/Al_2O_3 \sim 3.9$) and low water contents, as well as those with high alkali and low alumina contents. For the latter, not only was a characteristic slower strength development with increasing alkali content observed, but there was also a limit of alkali concentration ($Na_2O/Al_2O_3 \sim 1$) beyond which the strength deteriorated. Furthermore, SEM micrographs disclose that the fly ash precursor dissolves more readily in the sodium-based system compared to the potassium equivalent. The interrelation between microstructures of the respective formulations and their strength development are discussed. It is observed that the charge-balancing role of the alkali cations in the fly ash formulations may be dominant compared to initial alkali dissolution reaction of the aluminosilicate fly ash particles, which is partly responsible for initial strength development.

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1. Introduction

Inorganic polymers represent a family of emerging synthetic compounds produced by reactions between an aluminosilicate solid and an alkali silicate solution [1–3]. While metakaolin is the most widely researched aluminosilicate precursor [1], several studies on fly ash as an alternative raw material have also been published [4–6]. Fly ash has the advantage over metakaolin of being a waste resource produced in huge quantities by coal-fired power stations, making it an ideal environmentally friendly feedstock. It consists of fine, amorphous and reactive aluminosilicate particles. Class F fly ash, which is high in aluminosilicate and low in calcium, is the preferred grade for inorganic polymerisation [7], however being considerably less pure than metakaolin, fly ashes produce more complex inorganic polymer structures.

Previous microstructural investigations [4] of the condensed inorganic polymer phase in fly ash samples has shown that they consist of rounded growths. However, there has only been a cursory attempt to relate such microstructures to the composition and strength of inorganic polymer formulations. There are several reports on the compressive strengths of fly ash inorganic polymers in the literature [8, 9], but there are only the occasional SEM images. Thus, this study attempts to examine the relationships between formulation, structure and performance of these systems. The microstructure, studied by SEM, and the compressive strength of 15 different fly ash-derived inorganic polymer formulations have therefore been investigated to determine their dependence on the concentration of each of the four component oxides (Na_2O, SiO_2, Al_2O_3 and H_2O), as well as the corresponding effect of two alkali cations (Na and K).

2. Experimental

The inorganic polymers were prepared from fly ash, alkali silicate solution, alkali hydroxide and distilled

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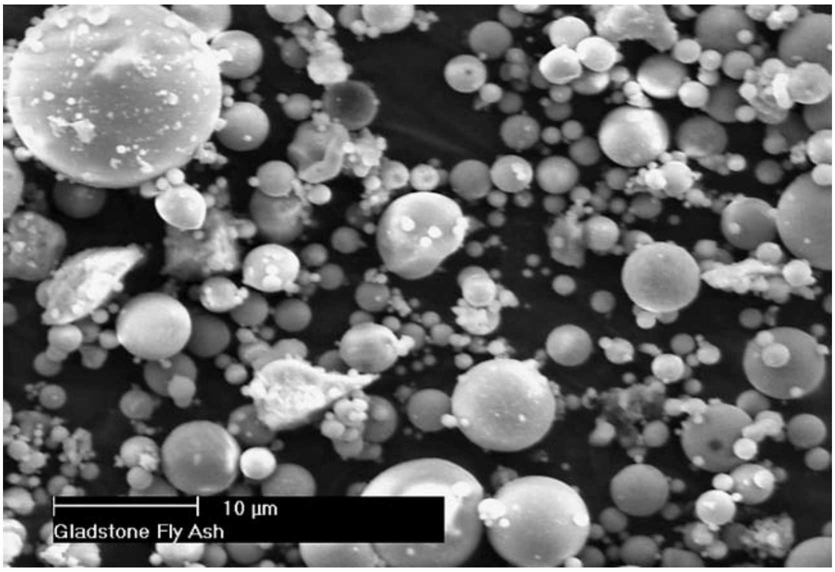

Figure 1 The fly ash inorganic polymer precursor material.

water. A Class F fly ash supplied by Pozzolanic Enterprises, Australia, with a composition by weight per cent of oxides of 47.9% SiO_2, 29.79% Al_2O_3, 13.93% Fe_2O_3, 3.29% CaO with minor amounts of other oxides was used throughout this work. The fly ash was mostly amorphous, however it also contained approximately 10% quartz, 20% mullite and 5% ferrite spinel. Fig. 1 shows an SEM image of the fly ash precursor. It consisted of spherical solid particles and cenospheres (hollow particles) with a broad size distribution, the majority of the particles passing minus 45 μm sieve.

The alkali silicate solutions were supplied by PQ Australia and had the following concentrations: sodium silicate (8.9 wt% Na_2O, 28.7 wt% SiO_2, 62.5 wt% H_2O) and potassium silicate (11 wt% K_2O, 24.5 wt% SiO_2, 64.5 wt% H_2O). Fifteen different inorganic polymer formulations were prepared (Table I), with the different proportions of ingredients selected to allow the effect of alkali, water, silica and alumina content to be assessed, along with a comparison between the alkali cations sodium and potassium. The sample labels refer to the variable being tested and its value, similar to the notation used in Part 1 of this study, i.e. FA for “fly ash”, followed by the variable being tested and its value; for example, FAH10 assesses the effect of H_2O at an H_2O/Al_2O_3 ratio of 10. Thus, while samples FANa1, FANa10, FASi30, FAAl10 and FAH10 have different notations, their chemical composition is identical. The formulations generally had higher liquid to solid ratios (L/S) than those used by previous researchers [3, 7]. This was not only due to the limitations set by the choice of ingredients and by the setting properties of the slurry, but partly to allow comparisons to be made with the metakaolin inorganic polymers described previously [1].

TABLE I Compositions of the fly ash inorganic polymers. L/S is the liquid to solid mass ratio, where the liquid is the “activator” solution containing the alkali, the silicate and the water, and the solid is the fly ash

Sample notation	Composition	L/S	Compressive strength (MPa)
FANa1	$Na_2O \cdot 3SiO_2 \cdot Al_2O_3 \cdot 10H_2O$	0.76	11
FAFK1	$K_2O \cdot 3SiO_2 \cdot Al_2O_3 \cdot 10H_2O$	0.84	2.1
FANa06	$0.6Na_2O \cdot 3SiO_2 \cdot Al_2O_3 \cdot 10H_2O$	0.69	2.8
FANa08	$0.8Na_2O \cdot 3SiO_2 \cdot Al_2O_3 \cdot 10H_2O$	0.73	3.1
FANa10	$1.0Na_2O \cdot 3SiO_2 \cdot Al_2O_3 \cdot 10H_2O$	0.76	11
FANa12	$1.2Na_2O \cdot 3SiO_2 \cdot Al_2O_3 \cdot 10H_2O$	0.80	7.1
FASi27	$Na_2O \cdot 2.7SiO_2 \cdot Al_2O_3 \cdot 10H_2O$	0.71	3.9
FASi30	$Na_2O \cdot 3.0SiO_2 \cdot Al_2O_3 \cdot 10H_2O$	0.76	11
FASi35	$Na_2O \cdot 3.5\ SiO_2 \cdot Al_2O_3 \cdot 10H_2O$	0.85	29
FASi39	$Na_2O \cdot 3.9\ SiO_2 \cdot Al_2O_3 \cdot 10H_2O$	0.92	47
FAAl07	$Na_2O \cdot 3SiO_2 \cdot 0.7Al_2O_3 \cdot 10H_2O$	1.29	13
FAAl09	$Na_2O \cdot 3SiO_2 \cdot 0.9Al_2O_3 \cdot 10H_2O$	0.90	20
FAAl10	$Na_2O \cdot 3SiO_2 \cdot 1.0Al_2O_3 \cdot 10H_2O$	0.76	11
FAAl11	$Na_2O \cdot 3SiO_2 \cdot 1.1Al_2O_3 \cdot 10H_2O$	0.65	6.3
FAH6	$Na_2O \cdot 3SiO_2 \cdot Al_2O_3 \cdot 6H_2O$	0.55	30
FAH8	$Na_2O \cdot 3SiO_2 \cdot Al_2O_3 \cdot 8H_2O$	0.66	14
FAH10	$Na_2O \cdot 3SiO_2 \cdot Al_2O_3 \cdot 10H_2O$	0.76	11
FAH12	$Na_2O \cdot 3SiO_2 \cdot Al_2O_3 \cdot 12H_2O$	0.87	3.8
FAH14	$Na_2O \cdot 3SiO_2 \cdot Al_2O_3 \cdot 14H_2O$	0.97	Crumbly

The compositions referred to in Table I indicate the overall mole ratios of the four oxides of interest. The calcium and iron oxide concentrations also vary between the samples due to the different L/S values. As 35% of the fly ash is crystalline and of low reactivity, the composition of the condensed inorganic polymer phase in the samples may be different to the overall composition.

The samples were prepared and analysed similarly to the metakaolin samples reported previously [1]. The alkali hydroxide, alkali silicate solution and water were initially mixed and cooled, followed by the fly ash. All samples were mixed then immediately poured into preheated moulds which were sealed. All formulations were cured at 85°C for 2 h, after which they were demoulded and cooled in a refrigerator to slow the reaction. Compressive strengths were measured on 25.4 mm cubes and SEM was performed on fracture faces.

3. Results

3.1. Setting characteristics

Most of the inorganic polymer formulations had low viscosities upon mixing; some had a viscosity similar to that of water. Samples FASi39 and FAH6 were the most viscous samples, however they were still relatively thin compared to the metakaolin-derived samples described previously [1]. Due to the rounded shape and comparatively large size of fly ash particles, it was expected that the fly ash mixtures would be much less viscous than clay-based mixtures. Despite their low viscosities, there was no evidence of settling of the fly ash particles in any of the samples. Most of the samples set, although not necessarily hardened, very quickly (i.e. within a few minutes), and all except FAH14 were hard after the 2 h at 85°C. FAH14 did not fully harden in 2 h and could be broken by hand after demoulding.

3.2. General comments

In general, the fly ash inorganic polymers looked similar to images previously published for these materials [2–4]. As was the case for the metakaolin inorganic polymer samples [1], the condensed inorganic polymer phase in the fly ash-derived samples consisted of rounded growths with bridging between them (Fig. 2). The different samples varied in the size, density of packing and the amount of bridging material between these spherical particles. Fly ash-derived inorganic polymers appear quite different to the metakaolin-derived systems discussed in Part 1 of this study [1] as they contain far more unreacted particles. The fractured sample surfaces typically contain voids left by extracted whole unreacted fly ash particles. Some of the samples have unreacted particles making up a significant proportion of their volume. These samples are composites and as such the strength of the unreacted particles and of the interfaces between them and the inorganic polymer matrix can be expected to have a significant bearing on the overall strength of the material. The unreacted particles, unlike those in metakaolin inorganic polymers [1], generally appear to have not reacted at all and pull out easily during fracture (there are no split fly ash particles), implying relatively low fly ash:matrix interface strength. It is unclear at this stage whether the particles that do not react are of a different composition to those that do. However, the amount of unreacted material varies from sample to sample and is very low in some samples, which implies that nearly all particles are reactive.

It was observed that unlike metakaolin inorganic polymers, the fly ash-based formulations had characteristically more complex microstructures and more structural variety. In particular, some of the samples contained some crystalline material, particularly those samples with the highest strength and the densest microstructure.

The compressive strengths of the samples followed similar trends to those found for metakaolin-derived inorganic polymers and in general could be related to both the composition and the microstructure in a logical way (Table I). The compressive strengths were generally quite low compared with metakaolin formulations of equivalent composition [1]. This was probably due to the high L/S of the samples investigated. High water content was used in the formulations to allow comparison of the results with equivalent metakaolin systems, and also to enable low aluminium (FAAl07), high silica (FASi39) and high alkali (FANa12) samples to be prepared. Given the constraint to achieve specified stoichiometry, the actual water content of some of the fly ash mixtures tended to be somewhat higher than desirable. In addition to restricted L/S ratios, selected formulations had to satisfy requirements of flowability and setting properties that allow practical preparation of samples. The characteristically high L/S ratio is expected to be the largest contributory factor to the relatively low strengths. The low strength of some of the samples was also partially due to the testing being done after only 2 h of curing. Palomo *et al.* [2] reported strengths of fly ash inorganic polymers after 2, 5 and 24 h and observed considerable increase in compressive strengths after 2 h, with the increase most marked in some of the samples that were weakest at 2 h.

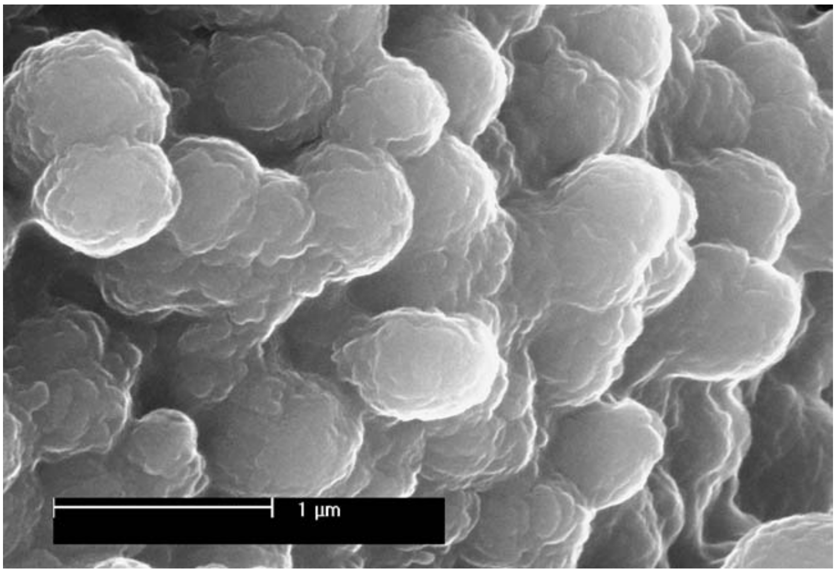

Figure 2 An example of the rounded growths that make up the inorganic polymer structure. Different samples have "balls" of different sizes, with different packing densities, between which there is bridging to different extents.

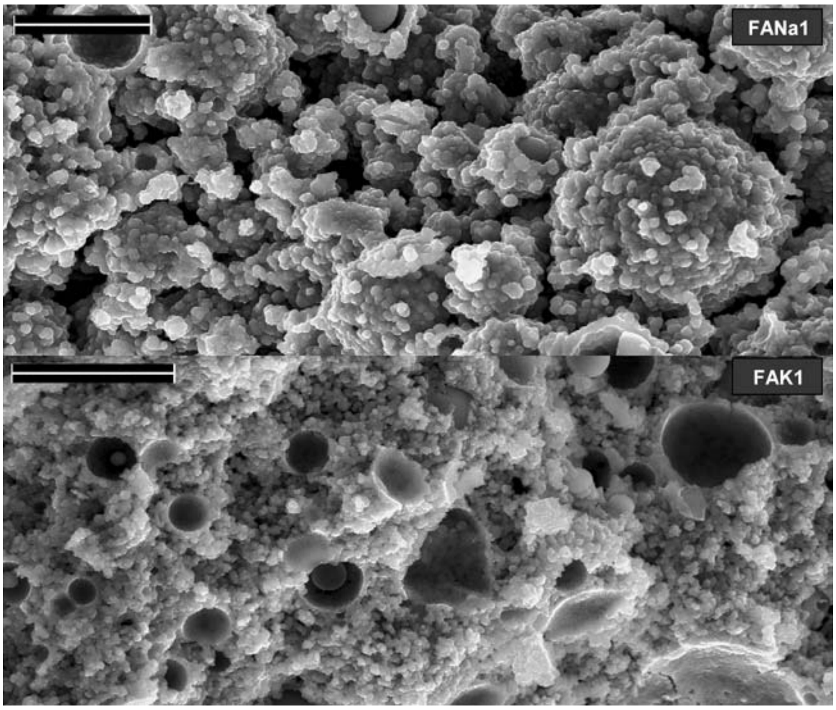

Figure 3 Inorganic polymer samples with similar compositions except that they contain different alkali cations. The sodium-based sample (FANa1) and its potassium equivalent (FAK1) have generally similar microstructures. Scale bar represents 10 μm.

3.3. The effect of the type of alkali cation

Two samples were prepared with different alkali cations present. Samples FANa1 (containing sodium) and FAK1 (containing potassium) had generally similar microstructures (Fig. 3). While no crystalline material was observed in FANa1, there were very occasional clumps of crystals in FAK1. FAK1 contained more unreacted particles than FANa1. Previous researchers have also found (by SEM [4] and by solution analysis [5]) that more of the fly ash precursor dissolves in the sodium-based system than in the potassium equivalent, and similar results were found for metakaolin [1].

As with the metakaolin system, the microstructure of FAK1 appeared to be less porous than FANa1, although the sizes of the spherical particles making up the fine structure were larger in FANa1 than in FAK1. Correspondingly, the surface areas of inorganic polymers made from the two alkalis previously reported by van Jaarsveld *et al.* [6] showed that the potassium containing sample had a comparatively higher surface area. By contrast, Silverstrim *et al.* [4] noted greater porosity in a potassium inorganic polymer than in the sodium equivalent by SEM. The relatively lower viscosity of the potassium silicate solution and its propensity for rapid water release partly accounts for the higher porosity levels observed in these systems.

The compressive strength measurements of the samples showed FANa1 to be much stronger than FAK1. As with the metakaolin system, this was an unexpected result as FAK1 had a denser structure than FANa1, although, as hypothesised for the metakaolin system, this may be due to the short curing time (i.e. the reaction rates of the FANa1 and FAK1 formulations are different, and hence the two-hour compressive strength may not relate to the ultimate compressive strength). The compressive strengths and porosities found for samples FANa1 and FAK1 are the opposite of those generally reported. The generally accepted trend in fly ash inorganic polymers is that potassium produces stronger materials than sodium [5–7], although there are other reports of the reverse [2]. Furthermore, the 2 h cure cycle adopted in this study is relatively short for extensive alumino-silicate network structure formation during the condensation stage of the reaction to occur. This situation may lead to a possible insufficient pore structure refinement. Thus, the reported microstructures and compressive strength results may be viewed primarily as those characteristic of early age development.

Both sets of results, whether those of the present studies in which sodium gives the stronger product or of the earlier studies in which potassium gave the stronger product, must contend with the conundrum of the more porous material having the higher strength. It appears logical that a denser structure would be stronger as there is simply more material in a given volume to resist the compressive force. As discussed below, a positive correlation between density (and hence low porosity) was found for the other samples.

Such a relationship has also been previously indicated by Jaarsveld *et al.* [8]. Spectroscopy studies (IR and NMR [6]) have not, however, indicated any distinct differences in the atomic structure of sodium and potassium inorganic polymers, which could have accounted for the greater strength of the more porous material, and should therefore be further investigated.

3.4. The effect of alkali content

Four samples were prepared with different alkali concentrations: FANa06, FANa08, FANa10 (= FANa1) and FANa12. Despite the range of compressive strengths in these four samples, there was not a great

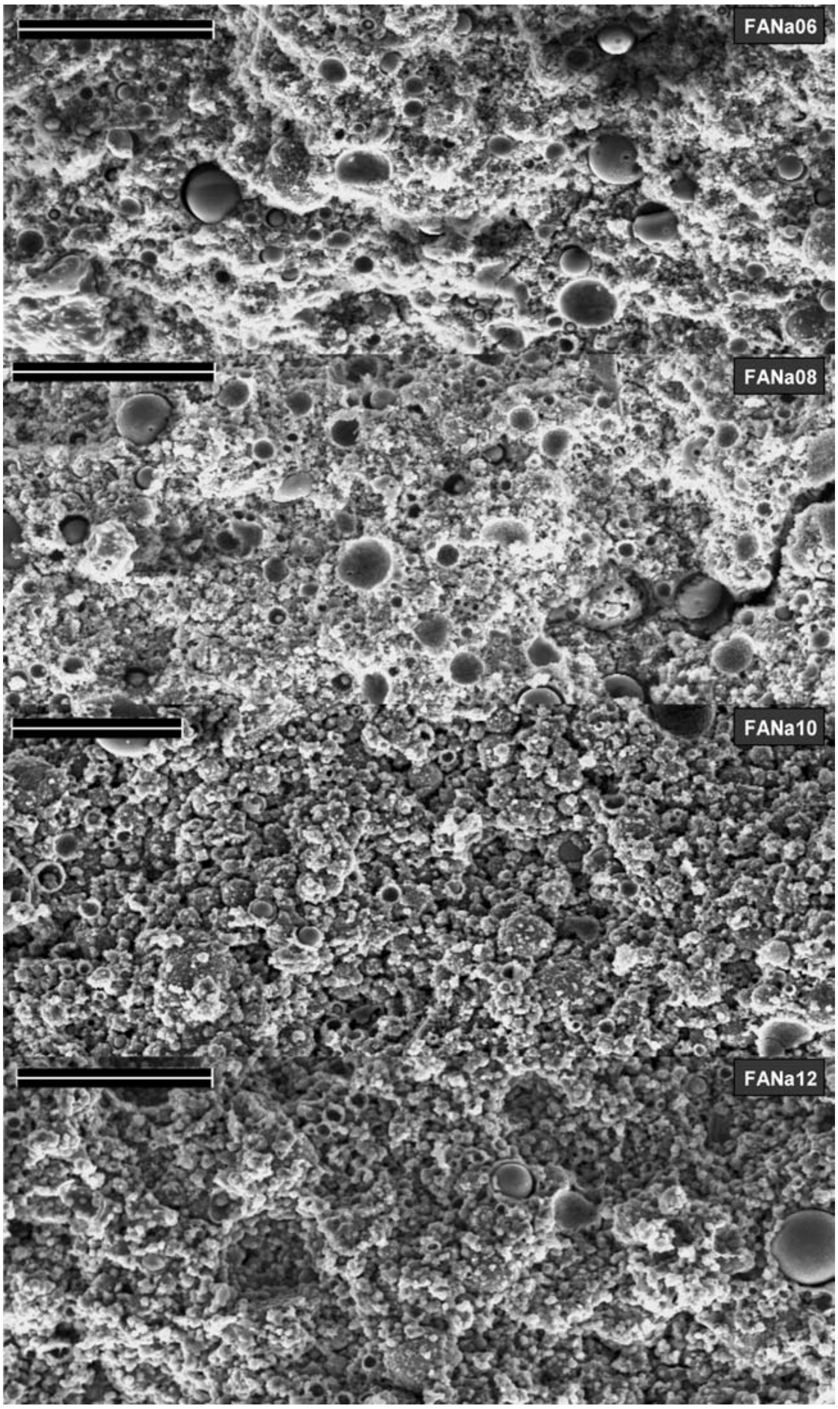

Figure 4 Inorganic polymers containing different amounts of alkali. The differences between the samples were not great, although there was a decrease in the number of unreacted particles with increasing alkali. Scale bar represents 50 μm.

difference in their microstructures. There was some decrease in the number of unreacted particles and an increase in the size of spherical-shaped particles with increasing alkali content (FANa06–FANa12), however the differences were not great. Samples FANa06, FANa08, FANa10 and FANa12 are shown in Fig. 4.

The compressive strengths of the FANa series samples show an increase from sample FANa06 to FANa10 then a decrease to FANa12. As the role of the alkali in inorganic polymers is partially to balance the charge of the aluminate groups in the tectosilicate, it is not unexpected to find that the compressive strength goes through a maximum when the alkali and alumina concentrations are equal, however, no such maximum was found in the equivalent samples in the metakaolin experiments [1]. The other role of alkali in the system is to increase the solubility of the aluminosilicate, as indicated by Equation 1.

Thus, in an alkaline medium (e.g. containing sodium ions) a conventional silica depolymerisation reaction is likely to occur, with any excess NaOH tending to disrupt internal Si-O-Si links of the silica tetrahedron after the acidic hydroxyl groups at the surface of the silica have been neutralised, as indicated by:

$$\text{Si-O-Si} + 2\text{NaOH} = \text{Si-O-Na}^{+} + \text{Na}^{+}\text{-O-Si} + \text{H}_2\text{O} \tag{1}$$

It is therefore possible that in the case of fly ash, the charge-balancing role is dominant, whereas in the metakaolin system, dissolution is dominant. The increase in strength with increasing alkali content of the metakaolin samples was much more pronounced than for the fly ash samples, which supports this theory.

Phair and van Deventer [5] measured the compressive strength of fly ash inorganic polymers (which also contained 6–12 wt% Portland cement) made at pH 12, 13 and 14. In agreement with the present results, the pH 14 sample was found to be much stronger than at lower pH (50 times the strength at pH 12). Indeed, given the present result that approximately twofold increase in Na_2O molar concentration (FANa06–FANa10) quadruples the strength, it is surprising that the pH 12 sample (with about 1% the alkali concentration of pH 14) set at all. The added cement may have been all that was holding the samples together.

Van Jaarsveld and van Deventer [7] studied the relationship between the compressive strength of inorganic polymers and the Na_2O/SiO_2 ratio. They found a maximum in compressive strength with various alkali concentrations which agrees with the present results. The information supplied was, however, insufficient to make direct comparisons with the results of this study. Van Jaarsveld and van Deventer [7] also found a variation in the reaction rate with Na_2O concentration. As the present compressive strength results are all recorded at one time interval (two hours), it is not possible to separate formulation effects and kinetic effects, however, kinetic considerations appeared to be important for equivalent samples made with metakaolin [1]. Samples FANa06–FANa12 may all reach similar strengths at longer time intervals.

3.5. The effect of silica content

Samples FASi27–FASi39 were produced to determine the effect of the silica concentration on the structure and strength of inorganic polymers. This variable had the most dramatic effect on the microstructure and the strength of all the variables tested. The difference between FASi30 (= FANa1) and FASi35 was greater than that between FASi27 and FASi30 or FASi35 and FASi39, as would be expected given the silica concentrations. The fineness of the texture and the density of the inorganic polymer increases greatly from FASi27 to FASi39, as seen in Fig. 5. Lower magnification images (Fig. 6) show that the higher silica samples contain more unreacted particles, and also that crystals have grown on a number of the unreacted fly ash particles, particularly in FASi39.

The compressive strengths of the Si series of samples followed the changes in the microstructure in the expected way, i.e. the densest, finest grained samples were the strongest. The change in strength with silica content was quite dramatic, in particular the small change (11%) from FASi35 to FASi39 gave a 62% strength increase.

The compressive strengths of the samples show a very clear correlation to the density of the microstructure (or, alternatively, an inverse relationship to the porosity). This is the intuitively correct result. It deserves mention because it is the opposite correlation to that found for the comparison between sodium- and potassium-based inorganic polymers, as discussed in Section 3.2.

The effect of silica concentration in fly ash inorganic polymers has not been widely reported in the past. Similar trends in structure with silica content have been reported for metakaolin-derived inorganic polymers, however, in that situation, the strength plateaued at high silica loadings [1]. As this result was not found for the fly ash samples of the present study, it can be assumed that if such a plateau exists in the fly ash system, it is at a higher silica concentration than in the metakaolin system.

Palomo *et al.* [2] compared fly ash inorganic polymers made with and without added silica by SEM. The samples had compositions of approximately $0.5Na_2O{\cdot}3.5SiO_2{\cdot}1.0Al_2O_34{\cdot}3H_2O$, referred to as “Solution 1”, and $0.4Na_2O{\cdot}3.9SiO_2{\cdot}1.0Al_2O_3{\cdot}3.4H_2O$, termed “Solution 3”. The SEM image of the latter formulation appears similar to those of FASi39 in the present study and it had a similar strength. The other formulation, without added silica, appeared more like FASi27, but with many more unreacted particles. It was considerably stronger (≈9.5 MPa), which could be due to the lower water content, as discussed in Section 3.7.

The series of samples FASi27–FASi39 differ in the proportion of the silica added in solution compared to that added as a solid (fly ash). As discussed previously [1], it is not possible when assessing the differences in the microstructure between these samples to determine whether the changes along the series are caused by the total silica content or the proportion of added soluble silica. The fly ash used in the study of Palomo *et al.* [2] had a higher Si/Al ratio than that used in the present study. Thus, corresponding to their Solution 1 sample and as indicated in Table II, the microstructure appears to be related to the proportion of silica added in solution rather than to the overall Si/Al ratio. The same is true, but to a lesser extent, for the compressive strength. This interesting result is discussed further in the next section.

3.6. The effect of alumina content

The four samples prepared with varying alumina concentrations (FAAl07, FAAl09, FAAl10 (= FANa1) and FAAl11) had microstructures similar to those of the FASi27–FASi39 series, however the trends are reversed, with the low alumina formulation giving the strongest and densest product. This may be expected as their Si/Al ratios follow similar, but reversed, trends and alkali and water concentration (the main variables apart from Si/Al between the FASi27–FASi39 and FAAl11-FAAl07 series) have been shown to have a less dramatic effects on the structure and properties of the fly ash formulations.

In the series of samples from FAAl07 to FAAl11, the amount of unreacted material, the amount of crystalline material, and the density and fineness of the microstructure decreased, as shown in Figs 7 and 8. Also, the strength generally decreased except for FAAl07,

TABLE II Samples with various silica concentrations. L/S is not stated for the SEM images in the original article and is taken to be 0.25 in this table

Sample	Formulation	Overall SiO_2/Al_2O_3 (mole)	Fly ash SiO_2/Al_2O_3 (mole)	Proportion silica added in solution (%)	Compressive strength (MPa)	Microstructure
Solution 1*	No silica in the liquid	3.47	3.47	0	9.3	Porous, large amount of unreacted fly ash
FASi27	Minimal silica in the liquid	2.70	2.69	0.5	3.9	Similar to above, less unreacted material
FASi35	High silica in the liquid	3.50	2.69	23	29	Dense, fine grained material, some crystals

*Refer: Sample made with Solution 1 of Palomo *et al*. [2].

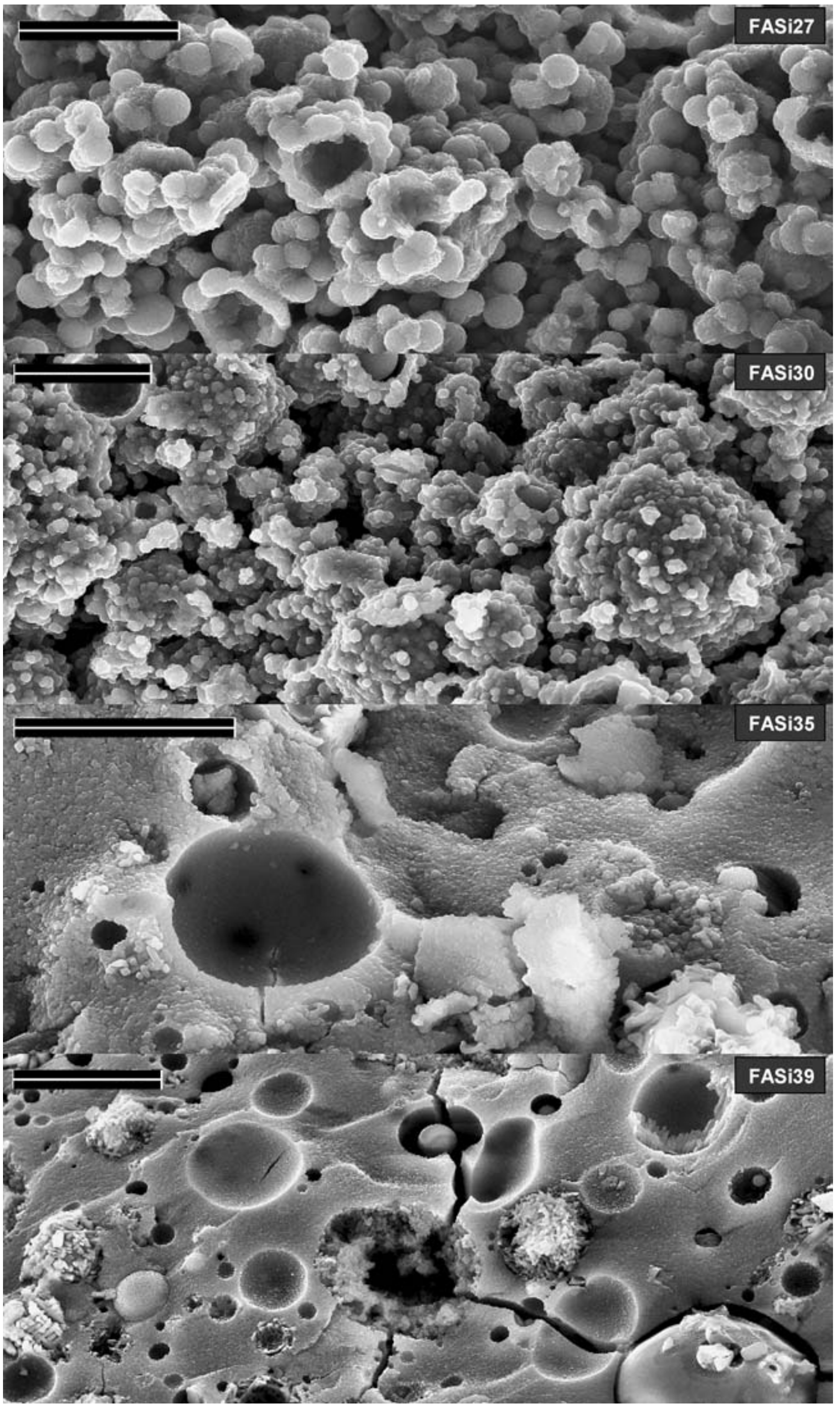

Figure 5 High magnification images of inorganic polymers containing different amounts of silica. The samples show a gradation in the fineness of texture. Note that samples FASi35 and FASi39 were coated with gold (rather than the carbon used on all the others) and this can be seen as small black lines on the surface. Scale bar represents 1 μm.

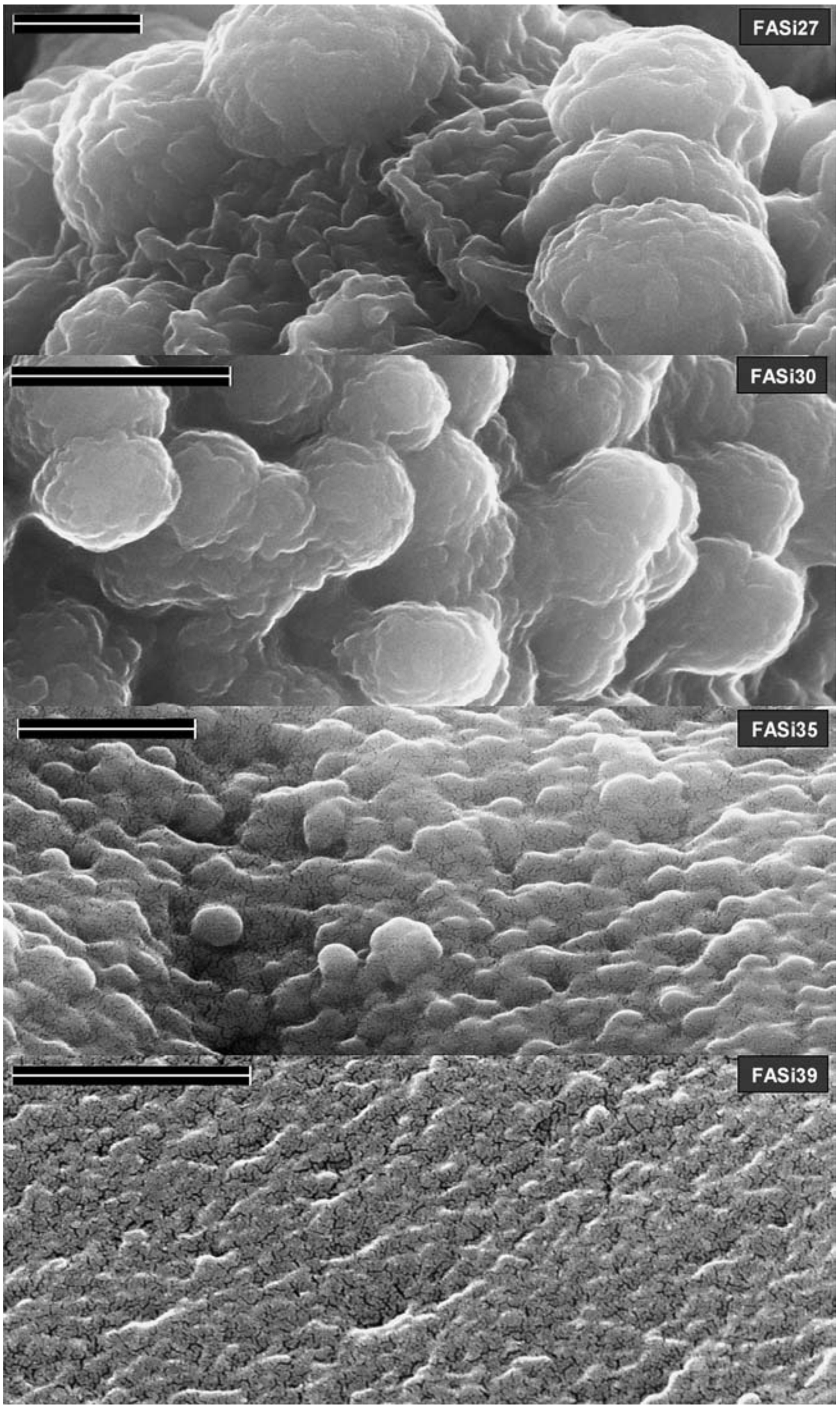

Figure 6 Low magnification images of inorganic polymers containing different amounts of silica. The samples show a very clear gradation in the fineness of texture. The amount of crystalline material also increases with silica concentration and this is particularly clear in FASi39. Scale bar represents 10 μm.

which was weaker than FAAl09. This appears to be an anomalous result as the structure of FAAl07 clearly follows the trend through the other Al samples, and the differences between FAAl07 and FAAl09 (FAAl07 is denser and finer grained) suggest that FAAl07 should be stronger. However, a repeat of the experiment produced the same results.

As shown in Fig. 9, FAAl07 had both the largest proportion of unreacted particles and the most crystallinity. These two factors could be expected to weaken the sample, as the strength is likely to be derived from the amorphous gel rather than crystalline or unreacted components, which may counteract the effect of the extra strength given to the binding phase by its density and fine grain. At an alumina concentration around that of FAAl08, a strength maximum is observed between these two counteracting factors.

FAAl11 had a unique structure, as shown in Figs 7 and 8. It was the only one of all the samples to be almost entirely free of unreacted fly ash particles (suggesting that most of the fly ash may have reacted), and thus it had an extremely uniform structure. The form of its structure at the highest magnification was distinctly different to that of the other samples. The spherical particles clearly have lenticular growths (compared with FAAl10; equivalent to FANa1, in the same figure). Sample FASi27 (another low silica formulation with a similar Si/Al ratio) showed some slight indications of

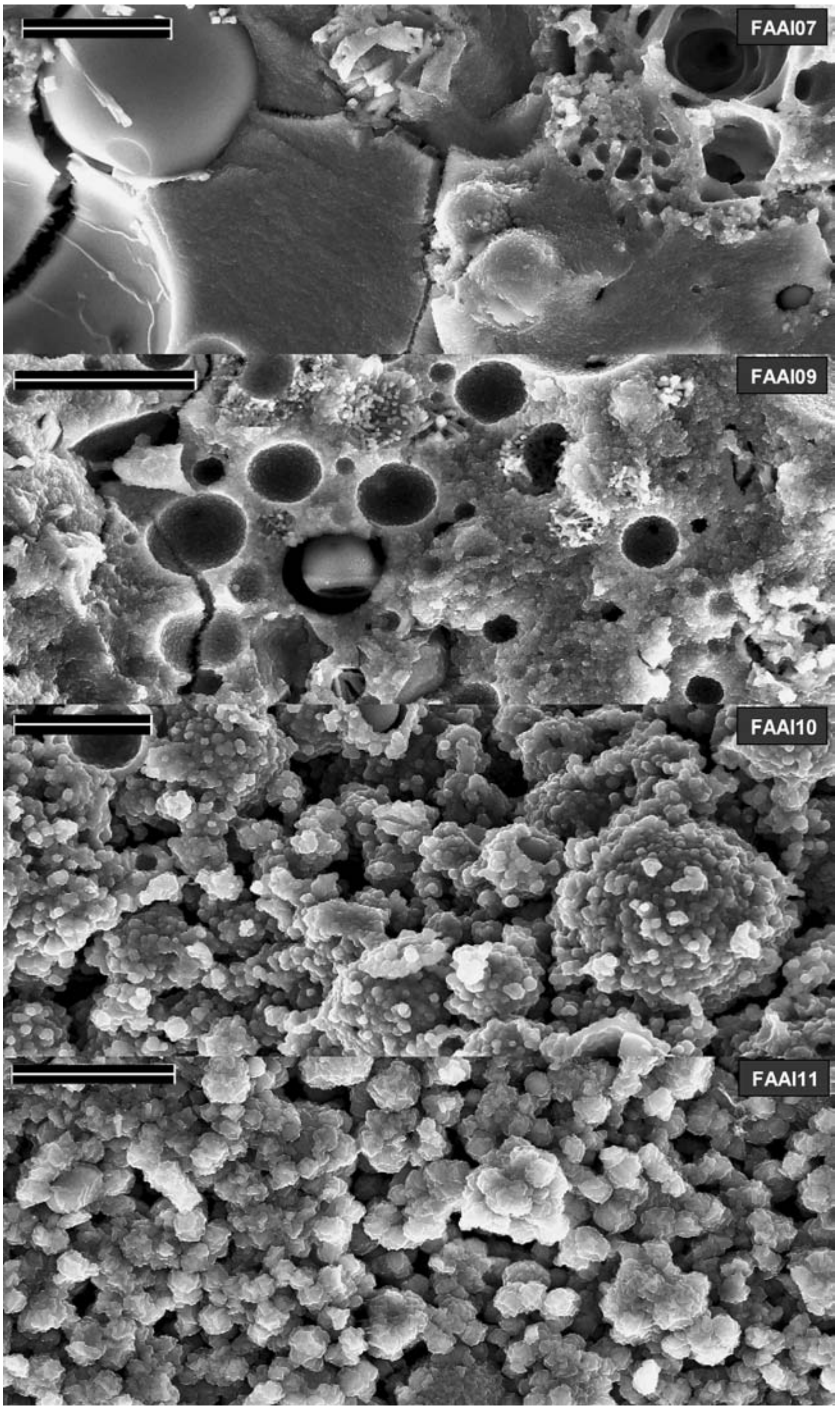

Figure 7 Low magnification images of inorganic polymers containing different amounts of alumina. The porosity and the fineness of the texture are clearly related to alumina concentration. Scale bar represents 10 μm.

similar growth (Fig. 5). Low Si/Al could be expected to greatly limit the growth of the inorganic polymer, as the depositing solution species are much more constrained in where they may condense in the growing polymer, as Al-O-Al linkages must be avoided (Lowenstein's rule). It is, however, unclear why FASi27 and FAAl11, which have approximately the same L/S, should have such different structures. Perhaps with a higher H_2O/Al_2O_3 (sample FAAl11) there is more dissolved aluminium available and hence the inorganic polymer is closer to Si/Al = 1, given that Al dissolution is believed to be a rate-limiting step in the synthesis [5]. This is supported by the apparent complete dissolution of the fly ash particles.

In the four FAAl samples, L/S was varied. This variable has been studied previously by several authors [2, 4]. Silverstrim *et al.* [4] found that the strength of inorganic polymer mortars substantially increased with increasing proportions of activator. Palomo *et al.* [2] found that there was little difference between formulations with 20 and 23% activator (L/S = 0.25 and 0.30). While these proportions are fairly similar, the data of Silverstrim *et al.* [4] implies that such small increments would make a measurable difference. The results of the present study clearly support the findings of Silverstrim *et al.* [4].

As with the FASi27–FASi39 series samples, the FAAl07-FAAl11 samples have different proportions

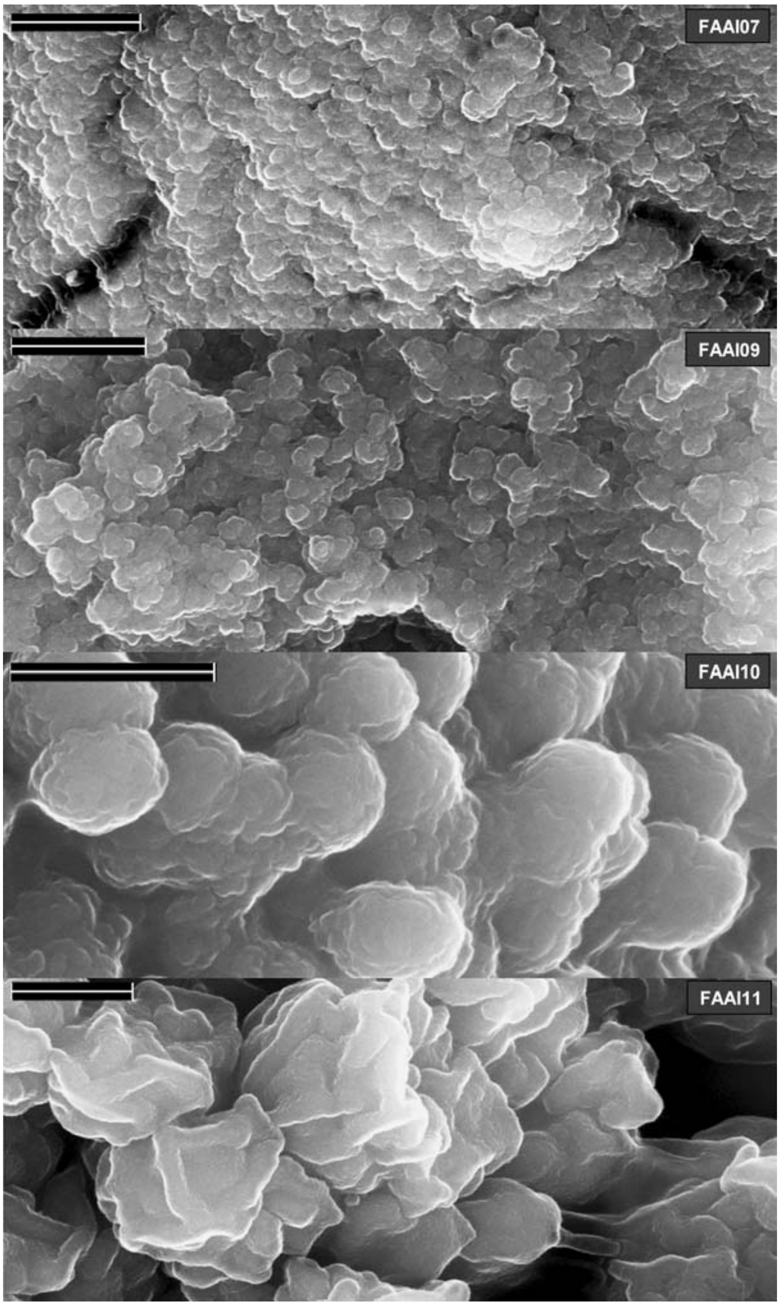

Figure 8 High magnification images of inorganic polymers containing different amounts of alumina. The porosity and the fineness of the texture are clearly related to alumina concentration. Scale bar represents 1 μm.

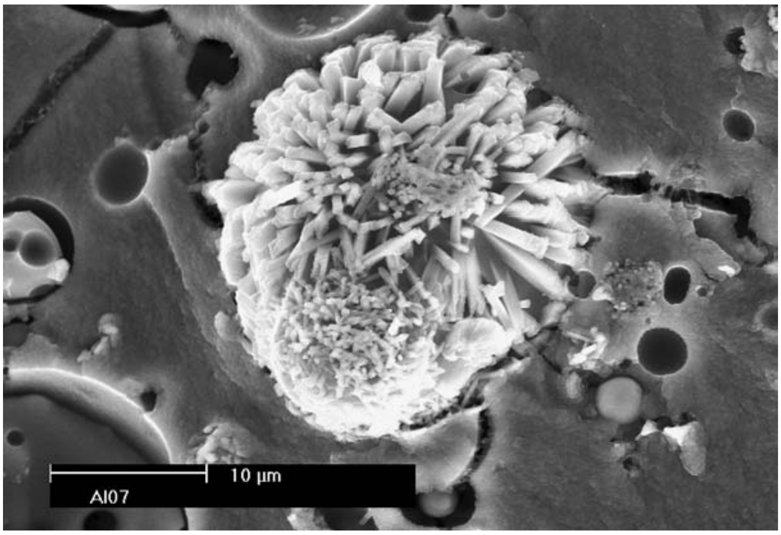

Figure 9 An example of crystal growth in sample FAAl07.

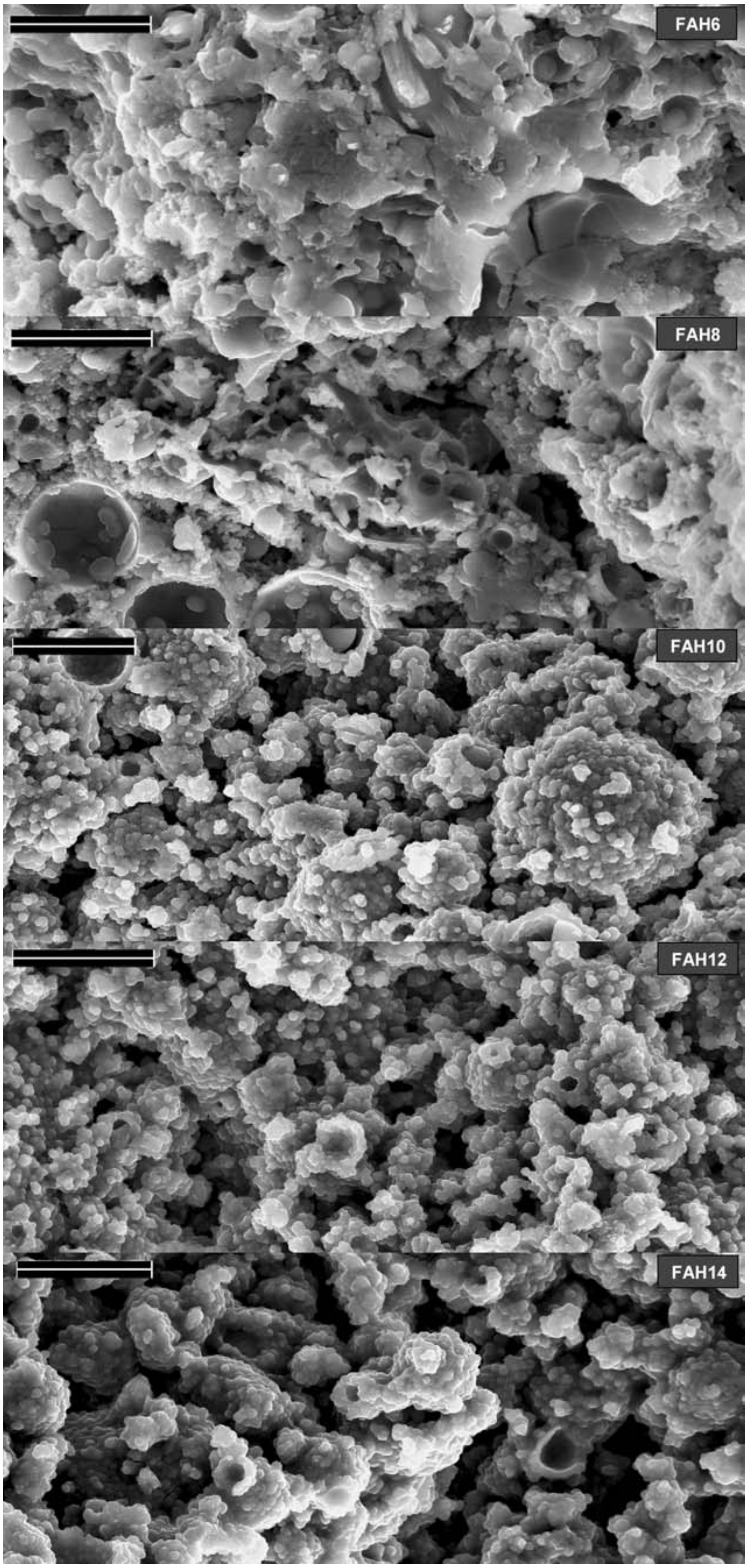

Figure 10 Inorganic polymers containing different amounts of water. An increase in porosity with water content is evident. Scale bar represents 10 μm.

of silica added as solution compared to solid (Table III). Given the comparison with the results of Palomo *et al*. [2] for a different fly ash precursor (described in the previous section) and also the similar (but reversed) microstructures of the FASi and FAAl series of samples, it may be inferred that it is the proportion of soluble silicate added (%$SiO_{2(liq)}$) that is the main factor contributing to the microstructures of the

TABLE III Proportion of the total silica added in solution (%$SiO2_{(liq)}$) for FASi27–FASi39 and FAAl07–FAAl11 samples showing a strong correlation between % $SiO2_{(liq)}$ and strength

Sample	$SiO2_{(liq)}$ (%)	Compressive strength (MPa)
FASi27	0.5	3.9
FAAl11	1.4	6.3
FASi30/FAAl10	10.3	11
FAAl09	19.3	20
FASi35	23.1	29
FASi39	31.0	47
FAAl07	37.2	13

FAAl07–FAAl11 samples. Indeed, if the microstructures of all the FASi27–FASi39 and FAAl07–FAAl11 samples are compared in relation to their % $SiO_{2(liq)}$, there is a definite trend of changing density, fineness of grain structure and porosity. Also, the correlation between the strength and the % $SiO_{2(liq)}$ is very good (a linear regression line gives a fit of $R^2 = 0.92$ with the outlier FAAl07 excluded).

Thus, for the FASi27–FASi39 samples as well as the FAAl07–FAAl11 series, there was a strong correlation between density and compressive strength, in contrast to the FANa1-FAK1 samples. Similar relationships were observed for the metakaolin system [1].

3.7. The effect of water content

Varying the water content of the inorganic polymers from FAH6 to FAH14 had a lesser effect on the microstructure of the material compared to silica or alumina concentration, however there was a decrease in the amount of unreacted particles and some increase in the porosity, as shown in Fig. 10. These two expected trends correlates well with the same variable in the metakaolin series [1] especially the latter of the two. As the samples with the higher water contents set slowest (FAH14 never fully set), there was more time during which there was sufficient mobility of ions in the system for the solid to dissolve, hence the very low level of unreacted material in FAH14. The porosity increase is to be expected, as there will be more water-filled pores in the product with increase in water content.

The compressive strengths of the samples show a clear trend of lower water contents giving the highest strengths, a finding that logically follows the trend in porosity. As with the FANa06–FANa12 series though, the small differences in microstructure would not appear to warrant the significant differences in strength. This is particularly so for samples FAH6 and FAH8 which had similar microstructures but a two-fold difference in strength. FAH14 was very weak to the extent that it could be crushed by hand.

The effect of varying the water content of fly ash inorganic polymers has not been widely reported in the past. Van Jaarsveld and van Deventer [7] report that a formulation with a water/fly ash ratio of 0.34 is around twice the strength of one with a ratio of 0.75 for various alkali concentrations, a similar trend to that seen in the present results. The water to fly ash mass ratios of the FAH6 and FAH14 samples vary from 0.15 to 0.57, respectively. It would appear that the drier the sample, the stronger it is, however, there are practical limitations to low water contents and, in practice, it is these limitations which would limit the strength that could be achieved by water reduction. Low water content greatly raises the viscosity of the liquid component reducing dispersal and ease of mixing. For example, an FAH4 sample was attempted, but even a small amount could not be reasonably mixed by hand. The practical importance of the viscosity of inorganic polymer formulations has been commented upon previously by other authors [6, 9]. Fast setting is also a problem with low water samples. For example, sample FAH6 was cast into moulds immediately after mixing to prevent it from setting in the mixing vessel. On a larger scale where casting takes more than a few seconds, a formulation such as FAH6 would be impossible to handle.

4. Conclusions

The effect of the concentration of each of the four most important oxide components of inorganic polymers was assessed by electron microscopy and by strength testing. Additionally, the effect of the type of alkali cation was determined. The results of this study demonstrated some clear correlations between composition, microstructure and strength, with some series of formulations following expected trends. It was observed that high strength was related to low porosity and a dense, fine grained microstructure, as was the case for the metakaolin-derived inorganic polymers previously reported [1]. Such a structure was found in inorganic polymers with high silica contents and low water contents. High alkali and low alumina contents also produced this structure, however there was a limit beyond which the strength deteriorated. Sodium was found to give a higher strength than potassium. In sets of samples with varying Si/Al ratios (FASi and FAAl series), the proportion of the total silica added as liquid also varied, and this appeared responsible for some of the observed structural and strength differences between these formulations.

While in general the correlations between structure and strength were clear, in some samples (e.g. those of the FANa and FAH series) the differences in strength appeared to be disproportionate to the changes in structure. Perhaps for these samples other analytical methods (such as FTIR and NMR) may unearth finer structural differences. It is reassuring that the results, in general, agreed with those of the metakaolin system and this reinforces the statement that the trends found would be generally true for certain classes of inorganic polymer systems.

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