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Relationships between composition, structure and strength of inorganic polymers

Part I *Metakaolin-derived inorganic polymers*

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"Inorganic polymers", or geopolymers, are novel synthetic binders produced by reactions between alkali silicate solutions and solid aluminosilicates. In Part 1 of this study, 12 metakaolin-derived inorganic polymers were produced with various compositions. The effect of the concentration of each of the four most important oxide components of inorganic polymers (Na_2O, SiO_2, Al_2O_3 and H_2O) was assessed by electron microscopy and by strength testing. Additionally, the effect of the type of alkali cation was determined. In general, the results followed expected trends and there were clear correlations between composition, microstructure and strength. It was found that high strength was related to low porosity and a dense, fine grained microstructure. Such a structure was found in inorganic polymers with high alkali contents ($Na_2O/Al_2O_3 = 1.2$) and low water contents ($H_2O/Al_2O_3 = 12$). High silica and low alumina contents ($SiO_2/Al_2O_3 = 3.5$–3.8) also produced this structure, however, there was a limit beyond which the strength deteriorated. In relation to the effect of alkali cations, sodium was found to give higher resin strength than potassium. The results of the study further confirm that the selection of precursor raw materials remains a critical factor to initial strength development. The relationship between different resin formulations and resulting microstructures are discussed.

1. Introduction

Inorganic polymers are novel synthetic binders produced by reactions between alkali silicate solutions and solid aluminosilicates. The solid aluminosilicate from which the inorganic polymers discussed in this article are made is metakaolin. Fly ash is another common precursor, and inorganic polymers made from it are discussed in Part 2 of this article [1]. Inorganic polymers set and harden in a physically similar process to Portland cement and potentially have similar applications. Inorganic polymers may also have applications in toxic waste stabilisation [2], advanced composites [3] and as cement additives [4]. Despite inorganic polymers having cost, environmental and performance advantages over current binder technologies, their great potential is only now being realised. One of the reasons for this is that there has been little fundamental research into the relationships between empirical formulations of inorganic polymers and their chemistry, structure and performance characteristics.

Broadly, inorganic polymers may be considered as three-dimensional framework aluminosilicates consisting of corner-sharing silicate and aluminate tetrahedra, and containing metal cations which balance the negative charge of the aluminate groups. They are typically made with compositions (in terms of oxides) of approximately $M_2O{\cdot}3SiO_2{\cdot}Al_2O_3{\cdot}12H_2O$, where M is an alkali metal cation (usually Na or K). X-ray diffraction has shown them to be amorphous [5] and MAS NMR and FTIR have shown them to contain Si and Al in coordination environments typical of tectosilicates [6, 7]. Several of these techniques and others have been employed to characterise metakaolin-derived inorganic polymer systems, in addition to published microstructural studies using various electron microscopy techniques [8] and mechanical performance assessment based on compressive strength measurements [7]. There is, however, limited data available correlating engineering performance of resins to their bulk microstructural properties such as pores, gel texture and unreacted particles. As such, the present study investigates the microstructures of different formulations of metakaolin inorganic polymers made with varying oxide compositions and alkalis, and assesses the effect of

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changes in resin chemistry on both microstructure and compressive strength.

2. Experimental

The inorganic polymers were prepared from metakaolin, alkali silicate solution, alkali hydroxide and distilled water. The metakaolin was made by calcining kaolin (Commercial Minerals, Australia, 47.3 wt% SiO_2, 35.7 wt% Al_2O_3, 3.1 wt% other oxides). 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). Twelve inorganic polymers were prepared with different formulations (Table I), with the different combinations 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 notation adopted starts with two letters designating the reference silicate source, i.e. MK for a "metakaolin" system or, as indicated in Part 2 of this paper, FA for "fly ash". This is followed by the variable being tested and its value; for example MKH12 assesses the effect of H_2O at an H_2O/Al_2O_3 ratio of 12. While samples MKNa1, MKNa10, MKSi30, MKAl10 and MKH12 have different notations, they have identical composition. The range of concentrations of each component was restricted by limitations on the choice of ingredients and by the setting properties of the respective slurries.

The inorganic polymer formulations that were selected for this study were designed so that five different variables (alkali choice and water, silica, alumina and alkali concentration) could be studied independently. However, there are other factors that vary between the samples. In all the five sets of samples there were changes in the liquid to solid ratio of the reactants (Table I). The change was most significant in the MKAl07–MKAl12 series where the liquid to solid ratio (L/S) changed by a factor of two. Changing the L/S would clearly have an effect on the synthesis of inorganic polymer. This ratio affects the mobility of ions, the concentration of dissolved species and the amount of new material that must be deposited to give a cured solid.

TABLE I Compositions of the 12 inorganic polymer samples. 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 metakaolin

Sample	Composition	L/S	Compressive strength (MPa)
MKNa1	$Na_2O{\cdot}3SiO_2{\cdot}Al_2O_3{\cdot}12H_2O$	1.31	29
MKK1	$K_2O{\cdot}3SiO_2{\cdot}Al_2O_3{\cdot}12H_2O$	1.44	25
MKNa07	$0.7Na_2O{\cdot}3SiO_2{\cdot}Al_2O_3{\cdot}12H_2O$	1.24	4.9
MKNa10	$1.0Na_2O{\cdot}3SiO_2{\cdot}Al_2O_3{\cdot}12H_2O$	1.31	29
MKNa12	$1.2Na_2O{\cdot}3SiO_2{\cdot}Al_2O_3{\cdot}12H_2O$	1.36	42
MKSi25	$Na_2O{\cdot}2.5SiO_2{\cdot}Al_2O_3{\cdot}12H_2O$	1.19	2.7
MKSi30	$Na_2O{\cdot}3.0SiO_2{\cdot}Al_2O_3{\cdot}12H_2O$	1.31	29
MKSi35	$Na_2O{\cdot}3.5SiO_2{\cdot}Al_2O_3{\cdot}12H_2O$	1.44	48
MKSi38	$Na_2O{\cdot}3.8SiO_2{\cdot}Al_2O_3{\cdot}12H_2O$	1.51	48
MKAl07	$Na_2O{\cdot}3SiO_2{\cdot}0.7Al_2O_3{\cdot}12H_2O$	2.11	34
MKAl08	$Na_2O{\cdot}3SiO_2{\cdot}0.8Al_2O_3{\cdot}12H_2O$	1.78	45
MKAl10	$Na_2O{\cdot}3SiO_2{\cdot}1.0Al_2O_3{\cdot}12H_2O$	1.31	29
MKAl12	$Na_2O{\cdot}3SiO_2{\cdot}1.2Al_2O_3{\cdot}12H_2O$	1.00	2.8
MKH12	$Na_2O{\cdot}3SiO_2{\cdot}Al_2O_3{\cdot}12H_2O$	1.31	29
MKH14	$Na_2O{\cdot}3SiO_2{\cdot}Al_2O_3{\cdot}14H_2O$	1.46	7.0
MKH16	$Na_2O{\cdot}3SiO_2{\cdot}Al_2O_3{\cdot}16H_2O$	1.61	2.0

Samples were prepared by mixing the alkali silicate, distilled water and alkali hydroxide (in that order) then allowing this activator solution to cool before mixing in the metakaolin. There are reports in the literature that this order of addition of the reagents reduces the early age (e.g. two-hour) compressive strength [7] (but does not affect the microstructure [8]). It has also been reported that the order of mixing the reagents can give undesired reaction products [9].

After mixing, the slurry was poured into moulds, which were sealed to prevent water loss, and placed into an 85°C oven. There was minimal aging time between mixing and curing. After two hours, the samples were removed from the oven, demoulded and stored in a refrigerator to facilitate rapid cooling to room temperature and limit further reaction.

Samples for SEM analysis were made in 34 mm diameter cylindrical moulds. The samples were fractured and the fragments were mounted on SEM sample stubs and carbon coated. The fracture faces were analysed on a Philips XL30FEG field emission SEM. Unless stated otherwise, all SEM images are representative of average parts of the samples.

In this study, only fracture faces of the inorganic polymers were examined. While this gave very good images of the microstructure, it prevented the use of composition analysis such as X-ray spectroscopy or backscattered imaging which require flat surfaces. These methods could be used to determine the distribution of aluminium and the alkali cation in the inorganic polymer, which would indicate the extent of reaction (aluminium is only present in the solid precursor and alkali is only present in the liquid precursor). The resolution of these instruments may, however, be too poor for worthwhile results as the composition is expected to be uniform down to the sub-micron level (the size of the metakaolin particles).

The samples for compressive strength testing (25.4 mm cubes) were cured in preheated (85°C) moulds. Two to six (usually three) cubes were tested for each formulation. Compressive strength testing was performed using Baldwin testing apparatus.

To minimise errors, the time delay between oven curing and the SEM analysis or strength measurement was kept to a minimum, all samples were treated similarly and all were stored in a refrigerator between curing and analysis. Metakaolin inorganic polymers take more than a week to cure in a refrigerator and hence the storage time in a refrigerator prior to analysis (1–2 days) was not significant compared to the oven time (where the inorganic polymers cure at least 100 times as fast). Previous research [8, 10] showed that inorganic polymer samples showed little difference in microstructure when cured for 1, 4 and 24 h, which implies that the

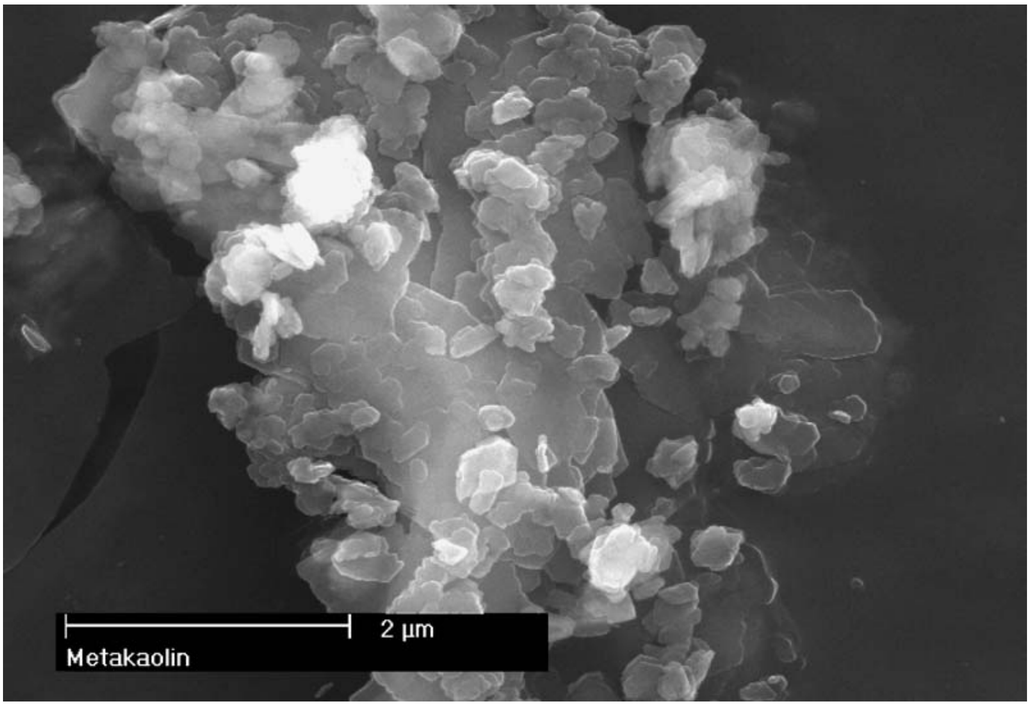

Figure 1 A typical agglomerate of particles in the metakaolin precursor.

small time differences in storage at low temperature will make no difference to the results.

3. Results

3.1. The microstructure of metakaolin

Fig. 1 shows the morphology of the metakaolin. The particles look little different to those of the precursor kaolin being layered and having angular edges and corners. The manufacturer states that 50% of the particles are smaller than 500 nm and >98% are smaller than 40 μm, although SEM suggests that there are many larger agglomerates.

3.2. Setting characteristics

All samples hardened within two hours at 85°C although some samples, particularly MKH16, were clearly not as hard as others. Most of the samples generated considerable amounts of heat during curing and some of the samples prepared for SEM (which were cured in less rigid moulds) cracked or became deformed. This deformation may have been due to the release of steam from some samples as their temperature increased to over 100°C due to the exothermic reaction. This variation in the heat released from each sample suggests that different samples experienced slightly different cure temperature regimes to the preset 85°C oven temperature.

3.3. General observations

All the inorganic polymer samples had a generally uniform microstructure, as has been reported in the past [9, 11]. At high magnification it was observed that the microstructure had a coarse texture made up of rounded balls with bridging between them. These balls were of different sizes in different samples but of consistent size within each sample, which implies that they are not the remains of the metakaolin precursor, but rather are pure inorganic polymer growths. The main differences between the samples were the size, the packing density and the extent of bridging between these spherical particles or "balls". The samples contained some proportion of unreacted or incompletely reacted particles such as that shown in Fig. 2. These particles, which clearly had a layered structure, were larger than the majority of the original particles, being up to 20 μm across. Why these particles remained unreacted is unknown, however they could be particles of a different, less reactive inorganic polymer (the kaolin precursor is commercial grade and is not pure kaolinite), although as their concentration varied amongst the samples they must react to some extent. It is generally understood that the small amount of quartz present in the original kaolin will not react during inorganic polymerisation and will be present in the final product [6, 7] and occasional quartz particles were observed in the samples.

The unreacted particles were generally uncommon and the inorganic polymer reaction is believed to be largely complete after two hours, thus the formulations given in Table I can be taken as approximate chemical formulae of the inorganic polymer. This finding agrees with that reached through spectroscopic analysis by Rahier *et al.* [11]. All the samples contained far less unreacted material than has been reported for fly ash inorganic polymers [1, 12]. The smaller particle size, higher reactivity and homogeneity of metakaolin compared to fly ash may be the reason for this observation.

Inorganic polymers are essentially gels and while the extent of porosity is clearly variable, previous studies have indicated that inorganic polymers may contain up to one-third pores by volume [6]. In the SEM the

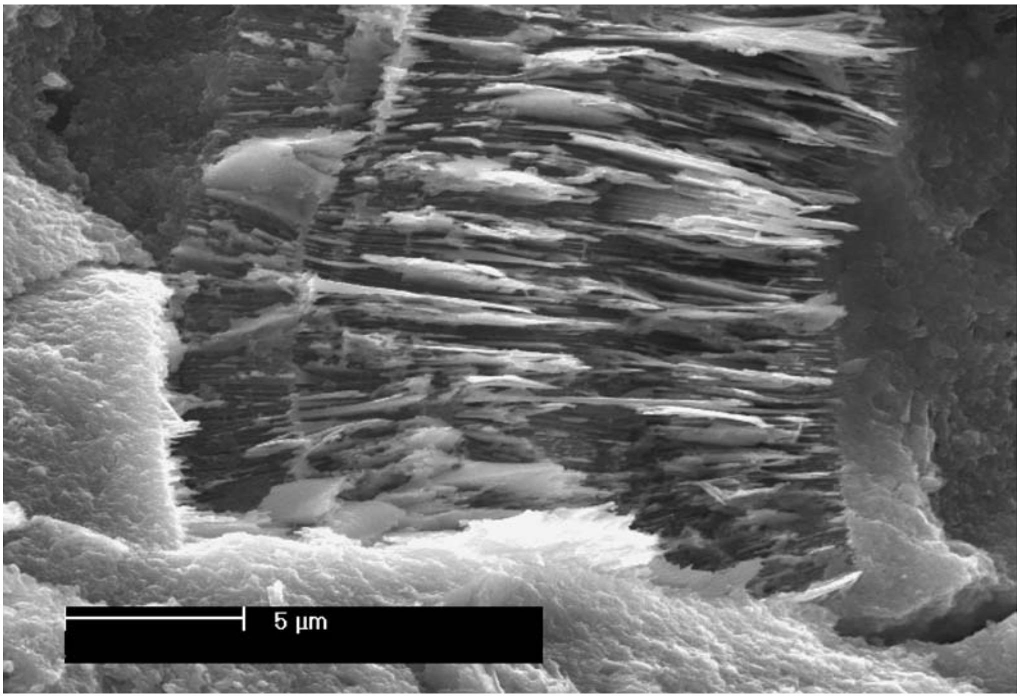

Figure 2 One of the incompletely reacted particles found in the metakaolin inorganic polymers. The particle clearly has a layered structure that has partially decomposed, either during calcining or during reaction with silicate solution.

samples are dried out by the high vacuum, thus the liquid phase is lost and any dissolved species in the liquid phase would precipitate onto the surface of pores. Table I lists the compressive strengths of the 12 inorganic polymer samples. The strengths were generally as one would logically expect and mostly correlated well to the value of the variable within each set of formulations. Some of the samples had quite low compressive strengths due to being measured after only 2 h curing. These strengths could be expected to rise with longer curing.

3.4. The effect of the type of alkali cation

Samples MKNa1 and MKK1 had identical compositions except they contained different alkali cations (sodium and potassium, respectively). These two samples, and in particular MKK1, contained some unreacted particles, however the reaction was still clearly almost complete. The fact that MKK1 contained more unreacted material than MKNa1 agrees with previous research which showed that metakaolin is more soluble in sodium hydroxide than in potassium hydroxide [13]. At low magnification, the images show a difference in the smoothness of the fracture faces—all the fracture faces of sample MKK1 were smoother than those of MKNa1. This is due to the considerably finer texture of the MKK1 inorganic polymer, which can clearly be seen in the higher magnification images (Fig. 3). The rounded balls making up the inorganic polymer are far more discrete in MKNa1 than in MKK1 which is much denser.

The sodium-based inorganic polymer was found to be stronger than its potassium-based equivalent. This is an unexpected result as the SEM analysis shows MKK1 to be denser. The greater density suggests it would be stronger, as a fine grained, dense microstructure is clearly related to strength in the other samples (discussed below). A similar result was also found in the equivalent samples in the set of fly ash-based inorganic polymers [1].

The relative strengths of metakaolin-derived inorganic polymers containing different alkalis has not been discussed in the past, however, in the case of fly ash, potassium has been found to give the stronger product [14]. Rahier *et al.* [11] found that metakaolin inorganic polymers derived from sodium silicate set at a faster rate than those derived from potassium silicate. Thus, the higher strength of MKNa1 compared to MKK1 could be due to the inorganic polymer synthesis reactions having progressed further in two hours and MKK1 could have a higher ultimate strength.

3.5. The effect of alkali concentration

Three samples (MKNa07, MKNa10, MKNa12) were prepared from which the effect of alkali concentration on the properties of metakaolin-derived inorganic polymers could be determined. MKNa04 and MKNa13 samples were also made, however MKNa04 did not set and MKNa13 flash set during mixing.

Alkali has two roles in inorganic polymer synthesis: it raises the pH which increases the solubility of the metakaolin, and it provides cations to balance the negative charge of aluminate groups in the product. The former role has been studied previously and metakaolin dissolution has been shown to be very pH dependent [10, 13]. The second role clearly requires only as much alkali as there is alumina (as it is the aluminate groups that require charge balancing), i.e., MKNa10 should have sufficient alkali. This is demonstrated by a previous report that Na^+ ions could be

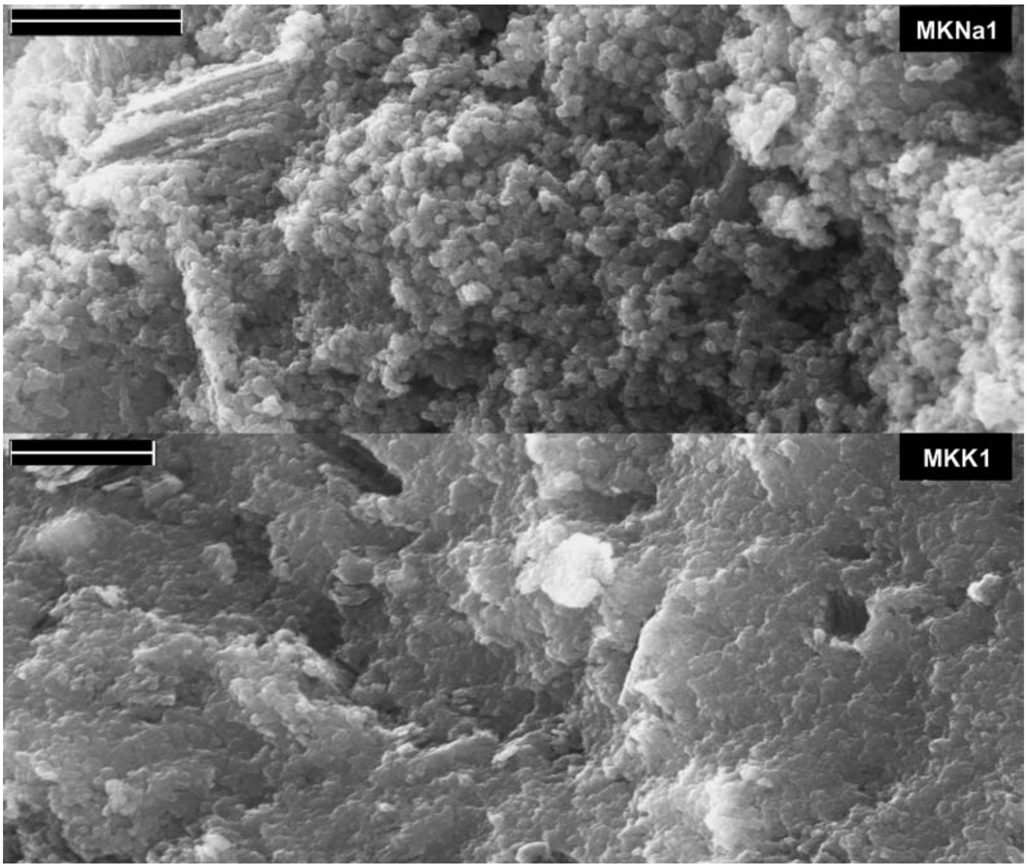

Figure 3 Inorganic polymer samples with similar compositions except that they contain different alkali cations. The sodium-based sample (MKNa1) is not as dense as its potassium equivalent (MKK1) and contains more discrete inorganic polymer balls. Scale bar represents 2 μm.

washed out of a sample with only a slight excess of alkali ($Na_2O/Al_2O_3 = 1.13$) [9].

When examined under the SEM, the three samples showed a gradation of density, surface smoothness and proportion of unreacted particles (Fig. 4), however the differences were not great, especially between MKNa07 and MKNa10. All three of these properties increased with increasing alkali concentration. The compressive strengths of the three samples also showed a clear relationship between alkali concentration and strength, and the strength increments were surprisingly large considering the minor changes in microstructure (cf. MKAl and MKSi series of samples discussed below). It is also interesting to note that the strength increased with increasing alkali beyond $Na_2O/Al_2O_3 = 1$ (MKNa10) showing the importance of the former on the two roles of the alkali.

It is intriguing that the stronger samples with the higher alkali contents had the highest proportion of unreacted particles, as it may be expected that the higher alkali content would result in more complete dissolution of the inorganic precursor. However, it is possible that it was the setting rate that determined the extent of reaction in these samples. Given that MKNa04 did not set and MKNa13 flash set, and considering the higher strengths of the samples with higher alkali contents (which is related to the extent of reaction), it appears that high alkali concentrations increase the setting rate. Rahier *et al.* [11] also report an increasing setting rate with decreasing SiO_2/Na_2O ratio. Faster setting gives less time for dissolution and hence there are more unreacted particles in the high alkali inorganic polymers.

3.6. The effect of silica content

There were very significant differences in the microstructures of samples containing differing amounts of silica, particularly through sample series MKSi25–MKSi35. However, sample MKSi38 was not greatly different to MKSi35. At low magnification there is a clear graduation in the smoothness of the fracture surface texture and density of the microstructure from sample MKSi25, through sample MKSi30, to sample MKSi35 (Fig. 5). This is shown even more dramatically at high magnification where the difference between sample MKSi25 and the other samples is striking (Fig. 6). Samples MKSi35 and MKSi38 have the finest texture with sample MKSi30 considerably more granular and sample MKSi25 far coarser and with the particles much smoother and more "sintered" and with a great deal of porosity.

The compressive strengths of the samples were clearly related to their microstructure, with the denser, finer textured samples being the strongest. Given the very high porosity of MKSi25, it is not surprising that its strength is so much lower than those of the other MKSi series samples. The very small proportion of silica added as silicate solution in MKSi25 may have meant that there was very little reactive liquid filler between the particles during curing, which led to high porosity. The effect of the proportion of liquid silicate added is discussed further in the next section.

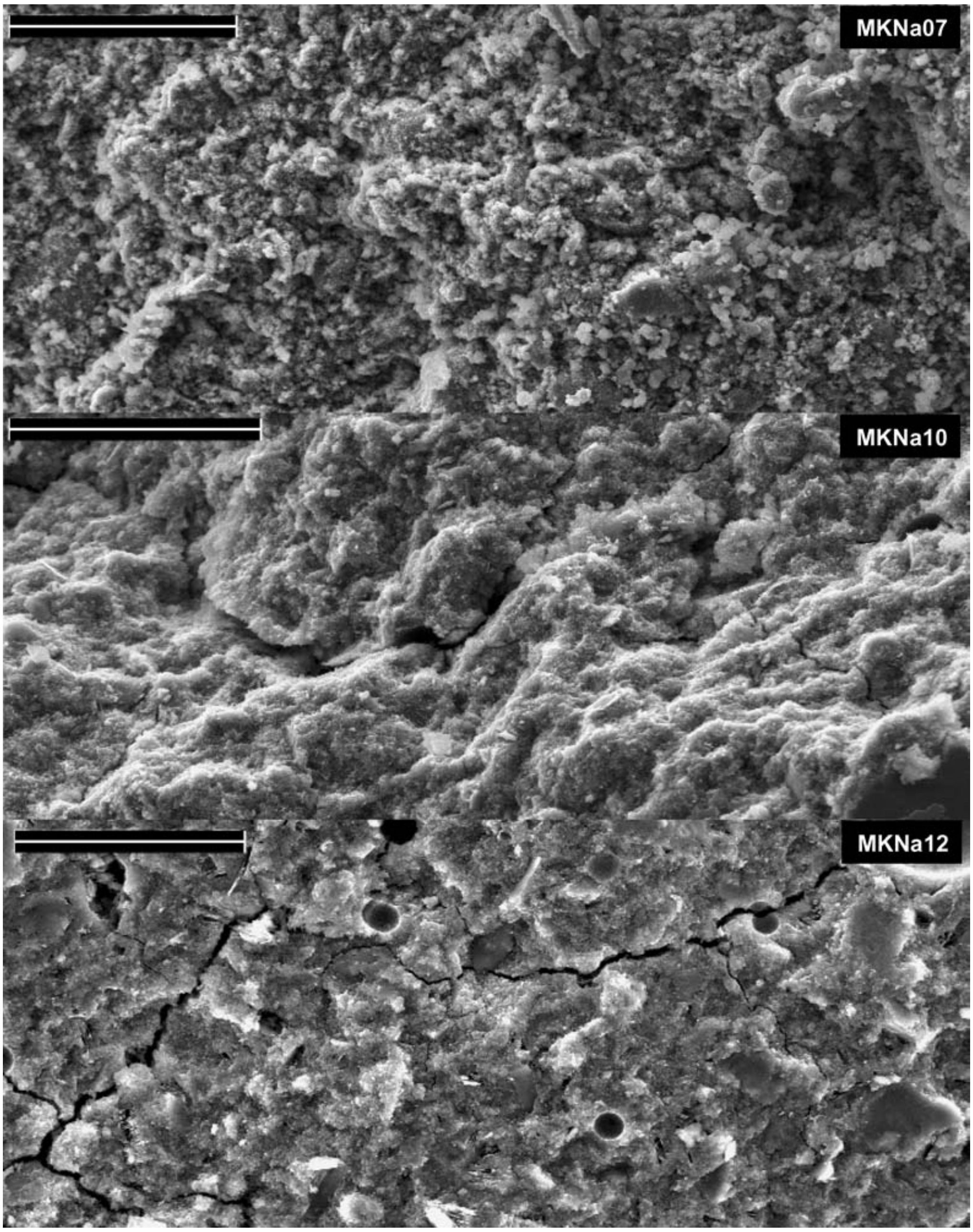

Figure 4 Inorganic polymers containing different amounts of alkali. The differences between the samples were not great. Scale bar represents 50 μm.

The similar strengths of MKSi35 and MKSi38 are in accordance with their similar structures. However, MKSi38 is neither stronger nor denser than MKSi35, given the observed trends in properties from samples MKSi25 to MKSi35. This implies there is a limit beyond which additional silica no longer improves strength, an implication that is supported by Barbosa *et al.* [6]. In their study, they tested the strengths of two metakaolin-derived inorganic polymer samples with different silica contents (approximately $1.5Na_2O\cdot xSiO_2\cdot Al_2O_3\cdot 15H_2O$, with $x = 3.3$ and 4.5) and found the lower silica sample to be considerably stronger (41 MPa cf. 28 MPa after 1 h). This implies that more silica than MKSi38 may result in a strength reduction (such a formulation could not, however, be tested with the raw materials used in this study without adding more water). By comparison, Davidovits [9] recommends silica concentrations of $SiO_2/Al_2O_3 = 3.5–4.5$ and suggests that 4.0 is ideal.

3.7. The effect of aluminium content

Metakaolin inorganic polymers with various amounts of aluminium were made by changing the amount of metakaolin added and compensating by adding more activator solution. Thus, L/S changes most dramatically in this series of samples (see Table I). This could be a reason for the significant structural changes between these four samples (Figs 7 and 8). In the samples, there is a clear gradation of structure types from MKAl08 to MKAl12, with MKAl08 having a much finer, denser microstructure than MKAl12. MKAl08 had the maximum density and fineness, with MKAl07 being coarser, but not as much as MKAl10 (=MKNa1) and especially MKAl12.

The compressive strengths of the samples gave the expected results given the SEM analysis. Strength decreased from MKAl08 to MKAl12, and MKAl07 had a strength between that of MKAl08 and MKAl10. As with the MKSi series samples, there was a maximum

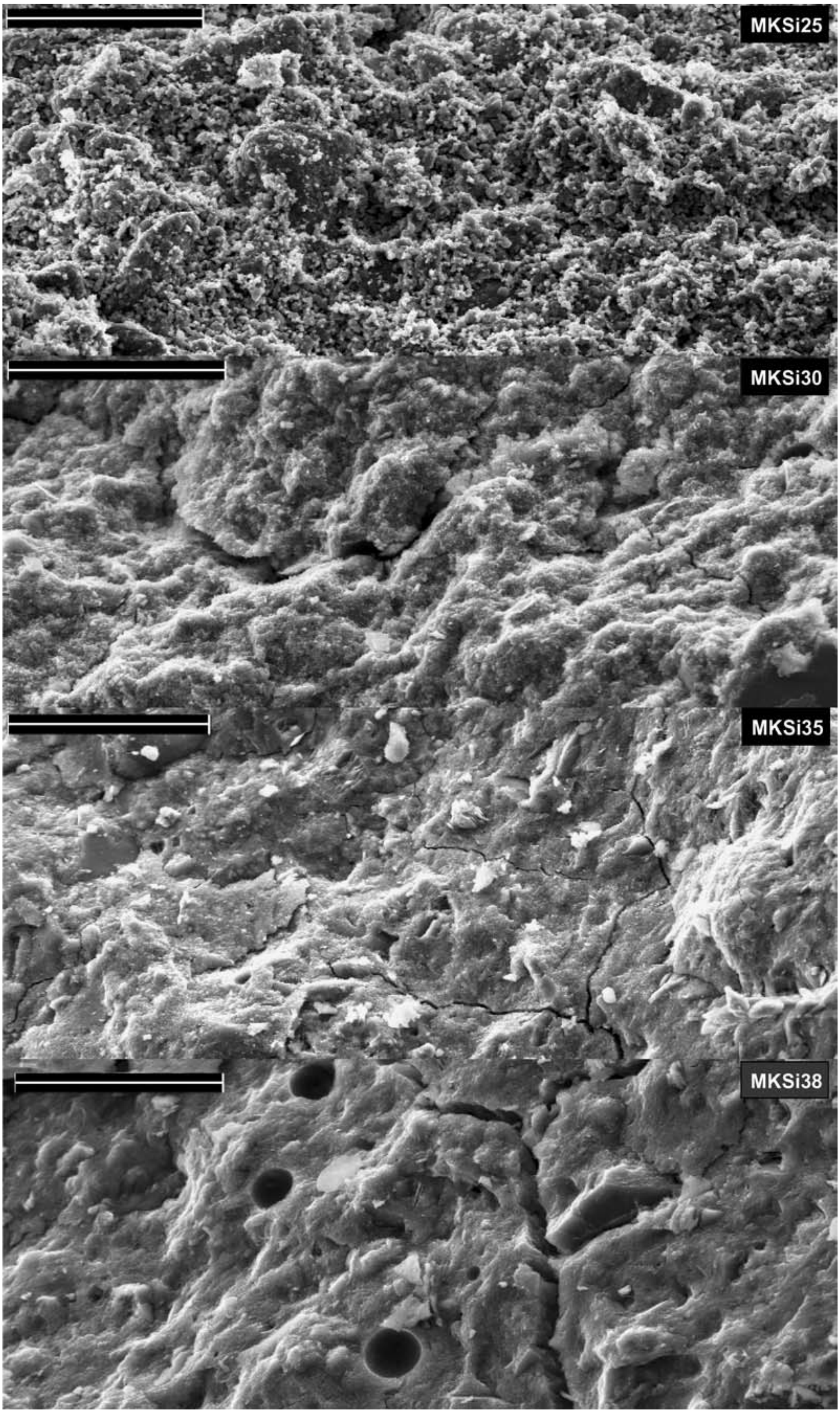

Figure 5 Low magnification images of inorganic polymers containing different amounts of silica. The samples show a gradation in density and surface smoothness which correlates to strength. Scale bar represents 50 μm.

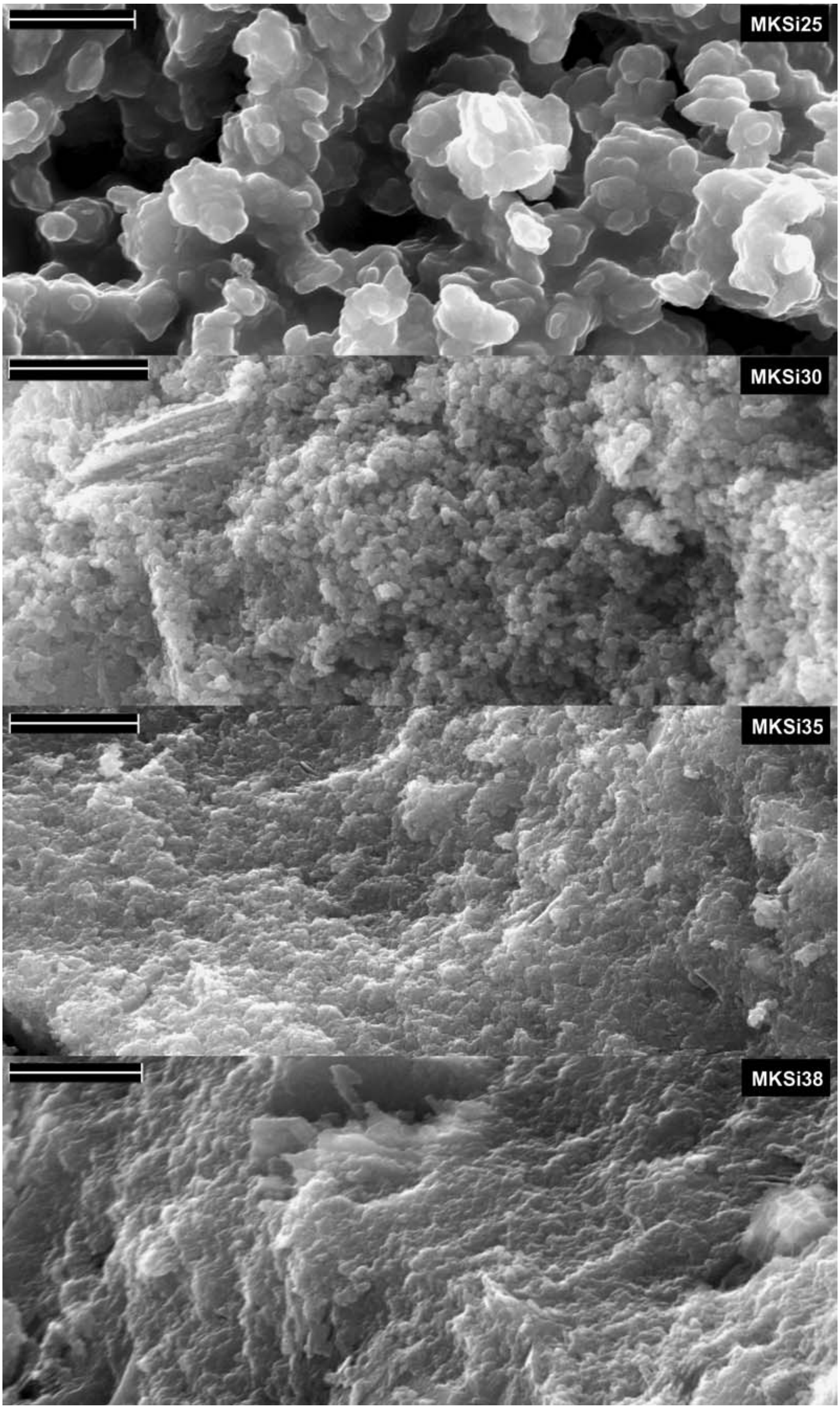

Figure 6 High magnification images of inorganic polymers containing different amounts of silica. The samples show a gradation in porosity, with MKSi25 in particular being far more porous than the others. Scale bar represents 2 μm.

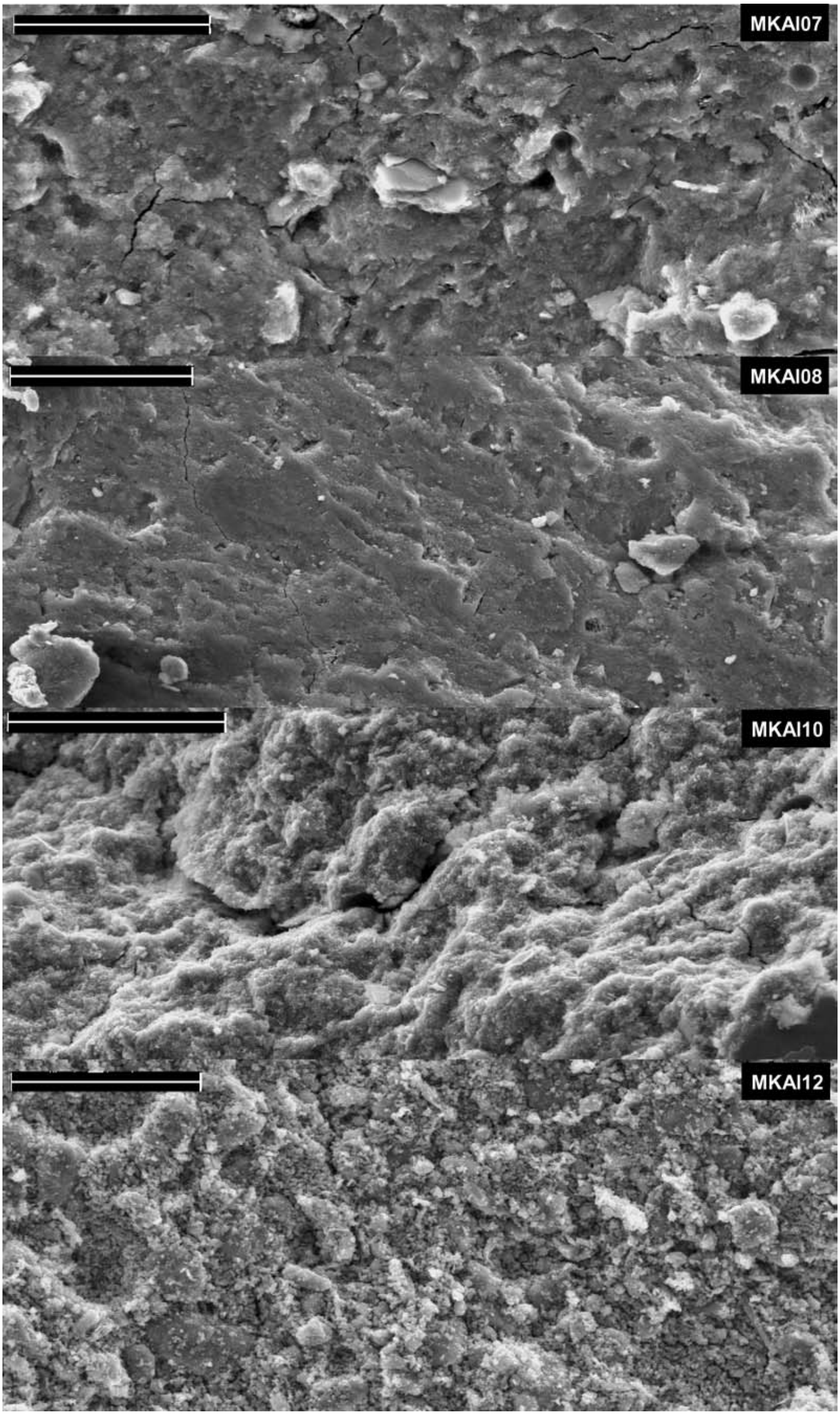

Figure 7 Low magnification images of inorganic polymers containing different amounts of alumina. The samples have densities, or fineness of texture, that correlate to their strengths. Scale bar represents 50 μm.

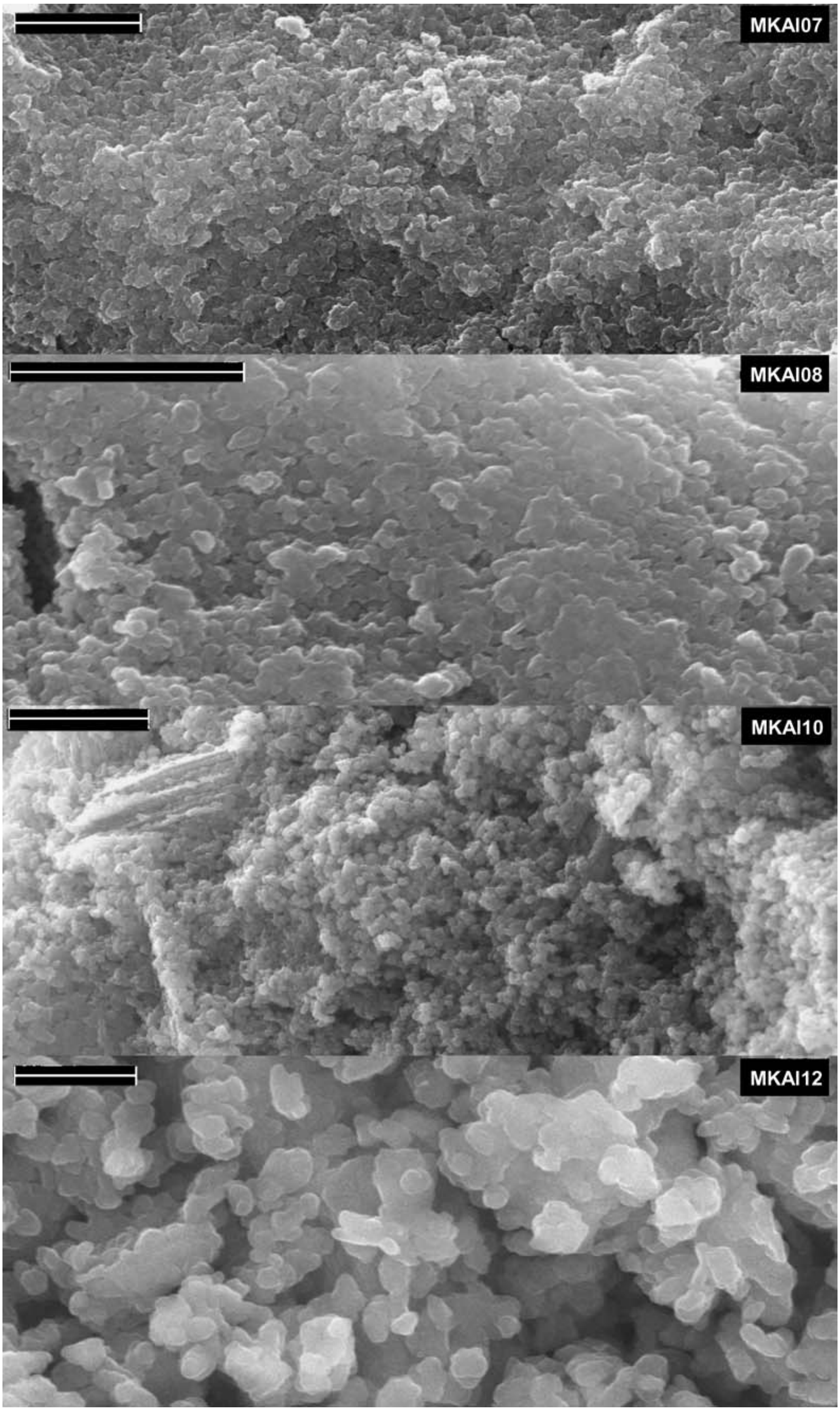

Figure 8 High magnification images of inorganic polymers containing different amounts of alumina. The samples have densities that correlate to their strengths. Scale bar represents 2 μm.

in the strength versus formulation relationship, and that maximum occurred at high SiO_2/Al_2O_3 ratios. In general, the trends within the MKAl series samples are similar to those of the MKSi samples, except that the order is reversed. The common link between these two series of samples is the variation of the proportion of the silica added in solution (% $SiO_{2(liq)}$). Table II gives these proportions of $SiO_{2(liq)}$ along with compressive strengths. It can be seen that for most of these samples there is a strong correlation between % $SiO_{2(liq)}$

TABLE II The relationship between compressive strength and proportion of silica added in solution in the MKSi25–MKSi38 and MKAl07–MKAl12 samples

Sample	$SiO_{2(liq)}$ (%)	Compressive strength (MPa)
MKSi25	10.0	2.7
MKAl12	10.0	2.8
MKSi30/MKAl10	25.0	29
MKSi35	35.8	48
MKAl08	40.0	45
MKSi38	40.8	48
MKAl07	47.5	34

and strength. With MKAl07 excluded (it has already been seen that this sample has too little aluminium for maximum strength and is outside the linear part of the relationship), the linear correlation coefficient (R^2) is 0.97. This very good correlation implies that it is the variation in % $SiO_{2(liq)}$ that is causing the differences between the MKSi25–MKSi38 and MKAl08–MKAl12 samples, rather than the overall silica or alumina contents.

To test this idea, two samples were prepared with different SiO_2/Al_2O_3 ratios (3.0 and 4.0) but with the same $SiO_{2(liq)}$ proportion (25%). The additional solid silica was sourced from high-purity silica fume and the samples were made and tested similarly to the others. The $SiO_2/Al_2O_3 = 4.0$ sample had a considerably denser microstructure than the $SiO_2/Al_2O_3 = 3.0$ sample (Fig. 9) and their strengths were 48 and 16 MPa, respectively. While the results cannot be directly compared to those of the pure metakaolin inorganic polymers as the raw materials are different, these results clearly indicate that SiO_2/Al_2O_3 does have an effect on structure and strength, in addition to % $SiO_{2(liq)}$. This result confirms the findings of Rowles *et al.* [15] who also observed strong dependence of compressive strength on the Si/Al ratio of different formulations. The researchers further observed that a displacement of the characteristic XRD diffuse halo occurred in all samples of low, medium and high strengths relative to the precursor metakaolin trace. This displacement highlights differences between the amorphous structures of initial unreacted material and the gel phase inorganic polymer matrix.

An alternative method that would separate the effect of alumina or silica concentration from % $SiO_{2(liq)}$ would be to use a variety of metakaolin sources, as this material is available with different compositions. Unfortunately this would bring in other variables (e.g. differences in crystallinity, aluminium coordination, reactivity) which may nullify any advantage.

From the work of Phair *et al.* [13] it is evident that the amount of silica that dissolves from metakaolin in alkaline solution is quite low, much lower than the concentration in the silicate solution. Thus, samples MKAl07 and MKAl12 (and MKSi25 and MKSi38) would have had very different solution concentrations of Si and Al during curing. These different concentrations may

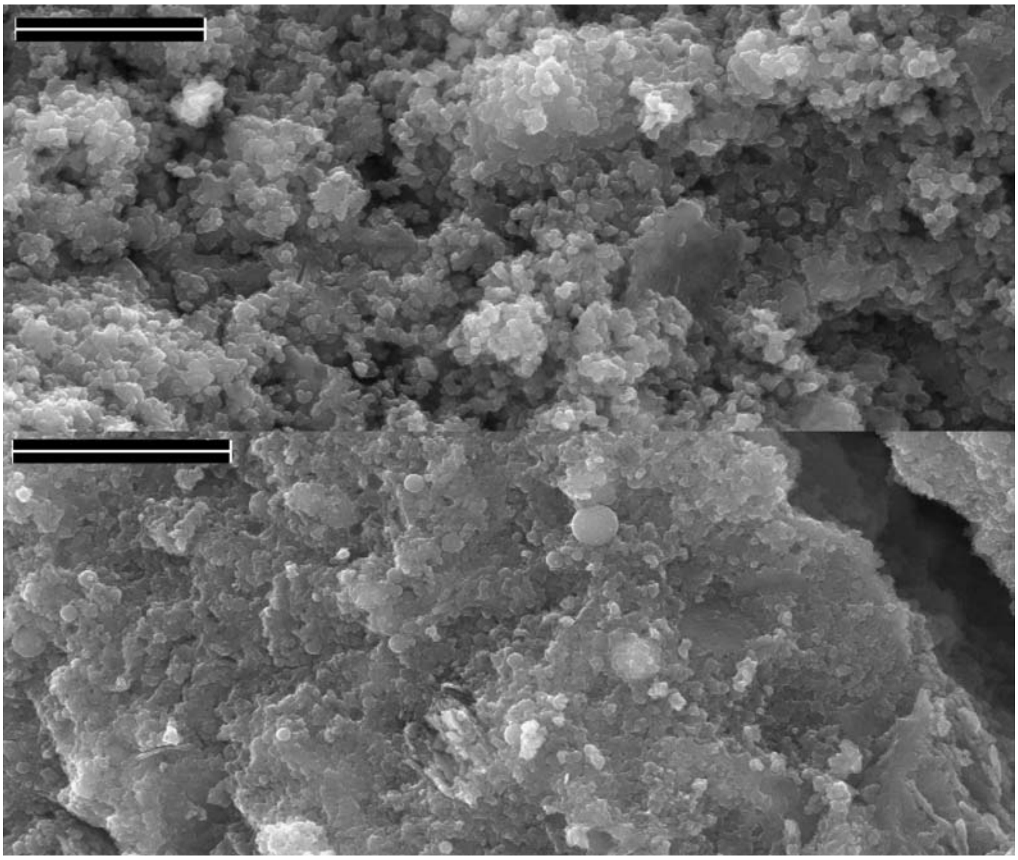

Figure 9 Metakaolin inorganic polymers with added silica fume to give different SiO_2/Al_2O_3 ratios (3 top; 4 bottom) but a constant proportion of silica added in solution (25%). The different microstructures show that Si/Al affects structure as well as % $SiO_{2(liq)}$. The unreacted spherical particles are aluminium-rich silica fume particles. Scale bar is 5 μm long.

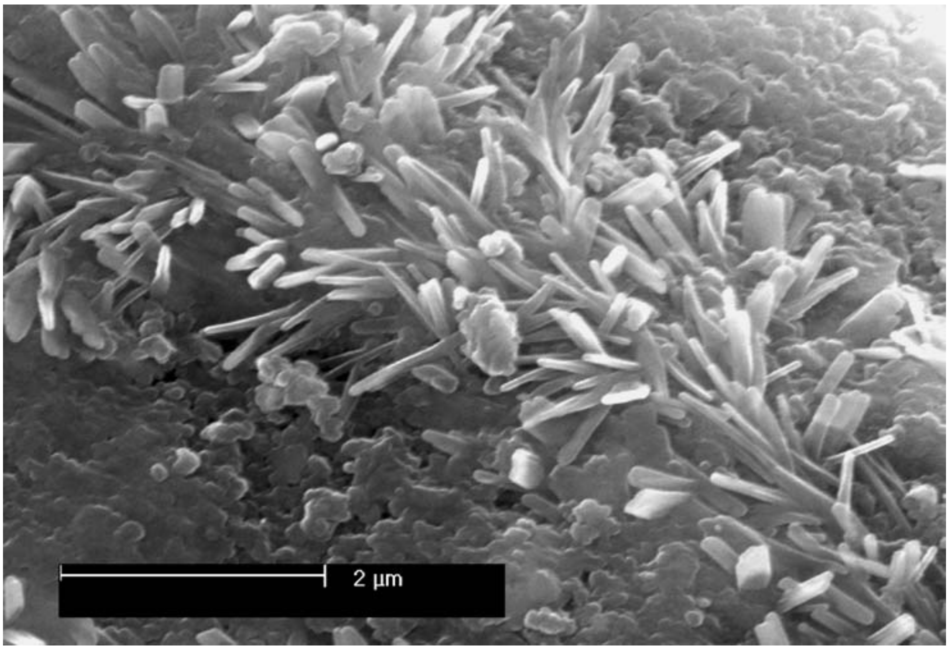

Figure 10 An example of the crystalline material that was common on the surface of MKAl08.

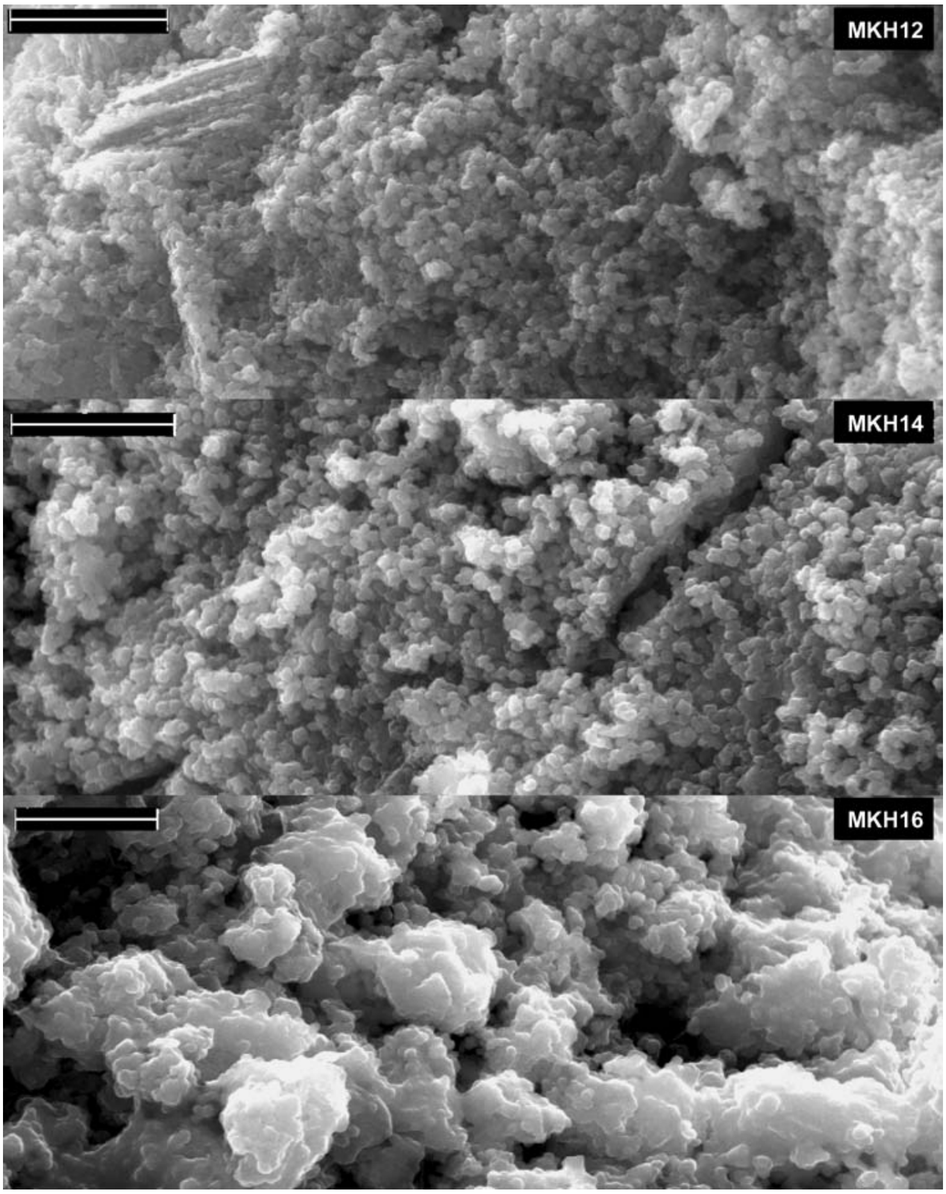

Figure 11 Inorganic polymer samples containing different amounts of water. The porosity clearly increases with increasing water. Scale bar represents 2 μm.

favour the formation of different complex aluminosilicate ions in solution. Inorganic polymers are believed to precipitate from these complex ions, thus their structure may affect that of the inorganic polymer. This may be why % $SiO_{2(liq)}$ has such a dramatic effect on strength and structure.

In the MKAl07–MKAl12 samples, the alkali/solid ratio changes (it decreases from MKAl07 to MKAl12). As it is the alkali which dissolves the metakaolin (hence enabling the inorganic polymer-forming reactions to take place), it would be expected that this ratio would be critical in determining the structure and final properties of the inorganic polymer. Indeed, the importance of this ratio has already been demonstrated by the results of the MKNa series of samples. Thus, the change in alkali/solid ratio may be one of the variables besides % $SiO_{2(liq)}$ which determines the structure and properties of the MKAl series samples.

MKAl08 contained more crystalline material than the other samples. In particular, there was a significant amount of crystalline phase on the surface (shown in Fig. 10). These crystals, which were sodium-rich aluminosilicates, did not correlate to lower strength as has been found in the past [8]. Interestingly, it has previously been reported that low Si/Al samples have the highest degree of crystallinity [11], which is in contradiction to the findings of the present work.

3.8. The effect of water content

Increasing the water content had a similar, but less dramatic, effect on the microstructure of the inorganic polymers compared to lowering the silica concentration or raising the alumina concentration. Four samples were prepared to determine the relationship between the water content and the microstructure and strength of inorganic polymers. In addition to the MKH12, MKH14 and MKH16 samples listed in Table I, an MKH10 sample was prepared, however it flash set during mixing and thus could not be poured into moulds. Increasing the H_2O/Al_2O_3 ratio from 12 to 14 to 16 increased the coarseness of the material and the amount of bridging material between the "balls" making up the microstructure (Fig. 11). The change between MKH14 and MKH16 was more distinct than that between MKH12 and MKH14.

The increasing porosity with increased water content can be partially attributed to the extra space taken up by water. The different shape of the microstructure (more discrete balls in the lower water samples) may be related to the polymerisation reaction proceeding more slowly with more water (sample MKH16 took the longest to set), allowing, more time for the dissolution and reprecipitation of the inorganic polymer. Such precipitation would occur as bridging material rather than on the balls (Ostwald ripening). Similar microstructures have been reported by Sun *et al.* [16] at very early ages using ESEM techniques although their attempt to obtain elemental maps of the matrix after 4 h only showed a uniform distribution of K, Si and Al without resolving specific details of compositional gradients.

The compressive strengths of the samples show a clear correlation to the water content and hence also to the microstructure. As expected, the low water sample (MKH12), which had lower porosity, was the strongest, and the high water sample (MKH16), which was highly porous, was the weakest.

4. Conclusions

In the sets of samples with varying Si/Al ratios (MKSi and MKAl), the proportion of the total silica added as liquid varied considerably. This may have been responsible for most of the structural and strength differences between these samples. It was, however, demonstrated that the Si/Al ratio alone has a significant effect.

These trends could be expected to hold for any inorganic polymer system containing predominantly the four oxides studied (it may be different for high calcium, mixed systems) although the exact concentrations of reactants for maximum strength would be different. These concentrations would depend on the composition and reactivity of the aluminosilicate. The physical limitations of mixing may also be a factor and may depend on the particle size, shape and surface chemistry, and the viscosity of the activator solution.

The results show the importance of correct selection of raw materials, as the physical properties of the raw materials have a significant effect on the handling and setting characteristics. For example, the particle size and shape of the metakaolin affect the viscosity of the slurry. It may be that with a different metakaolin, samples MKH10 and MKNa13 would have been successful and potentially significantly stronger than MKH12 or MKNa12. Studying some of these formulations over time is clearly crucial to further developing our understanding of inorganic polymer reaction kinetics.

The choice of raw materials also limits the range of combinations of variables possible. For example, the results of this study would indicate that a formulation $1.2Na_2O{\cdot}3.5SiO_2{\cdot}0.8Al_2O_3{\cdot}12H_2O$ would be the strongest inorganic polymer, however with the raw materials used here this would not be possible, and $1.2Na_2O{\cdot}3.5SiO_2{\cdot}0.8Al_2O_3$ would require $24H_2O$ which would be unlikely to set. Thus, as many studies have shown in the past, raw materials selection is the key to high-performance inorganic polymers.

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