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Chemical Engineering Journal 89 (2002) 63–73
Chemical Engineering Journal
www.elsevier.com/locate/cej

The effect of composition and temperature on the properties of fly ash- and kaolinite-based geopolymers

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Accepted 4 February 2002

Abstract

Fundamental research into the geopolymerisation process is increasing rapidly because of the potential commercial application of this technology. Despite this, however, very little work has been undertaken to determine the relationship between composition and temperature on the final chemical and physical properties of geopolymeric products derived from waste materials. The present study shows that the differences in reactivity of source materials, used during the synthesis of waste-based geopolymers, significantly affect the final properties of the geopolymeric material. It is proposed that these observed changes in material properties are due to the incomplete dissolution of the waste material. The water content, the fly ash/kaolinite ratio, as well as the type of metal silicate used have a substantial effect on the final properties of the geopolymer. In particular, the current work shows that the thermal history of the source materials, such as kaolinite, as well as the curing regime for the geopolymer are important factors that must be taken into consideration when designing a geopolymer product for a specific application.

Keywords: Geopolymer; Aluminosilicate; Waste materials; Inorganic polymer

1. Introduction

Geopolymers are the synthetic analogues of natural zeolitic materials. Geopolymeric materials possess excellent mechanical properties, including fire and acid resistance [1,2]. These properties make geopolymers an alternative construction material compared to Portland cement, and as a consequence, geopolymer technology has attracted a great deal of attention internationally in the past 20 years [3–5].

Most waste materials such as fly ash, blast furnace slag and mine tailings contain sufficient amounts of reactive alumina and silica that can be used as source materials for in situ geopolymerisation reactions. In previous work, many Al–Si containing source materials such as building residues, fly ash, furnace slag, pozzolan and some pure Al–Si minerals and clays (kaolinite and metakaolinite) have been studied [6–8]. Nevertheless, most of these studies have used the source materials on an arbitrary basis without consideration of the mineralogy or paragenesis of the individual minerals. It is important to note that the interrelationship between mineralogy and reactivity of individual minerals is extremely complex, and so further research on the ability of a wide variety of different materials to undergo geopolymerisation is required in order to elucidate the underlying chemical mechanisms.

The exact chemical mechanisms responsible for the dissolution and gel formation reactions in geopolymeric systems are still unknown. However, it is apparent that in many cases where materials such as fly ash and clays are used, the dissolution of the starting materials is not completed before the final hardened structure is formed [6]. In most cases, only small amounts of the silica and alumina present on particle surfaces need to take part in the reaction for the whole mixture to solidify. It is therefore generally believed that a surface reaction is responsible for bonding the undissolved waste particle into the final geopolymeric structure [9].

It is reasonable to assume that the type and nature of the starting materials used will directly affect the final physical and chemical properties of a geopolymer derived from waste materials. The current work therefore investigates the effect of various compositions of fly ash and kaolinite mixes on the physical and chemical properties of geopolymers. The effect of curing regime on final properties of the geopolymer has also been investigated.

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PII: S1385-8947(02)00025-6

2. Background

The term "geopolymer" was first used by Davidovits [9,10] to describe a family of mineral binders closely related to artificial zeolites. These structures consist of a polymeric Si–O–Al framework, similar to that found in zeolites. The main difference to zeolitic structures is that geopolymers are amorphous to X-rays, although the exact nature of this amorphicity is still not fully quantified.

The formation of geopolymeric materials follows much the same route as that for most zeolites, i.e. the three main steps: (1) dissolution with the formation of mobile precursors through the complexing action of hydroxide ions, (2) partial orientation of mobile precursors as well as the partial internal restructuring of the alkali polysilicates and (3) re-precipitation where the whole system hardens to form an inorganic polymeric structure. Amorphous to semi-crystalline geopolymers are therefore formed by the co-polymerisation of individual alumino and silicate species, which originate from the dissolution of silicon and aluminium containing source materials at a high pH in the presence of soluble alkali metal silicates [6,9].

Geopolymers are sometimes referred to as alkali-activated aluminosilicate binders. These materials differ substantially from ordinary pozzolanic cements, because geopolymers use a totally different reaction pathway in order to attain structural integrity. Whereas pozzolanic cements generally depend on the presence of calcium, geopolymers do not utilise the formation of calcium–silica-hydrates (CSHs) for matrix formation and strength. Instead, geopolymers utilise the polycondensation of silica and alumina precursors and a high alkali content to attain structural strength.

Various authors [6,11–15] have mentioned the importance of the H_2O/SiO_2 molar ratio in both the synthesis of geopolymers as well as other aluminosilicates such as zeolites. The mineralising and stabilising actions of water play important roles during both dissolution and polycondensation of zeolite and geopolymeric precursor species and therefore merit discussion in terms of their effect on the final properties of fly ash-based geopolymers. For the systems used in the current work it will be necessary to also consider factors such as the total amount of kaolinite present in the matrix. This is important to consider because a portion of the kaolinite will stay unreacted and will therefore affect the final structural properties of the geopolymer matrix.

3. Experimental procedures

3.1. Materials

Fly ash used in the synthesis of all geopolymer matrices was obtained from Tarong power station in Queensland, Australia. Other fly ash samples originated from Lake Macquarie, New South Wales. All fly ashes are of coal origin with chemical compositions as shown in Table 1. Kaolinite, grade HR1, was obtained from Commercial Minerals, Sydney, Australia, with compositions given in Table 2. All experiments were performed using the same batches of reagents and starting materials. Distilled water was used throughout.

Table 1
Composition of fly ash as determined by XRF analysis (mass, %)

Element as oxide	Tarong	Macquarie
SiO_2	61.4	59.9
Al_2O_3	33.0	21.6
CaO	0.6	2.9
Fe_2O_3	1.1	4.7
MgO	0.3	1.4
TiO_2	2.0	0.8
Na_2O	0.1	0.4
K_2O	0.1	2.3
SO_3	0.0	0.2
Loss on ignition	1.4	5.8

3.2. Synthesis

Sample preparation was performed as described previously [7] with at least a 7-day waiting period being observed before any tests were performed. In each case the samples were cast in 50 mm cubes, vibrated for 5 min and allowed to set at 30 °C for 24 h before being removed from the moulds and kept at room temperature for another 6 days. Various quantities of sodium or potassium silicate and sodium or potassium hydroxide were used for the synthesis of each geopolymer sample.

3.3. Yield strength measurements

In order to investigate the effect of using different fly ashes on the setting characteristics of the geopolymer paste, the early yield strengths of various mixes were measured by a vane rheometer as described by De Kretser [16]. A fresh mixture was made for every measurement and all experiments were repeated three times. Care was taken not to disturb the gel structure before any measurements were made.

Table 2
Composition of kaolinite as determined by fusion and XRF analysis (mass, %)

Element as oxide	Commercial minerals (HR1)
SiO_2	51.3
Al_2O_3	32.6
CaO	0.1
Fe_2O_3	1.1
MgO	0.3
TiO_2	1.1
Na_2O	0.2
K_2O	0.3
SO_3	0
Loss on ignition	13.0

3.4. Compressive strength testing

Compressive strength testing was performed as per AS 1012.9 [17] using 50 mm diameter cylinders with a 1:2 diameter to length ratio. Three cylinders of each sample were tested, with the experimental values being averaged. All samples were tested after 14 days. An Amsler FM 2750 compressive strength testing apparatus was used for all tests.

3.5. Specific surface area, infrared analysis and X-ray diffraction

BET surface areas were determined for all samples by using a Micromeritics Flowsorb ASAP 2020 with a 30/70 ratio of N_2 and He, degassing for 18 h at 95 °C. Infrared spectra were recorded on a Mattson Galaxy 2020 spectrometer using the KBr pellet technique (0.5 mg powder sample mixed with 250 mg of KBr). X-ray powder diffraction data were obtained using a Phillips PW 1800 diffractometer with Cu Kα radiation.

4. Results and discussion

4.1. The effect of clay and water content

Mostowicz and Berak [18] mentioned the tendency of zeolitic synthesis mixtures to form larger crystals when the total amount of water in the reaction mixture is increased. It seems that this is also the case for fly ash-based geopolymers. An increase in the size of regions of pseudocrystallinity will lead to a decrease in the specific surface area for each sample. This is because the total amount of inter-grain boundaries and surfaces will decrease accordingly while the internal specific surface area of each grain or area remains the same. Table 3 illustrates this point with the BET surface area values decreasing steadily as the amount of water is increased. It is significant to note that the surface area values are quite low compared to those found in zeolites (ca. 1000 m^2/g) and therefore the inter-grain boundaries contribute significantly towards the total measured specific surface area of the matrix.

It was mentioned previously [15] that the nucleation mechanism involves the ordering of water molecules by the alkali metal cations present. In particular, smaller alkali metal cations were mentioned [12] as being able to better order water molecules, compared to larger cations that are usually thought to disrupt the order of water molecules. The more disordered system, however, was reported [12] as having a higher degree of polycondensation which could also be the case where a higher water concentration is present with less cations to order it, resulting in a matrix with a higher degree of condensation and a lower surface area. This hypothesis has, however, not been proven conclusively as a multitude of other factors also affect the final surface area values observed in both geopolymers and synthetic zeolites. It should also be noted that reaction systems existing for geopolymer synthesis generally have water contents 10 or more times less than that used for conventional zeolite synthesis and many of the trends discussed here will therefore not necessarily be true for zeolite synthesis under hydrothermal conditions. It was also shown [18] that, although the hydroxyl ion concentration affects structure formation, this effect is less pronounced at very high alkali concentrations. At conditions such as that used in geopolymer synthesis a moderate increase in water content will therefore not dramatically affect the sizes of newly formed crystals or regions of pseudocrystallinity as the alkali content remains high. Water content, however, seems to have a limited effect on measured BET surface area values.

Table 4 presents a comparison between two systems containing no fly ash (matrices A1 and A2) and two systems with varying amounts of fly ash (matrices A3 and A4). In the case of matrices A1 and A2 the kaolinite used had an original specific surface area of 23 m^2/g, with both the geopolymer samples synthesised from this kaolinite having surface area values of around 3 m^2/g. This indicates that some form of polycondensation has taken place resulting in a less porous

Table 3
The effect of water content on BET values of matrices containing Tarong fly ash

Matrix	Hydroxide	Silicate	$(K_2O + Na_2O)/SiO_2$ (molar)	Clay (mass, %)	Water/fly ash (mass)	Surface area (m^2/g)
B1	K	Na	1.1	11	0.91	6.9
B2	K	Na	1.1	10	1.11	4.4
B3	K	Na	1.1	9	1.21	3.9

Table 4
BET values of matrices containing clay and Tarong fly ash

Matrix	Hydroxide	Water (mass, %)	$(K_2O + Na_2O)/SiO_2$ (molar)	Clay (mass, %)	Clay/fly ash (mass)	Surface area (m^2/g)
A1	K	11.6	1.2	73	∞	3.1
A2	K	6.8	1.2	84	∞	3.0
A3	K	10.2	1.2	64	5.0	2.2
A4	K	6.8	1.2	60	2.3	4.9

and more dense structure. It is also interesting to note that A1 contains double the relative amount of water present in A2 with virtually no effect on the measured surface area. The reason for this could be twofold. Firstly, it is possible that high alkali content mixtures are not affected significantly by the moderate addition of water. The second reason is that a large part of the kaolinite remains unreacted with water trapped in the layer structure and being prevented from evaporating by a surface geopolymerisation reaction as was proposed earlier [15]. Consequently, the effect of entrapped water moderates small changes in the quantity of added water.

With the addition of fly ash to the mix design of matrix A1, the resultant matrix A3 shows a marked drop in surface area measured. The main reason for this is an increased reaction between the soluble silicate species and aluminosilicate species dissolved from the amorphous glassy phases of the fly ash. In the case of matrix A3, the relatively small amount of spherical fly ash particles should also create denser packing with the plate-like structure of any unreacted kaolinite. Matrix A4 again shows the tendency for a higher surface area resulting from a lower total amount of water as compared to A3. The fact that relatively more fly ash is present that leads to disturbances in the packing of clay particles should also be considered. Clearly the water content affects surface area, but the effect for different kaolinite/fly ash ratios is still convoluted.

Table 5 presents information regarding the effect of an increase in clay content on both the measured specific surface area values as well as compressive strengths observed for a range of matrices containing Na or K as the primary alkali activator. It is significant to note that in the case of matrices S11, S6, S8 and S25 there seems to be a limit as to the amount of clay content that can be tolerated by the structure. This suggests that an optimum clay content exists to obtain a maximum in the compressive strength of the material. In the case of S25 this optimum has clearly been exceeded resulting in a sudden drop in measured compressive strength. The fact that the BET values do not closely follow the expected trend with respect to compressive strength has been dealt with elsewhere [15], although the internal surface area of matrix S25 is slightly higher, which agrees with its lower measured compressive strength when compared to S11, S6 and S8.

For matrices S12, S7 and S9, which contain Na, it can be seen that this sensitivity to clay content is not as obvious. The interactions of Na and K with synthesis species during geopolymerisation were shown [15] to be substantially different, resulting in altogether different amorphous structures exhibiting differing physical properties. Again the packing arrangement of individual particles will greatly change when the amount of kaolinite is either increased or decreased, causing changes in both compressive strength and internal surface area. The specific structure and its ability to tolerate high amounts of unreacted material will in each case determine the degree of change in these physical parameters while the nature of the structure is very dependent on the type of alkali cation used as was discussed earlier [15]. The interactions of different alkali metal cations with source materials such as fly ash are thought to account for the results in Table 5 where the two sets of data do not show the same trends with respect to an increase in clay content.

Fig. 1 indicates that a large part of the kaolinite remains unreacted in geopolymer samples. In particular, a number of characteristic kaolinite peaks can be seen where the spectra for matrices S11, S6, S8 and S25 are compared with that of kaolinite. The distinctive kaolinite peaks at 2θ values of 12.3, 19.8, 24.9, 45.4, 55.1 and 62.2° can be seen to increase in accordance with an increase in total clay content. As many of these peaks are absent in the spectrum of S11 and S6, while the clay content in these matrices is above the detection limits of the diffractometer, one could conclude that at smaller amounts of clay content, the kaolinite is almost fully digested to take part in the geopolymerisation reaction. At larger additions, however, the clay becomes a partially reacted filler that also serves to weaken the structure in most cases. Fig. 2 shows that this is also the case for the Na containing matrices S12, S7 and S9.

Table 6 presents the main infrared absorption peaks for the above matrices together with those of the fly ash and kaolinite used in their synthesis. The differences between absorption frequencies for the starting materials and synthesised geopolymers are an indication of the transformation that takes place during synthesis. The peaks around 467 cm^{-1} are attributed to in-plane bending of Si–O and Al–O linkages originating from within individual tetrahedra [19]. For the matrices under consideration there seems to be a slight shift in this wavenumber as more kaolinite is added.

Table 5
Compositions, specific surface area values and compressive strengths of matrices prepared from Tarong fly ash with all matrices having $M_2O/SiO_2 = 1.05$

Matrix	Hydroxide	Clay (mass, %)	Water (mass, %)	Water/fly ash (mass)	Strength (MPa)	Surface area (m^2/g)
S11	K	7	20	0.33	11.0	0.8
S6	K	14	20	0.35	11.0	1.0
S8	K	21	20	0.43	11.4	0.7
S25	K	41	20	0.75	5.0	1.1
S12	Na	7	20	0.33	8.5	0.3
S7	Na	14	20	0.36	8.0	0.6
S9	Na	21	20	0.43	10.6	0.2

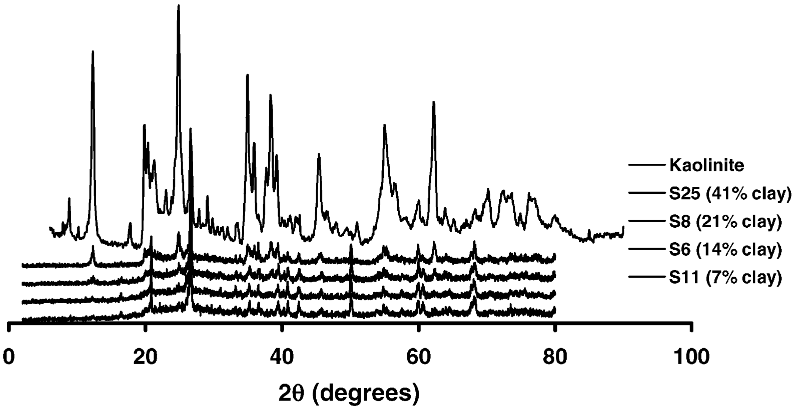

Fig. 1. The effect of increased clay content on the X-ray diffraction spectra of matrices containing Tarong fly ash and KOH.

Table 6
Main FT-IR absorption peaks for matrices in Table 5

Matrix	Clay (mass, %)	Wavenumber (cm^{-1})					
Fly ash	–	467	537	–	–	1033	1096
Kaolinite	100	470	539	938	1009	1033	1106
S11	7	469	539	–	1013	1035	1079
S6	14	469	540	942	1011	1035	1085
S8	21	469	539	939	1010	1033	1090
S25	41	471	540	939	1010	1033	1094
S12	7	468	538	–	1013	1038	1093
S7	14	469	540	942	1013	1036	1085
S9	21	472	539	939	1012	1033	1090

This is a result of a physical increase in kaolinite and not because of any chemical changes that have taken place during synthesis. This result suggests that a large amount of the kaolinite remains unreacted.

The peaks around 539 cm^{-1} originate from Si–O–Al bonds [20], where Al is present in octahedral co-ordination. For most of the synthesised geopolymer matrices these wavenumbers are shifted from those of the starting materials, suggesting that a change in the chemical bonding of the system has taken place. A change in the co-ordination number of Al from 6 to 4 would cause peaks to appear at approximately 850 cm^{-1} [20]. However, these were only found in matrices containing small amounts of kaolinite, typically <7% (by mass). It seems therefore that when small amounts of kaolinite are present some dissolution takes place at a high pH, with subsequent formation of tetrahedral Al. It is possible that when large amounts of kaolinite are added, reaction takes place at the surface predominantly, which strengthens the Si–O–Al bonds, but does not dissolve the Al. This leaves the latter to retain its octahedral nature. This changing of the environment of the Al is also reflected in the measured vibrational peaks around 939 cm^{-1}, which are characteristic of the Al–OH bending mode [21]. Bending of these bonds requires a higher energy than that associated with bending of the same bonds in the kaolinite structure. Again the addition of substantial amounts of kaolinite seems to mask this effect, with the wavenumber decreasing as the total amount of kaolinite increases.

Characteristic vibrations at 1009 and 1033 cm^{-1} have been assigned to asymmetric stretching of Al–O and Si–O bonds originating from within individual tetrahedra [19]. The fact that both of these vibrational frequencies are higher

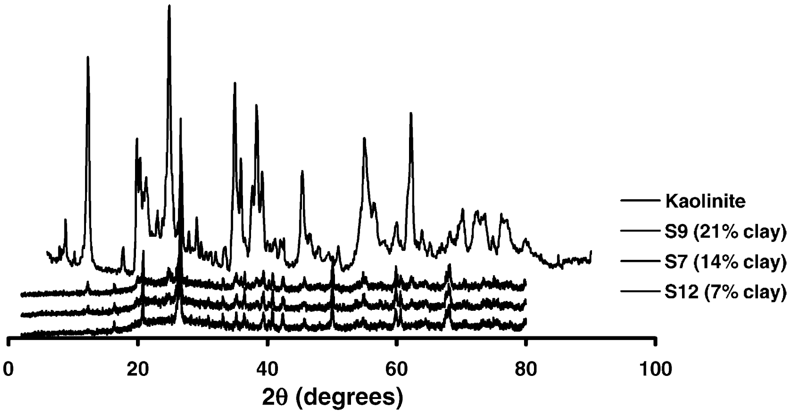

Fig. 2. The effect of increased clay content on the X-ray diffraction spectra of matrices containing Tarong fly ash and NaOH.

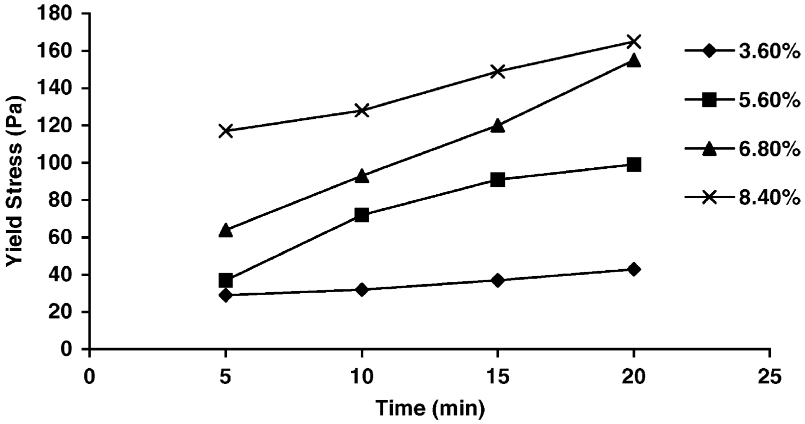

Fig. 3. The effect of increased kaolinite content on the initial yield stress of a geopolymer paste containing Port Augusta II fly ash with the following compositional variables. Water/fly ash (mass) = 0.24, $M_2O/SiO_2 = 0.25$ and K as alkali metal activator. Mass (%) of kaolinite is indicated.

in the geopolymer matrices than in any of the starting materials again signifies that a change has taken place in the bonding structure within individual tetrahedra. The characteristic vibrations around 1087 cm^{-1} have been assigned to asymmetric stretching of linkages between tetrahedra and these are generally of a lower value in the synthesised products when compared to those found in any of the starting materials. This effect is, however, again overshadowed when the clay content is increased substantially but points to a markedly different association between individual tetrahedra after geopolymerisation has taken place.

Fig. 3 gives the yield stress at constant shear for the initial setting of a geopolymeric paste when the kaolinite content is increased. An increased solid content of the paste would result in higher measured yield stress values and this is apparent for all the data points in Fig. 3. The rate of change of the yield stress seems to be affected the most at kaolinite contents of 5.6 and 6.8%. This indicates that some stoichiometric reaction between the soluble silicate and the kaolinite is taking place, as was proposed for metakaolinite by Rahier et al. [22]. The compositional molar ratios of kaolinite to soluble silicate are very close to unity at kaolinite contents of 5.6 and 6.8%, which are in agreement with the values found by Rahier et al. [22] for a metakaolinite system. An increase in kaolinite content to 8.4% overshadows this effect with no differences in the rate of change of the yield stress values when compared to the system containing 3.6% kaolinite, except for the baseline shift caused by a system containing more solid material. At higher contents of kaolinite some reaction will therefore take place although it could again be concluded that a large part of the kaolinite stays unreacted.

In summary, the inclusion of kaolinite serves to provide structure forming species to the overall geopolymerisation process. However, a large amount of added kaolinite may not take part in the synthesis reaction at all. The mechanism through which kaolinite reacts with fly ash and the alkali present, involves both digestion of the clay to form soluble species as well as a surface reaction where clay particles are unable to fully dissolve.

4.2. The effect of curing conditions and calcining temperature

It has been reported previously that for metakaolinite-based systems the temperature at which samples are cured greatly affects its final compressive strength [23]. The results presented in Table 7 testify to the fact that this is also the case for fly ash-based systems. Khalil and Merz [23] do not discuss their data that indicate an almost 100% improvement in compressive strength when geopolymer samples are cured at 50 and 80 °C as opposed to curing at room temperature. It is significant, however, that initial curing at higher temperatures does not increase compressive strength substantially above that achieved by curing at room temperature. Curing at higher temperatures for more than a couple of hours does seem to positively affect the development of compressive strength. These trends are also apparent from Table 7 where curing at 70 °C seems to substantially improve

Table 7
The effect of curing conditions on the compressive strength of a matrix containing Macquarie fly ash with compositional variables: clay (kaolinite) content = 15% (mass), water/fly ash (mass) = 0.31, $M_2O/SiO_2 = 1.14$, $Al_2O_3/SiO_2 = 0.57$ and K as alkali metal activator[a]

Time (h)	Temperature (°C)					
	30	50	70	30 B	50 B	70 B
6	6	–	14	19	–	28
12	15	26	34	7	22	21
24	20	12	33	19	24	29
48	19	–	28	21	–	15
Average (12/24 h samples)	17	19	34	13	23	25

[a] Samples were cured in an oven, open to the atmosphere except for samples denoted by "B" which were cured in sealed plastic bags under the same conditions. Compressive strength values in MPa.

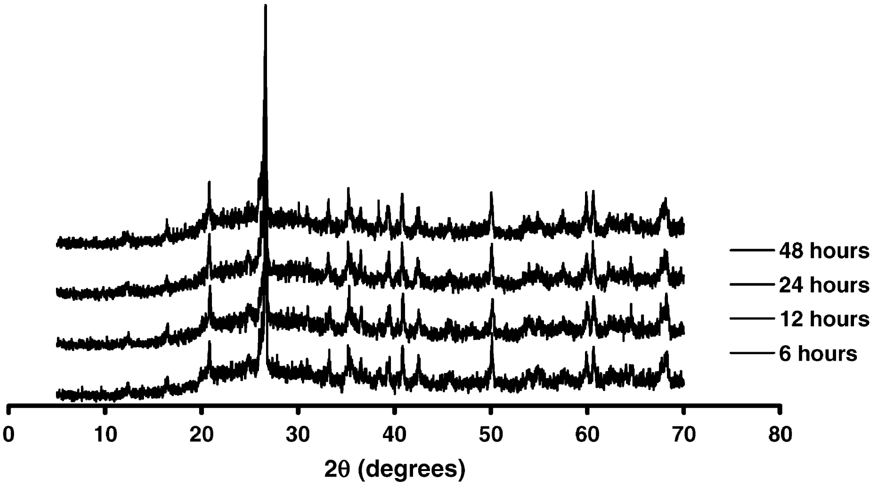

Fig. 4. The effect of curing time on the X-ray diffraction spectra of a geopolymer sample containing Macquarie fly ash with compositional variables: clay (kaolinite) content = 15% (mass), water/fly ash (mass) = 0.31, $M_2O/SiO_2 = 1.14$, $Al_2O_3/SiO_2 = 0.57$ and K as alkali metal activator. Curing took place at 30 °C.

compressive strength compared to curing at 30 °C for the same period of time. It is of interest to note that curing for longer periods of time at elevated temperature appears to weaken the structure, suggesting that small amounts of structural water need to be retained in order to reduce cracking and maintain structural integrity. This reduction in compressive strength at longer curing times is also supported by the work of Khalil and Merz [23]. It seems that prolonged curing at elevated temperatures breaks down the gelular structure of the geopolymer synthesis mixture, resulting in dehydration and excessive shrinkage as the gel contracts without transforming to a more semi-crystalline form.

Fig. 4 shows that longer curing times do not affect significantly the crystalline part of the geopolymer sample. This again indicates that the changes responsible for the differences in compressive strength originate and take place within the amorphous part of the structure, as supported by earlier work [7]. Fig. 5 indicates much the same trend with no apparent crystalline effects being observed when curing at different temperatures is considered, again signifying that any changes affecting structural integrity take place within the amorphous gel structure. From Table 7 it can also be seen that the samples cured at higher humidity in sealed plastic bags do not exhibit improved compressive strengths. This is in contrast with what could be expected from the curing of conventional cementitious products.

These effects are, however, very subtle as can be inferred from the infrared data presented in Table 8 where most peaks do not differ substantially from one another where the samples were cured with or without sealed bags. For samples cured at 30 °C, the peaks at 468 and 539 cm^{-1} are not affected by the curing method used and this is also the case for

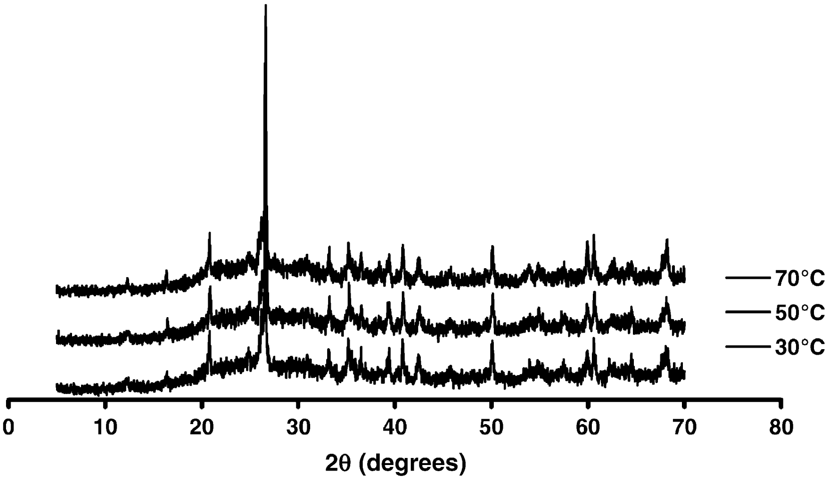

Fig. 5. The effect of curing temperature on the X-ray diffraction spectra of a geopolymer sample containing Macquarie fly ash with compositional variables: clay (kaolinite) content = 15% (mass), water/fly ash (mass) = 0.31, $M_2O/SiO_2 = 1.14$, $Al_2O_3/SiO_2 = 0.57$ and K as alkali metal activator. Curing took place at 30, 50 and 70 °C for a period of 24 h.

Table 8
Selected FT-IR absorption peaks for matrices in Table 7

Temperature (°C)	FT-IR absorption peaks (cm^{-1})			
	6 h	12 h	24 h	48 h
30	468	467	468	466
	539	539	539	541
	1034	1034	1035	1036
30 (sealed bag)	467	467	468	470
	540	539	540	539
	1035	1034	1034	1032
70	471	471	467	470
	539	539	539	539
	1031		1037	1038
		1082	1086	1086
70 (sealed bag)		466	466	470
		539	540	539
		1033	1033	

Table 9
The effect of calcining conditions of metakaolinite on the compressive strength of a matrix containing Macquarie fly ash with the following compositional variables: clay (metakaolinite) content = 14% (mass), water/fly ash (mass) = 0.31, $M_2O/SiO_2 = 1.14$, $Al_2O_3/SiO_2 = 0.57$ and K as alkali metal activator[a]

Time (h)	Temperature (°C)						
	300	400	500	600	700	800	900
1	14	14	30	54	17	7	8
6	11	31	13	9	15	7	15
12	12	47	28	25	14	3	15
24	6	32	31	18	6	15	12

[a] Compressive strength values in MPa.

samples cured at 70 °C. The peaks around 1033 cm^{-1}, which correspond to the asymmetric stretching of Si–O and Al–O bonds, seem to be affected by curing of the sample in sealed bags and their wavenumbers are generally slightly lower than for samples cured without bags. The slightly lower wavenumbers are indicative of weaker intra-tetrahedral bonding and could contribute to the lower compressive strengths measured for samples cured in sealed bags. It is also of interest to note that the wavenumbers of peaks around 1033 cm^{-1} seem to increase with increasing curing time in the case of samples cured without bags at both 30 and 70 °C, indicating a process of bond strengthening taking place. This is not the case where samples are sealed in bags, with these values staying constant for the 70 °C samples and decreasing with time for the 30 °C samples. It is proposed that the saturated atmosphere in the bags results in conditions more suitable to the formation of slightly weaker bonds.

The dehydroxylation or calcining of kaolinite to form metakaolinite has been studied extensively [24,25], and the process involves the transformation of the octahedral co-ordinated Al sheet in kaolinite to a tetrahedral co-ordinated form through the loss of water resulting from the breaking of OH bonds. Davidovits [26] used this more reactive form of kaolinite as the main solid reactive component of geopolymer systems. Although the work of Rahier et al. [22] contributed significantly to understanding of the reaction mechanism of metakaolinite-based geopolymers, the fly ash system with small additions of kaolinite discussed here remains largely unstudied as far as its reaction mechanism is concerned. In order to quantify the role of metakaolinite in a fly ash-based system, a limited investigation was conducted to determine the optimum calcining parameters for maximum compressive strength development in the final product. The results and composition of the matrix used are presented in Table 9. It is significant to note that maximum compressive strengths were achieved

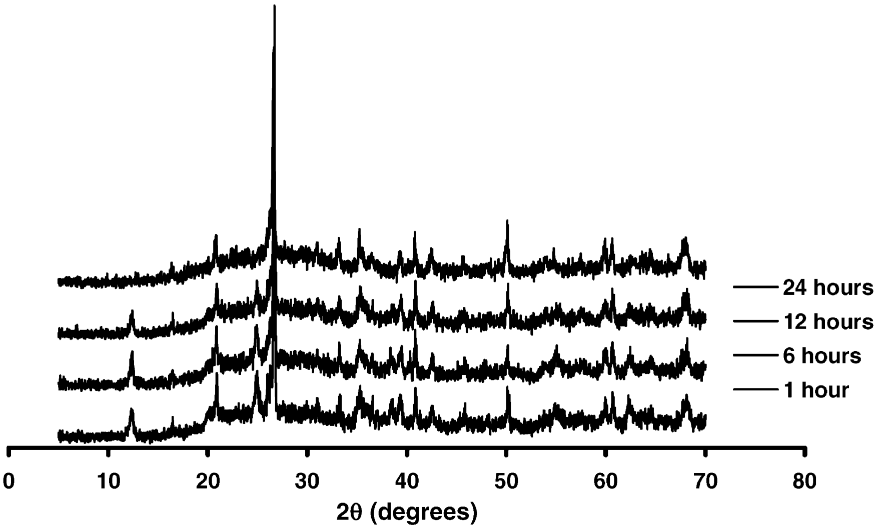

Fig. 6. The effect of calcining conditions of metakaolinite on the X-ray diffraction spectra of a matrix containing Macquarie fly ash with the following compositional variables: clay (metakaolinite) content = 14% (mass), water/fly ash (mass) = 0.31, $M_2O/SiO_2 = 1.14$, $Al_2O_3/SiO_2 = 0.57$ and K as alkali metal activator. Spectra presented include metakaolinite calcined at 400 °C for 1, 6, 12 and 24 h.

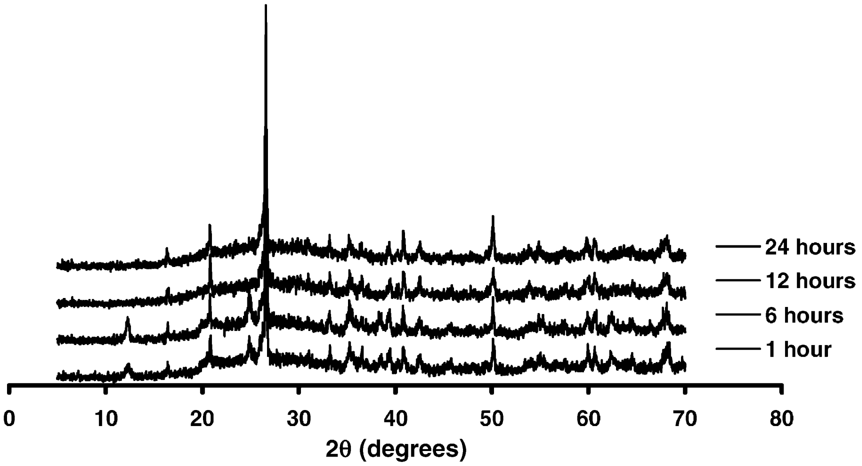

Fig. 7. The effect of calcining conditions of metakaolinite on the X-ray diffraction spectra of a matrix containing Macquarie fly ash with the following compositional variables: clay (metakaolinite) content = 14% (mass), water/fly ash (mass) = 0.31, $M_2O/SiO_2 = 1.14$, $Al_2O_3/SiO_2 = 0.57$ and K as alkali metal activator. Spectra presented include metakaolinite calcined at 500 °C for 1, 6, 12 and 24 h.

when metakaolinite calcined between 400 and 600 °C was used. The higher the temperature used during the calcination process, the shorter the time needed to obtain a metakaolinite that gives a maximum compressive strength. This means that longer calcining times are required at 400 °C and significantly shorter times at 600 °C.

The reasons for the above-mentioned observation are well explained in the literature and involve a transformation to mullite when kaolinite is subjected to thermal treatment [24,25]. Metakaolinite is an intermediate in this process and kaolinite calcined at higher temperatures or for longer times at slightly lower temperatures will contain more of the mullite phase as well as amounts of segregated silica making it less soluble and less reactive in the geopolymer system. The X-ray diffraction spectra presented in Fig. 6 show that the characteristic kaolinite peaks at $2\theta = 12.2$ and 24.7° only disappear from the spectra after 12–24 h of calcining at 400 °C, whereas the same peaks are absent from the spectra in Fig. 7 after 6–12 h of calcining. It should be kept in mind, however, that the X-ray diffraction spectra include unreacted fly ash as well as the reaction products of the various reactions that have taken place in hardening of the matrix. From Fig. 8 the differences in crystallinity between the spectra of kaolinite and a standard metakaolinite can be observed, notably the relatively large amorphous component present in metakaolinite and the absence of the characteristic kaolinite peaks at $2\theta = 12.2$ and 24.7°. These peaks are also present in the spectrum of the geopolymer matrix in Fig. 8, containing metakaolinite calcined at 500 °C for 6 h.

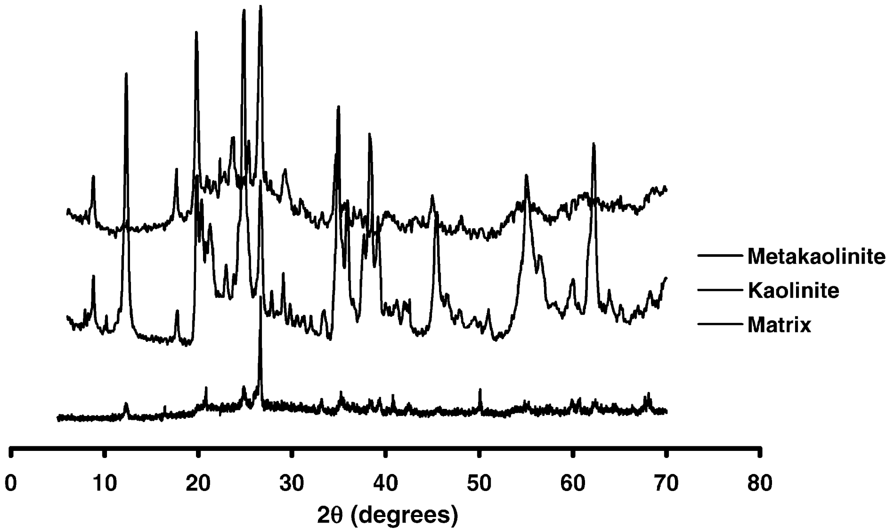

Fig. 8. The X-ray diffraction spectra of kaolinite, metakaolinite calcined at 750 °C for 24 h and a fly ash-based geopolymer matrix containing Macquarie fly ash with the following compositional variables: clay (metakaolinite calcined at 500 °C for 6 h) content = 14% (mass), water/fly ash (mass) = 0.31, $M_2O/SiO_2 = 1.14$, $Al_2O_3/SiO_2 = 0.57$ and K as alkali metal activator.

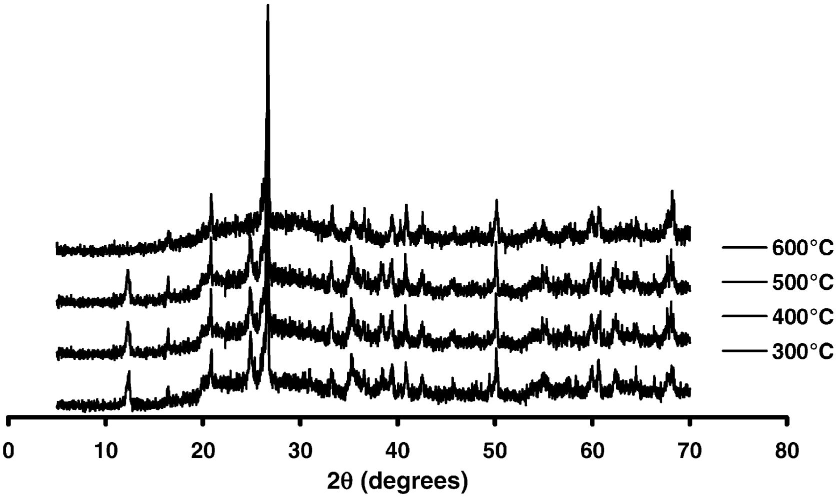

Fig. 9. The X-ray diffraction spectra of geopolymer matrices containing Macquarie fly ash with the following compositional variables: clay (metakaolinite calcined for 6 h) content = 14% (mass), water/fly ash (mass) = 0.31, $M_2O/SiO_2 = 1.14$, $Al_2O_3/SiO_2 = 0.57$ and K as alkali metal activator. Calcining of metakaolinite used took place at 300, 400, 500 and 600 °C.

Spectra published by Madani et al. [21] showed that these peaks were absent in metakaolinite, although they reappeared after contacting the metakaolinite with NaOH for 50 h. A reduction in size of these peaks was observed after a further 100 h of reaction with NaOH. These changes were attributed to zeolite formation and could account for the fact that the peaks at $2\theta = 12.2$ and 24.7° seem to increase in height when the 6 h spectrum is compared to the 1 h spectra in Fig. 7. It is significant to note that the compressive strength values presented in Table 9 do not seem to correlate well with differences in the degree of sample crystallinity when compared to the spectra in Fig. 9. This again confirms that most of the reaction products of geopolymer reactions are amorphous to X-rays.

Table 10 presents some infrared absorption data for the matrices under discussion. The elimination of the OH bending frequency at 913 cm^{-1} is evident as samples are calcined at higher temperatures. The presence of this band in samples containing metakaolinite calcined at 400 °C is also evidence of a portion of unreacted kaolinite remaining in the sample matrix. The band at 538 cm^{-1} (characteristic of octahedral co-ordinated Al [20]) also disappears at higher temperatures or longer times before reappearing at 553 cm^{-1}. A shift in the band at 468 cm^{-1} to lower wavenumbers around 455 cm^{-1} could point to the formation of a zeolitic phase [21] where kaolinite calcined at higher temperatures was used. It is also of interest to note that the position of the main peak around 1033 cm^{-1} stays fairly constant until higher calcining temperatures are used. This is an indication that more drastic changes take place, affecting the Al–O and Si–O bonds inside individual tetrahedra. Again it is difficult to determine to what extent the geopolymerisation reaction contributes to this shifting of the main peak, although data published by Madani et al. [21] suggest that reaction with an alkali could lead to this peak shifting to lower wavenumbers.

Table 10
Selected FT-IR absorption peaks for matrices containing metakaolinite calcined under different conditions

Temperature (°C)	FT-IR absorption peaks (cm^{-1})			
	1 h	6 h	12 h	24 h
400	468	467	467	461
	538	539	539	
	914	915	916	
	1033	1033	1033	1034
600	464	457	452	452
	538			
	1032	1030	1030	1032
700	460	460	453	453
		554	553	
	1025	1032	1032	1024
900		458		461
		1061		1075

5. Conclusions

There exists an interrelationship among the various material parameters that affect the final structure and property of fly ash-based geopolymers. It was shown that the water content, curing as well as calcining conditions affect the final properties of a geopolymer with less water not always being desirable when mix designs are considered. The clay content also impacts on the structural properties with a surface reaction expected to bind the clay into the structure, although unreacted clay particles could pose problems due to water absorption and retention. Mild curing seems to improve physical properties while curing under higher humidity is not usually beneficial. Rapid curing and/or curing at too high temperatures will result in cracking and thus have a negative effect on physical properties. The current work has therefore shown that the manufacture of a geopolymer product for specific applications requires careful consideration of process conditions such as curing temperature and humidity, in addition to the initial mix design.

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