Reviews

Do Geopolymers Actually Contain Nanocrystalline Zeolites? A Reexamination of Existing Results

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Geopolymers are a class of aluminosilicate materials synthesized by alkaline or alkali-silicate activation of solid alumina- and silica-containing precursor materials at ambient or higher temperature. These products have highly significant commercial and technological potential, but the exact physicochemical nature of the geopolymeric binder phase has never before been determined. Through analysis of existing experimental results from the literature and comparison with related systems, in particular the hydrothermal synthesis of zeolites, geopolymeric binders are identified as being comprised of agglomerates of nanocrystalline zeolites compacted by an amorphous gel phase. The degree of crystallinity is largely determined by product formulation and synthesis conditions. Results from powder X-ray diffraction, microscopy, electron diffraction, mechanical strength testing, and calorimetry are analyzed and shown to be consistent with the theory presented. The implications of nanocrystallinity are discussed, and areas to be targeted in further experimental investigations are identified.

1. Introduction

"Geopolymer" is the name that, since the late 1970s, has been applied to a wide range of alkaline- or alkali-silicate-activated aluminosilicate binders of composition $M_2O \cdot mAl_2O_3 \cdot nSiO_2$, usually with $m \approx 1$ and $2 \leq n \leq 6$, and where M represents one or more alkali metals.[1,2] Some geopolymers also contain alkaline earth cations, particularly Ca^{2+} in products based on industrial wastes such as granulated blast furnace slag or fly ash. Geopolymers may be synthesized at ambient or elevated temperature by alkaline activation of aluminosilicates obtained from industrial wastes,[3−7] calcined clays,[8−10] melt-quenched aluminosilicates,[11] natural minerals,[12] or mixtures of two or more of these materials.[13] Activation is achieved by addition of highly concentrated alkali metal hydroxide or silicate solutions. Filler materials including conventional concrete aggregates such as basalt may be used to enhance desired properties including strength[8,14−16] and density.[17] However, structural characterization of both waste-based materials and the geopolymers synthesized from these materials is greatly complicated by the highly impure nature of these systems, and the use of natural minerals or melt-quenched materials in geopolymerization is not yet widespread. Composites consisting of a fiber matrix and a geopolymeric binder phase have also been shown to have interesting and potentially very useful properties.[18,19] Geopolymer−calcium phosphate composites are also being investigated for potential application as a biocompatible synthetic bone replacement material.[20,21] Preliminary testing of activation by sodium aluminate solution displayed some

potential for further development,[22] but further work in this area has not been performed. The primary focus of this investigation will therefore be the formation of geopolymers by alkali metal hydroxide or silicate activation of calcined clays, particularly calcined kaolinite clay (metakaolin).

The term "geopolymer" has been a source of some confusion, with some authors[23,24] using the same word to describe organic materials polymerized under geothermal conditions. However, the use of the term "geopolymer" as a description of alkaline- or alkali-silicate-activated aluminosilicate materials is sufficiently widespread that it will be used in this study without further comment. The terms "polysialate" and compositional variants thereof[1,2] are sometimes used in the general description of geopolymeric binders. However, these terms will not be used in this investigation due to their limited applicability in the description of such a complex composite system, as the implication of the polysialate nomenclature system is that only integer Si/Al ratios are possible. This is clearly not true, suggesting that "polysialate" descriptions do not adequately represent the full range of possible geopolymeric structures. "Inorganic polymer glass"[10] and "hydroceramic"[25] are alternative terms used to describe materials that can also be classified as geopolymers, but neither term is currently in widespread use. Also, each of these terms have only ever been applied to a limited subset of the class of materials that can be described as geopolymeric, and so are not generally applicable in a wider sense.

The geopolymeric binder phase is often described as "X-ray amorphous".[9,26] Many authors have noted formation of phases described as either semicrystalline or poly-

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crystalline,[9,27−29] particularly in products synthesized at a higher temperature.[2,30] However, the chemical and physical nature of these phases has rarely been subjected to detailed analysis, and is very difficult to determine due to the complex and intergrown nature of the binder phases and the presence of significant quantities of unreacted raw materials. The early work of Rahier et al. presented claims of geopolymeric materials, "inorganic polymer glasses", in which full reaction of metakaolin was achieved.[10,31] However, more recent reports from these workers have not mentioned these claims of complete reaction,[32] and every microscopic or spectroscopic study of geopolymers has revealed the presence of significant quantities of unreacted material.

Hydrothermal techniques have been used in mineral synthesis processes for more than 50 years,[33] particularly in the production of a wide range of synthetic aluminosilicate structures both with and without naturally occurring analogues. Some of these synthetic compounds are zeolitic, and have therefore received much attention over the past several decades in their applications as catalysts and molecular sieves. Much is therefore known about the hydrothermal synthesis of zeolites, and this knowledge may be used to gain a further understanding of the chemistry of related systems. It has been stated that geopolymers may be viewed as the amorphous analogue of zeolites,[12,34] as synthesis may be carried out under similar hydrothermal conditions, and the presence of "zeolitic water" has been noted in DTA experiments.[3,8] Early in the development of geopolymers as a commercial product, synthesis temperatures of up to 150 °C were used,[2] making geopolymerization a true hydrothermal process. More recently, ambient temperature synthesis has been shown in some circumstances to give a stronger product,[30] but the classification of geopolymerization as a hydrothermal process remains valid at these lower temperatures.

The proposed amorphous geopolymer structure is often categorized as an aluminosilicate gel.[9,35−37] It has therefore been proposed that this structure is related to the aluminosilicate precursor gels from which zeolites are hydrothermally generated.[5,38,39] Due primarily to the difficulties inherent in detailed structural analysis of gel-phase systems, this suggestion has not yet been subjected to rigorous investigation. The fact that zeolitic materials are often detected in geopolymeric systems[2,9,29,36,40] suggests that this proposal is definitely worthy of further study.

Some authors[2,6,10,26,27,32] have also described the geopolymer phase as "glassy". This claim is based primarily on the apparent amorphicity of the geopolymeric binder and analogies drawn between geopolymerization and sol−gel glass processing. However, little detailed structural analysis has been carried out in this area, and the absence of organic species from the geopolymer reaction slurry will doubtless cause significant structural differences from the more common alkoxysilane-derived sol−gel glasses. The effect of the presence or absence of small organic species on geopolymer or sol−gel glass structure is an area worthy of further investigation, but such analysis will only be truly possible once the physicochemical nature of geopolymeric materials is better understood.

Table 1. Products Formed by Hydrothermal Treatment of Solid Aluminosilicates at Different Temperatures and Water Contents

water content	temperature	
	low	high
low	geopolymer[a]	geopolymer[b] or zeolite[c]
high	aluminosilicate gel[d]	zeolite[e]

[a] From refs 4 and 30. [b] From refs 2, 25, and 38. [c] From refs 42 and 46. [d] From refs 47 and 48. [e] From refs 33, 49, and 50.

Taking into account the existing confusion and disagreement regarding the exact chemical nature of geopolymers which is currently hindering the commercialization and application of this highly promising technology, the purpose of this paper is therefore 2-fold. First, to provide the first broad overview of the literature of geopolymers, and second to reexamine existing results in the light of the new structural theory proposed. The concept of a geopolymer as consisting of an agglomeration of nanocrystalline zeolitic phases bound together by an aluminosilicate gel is highly plausible from a chemical thermodynamic and mechanistic standpoint, and assists in the interpretation of several features of existing experimental data that have to-date resisted comprehensive analysis.

2. Critical Literature Evaluation and a Proposition

2.1 Geopolymerization as a Hydrothermal Mineral Synthesis.

Hydrothermal synthesis using calcined clays, particularly metakaolin (calcined kaolinite), has long been used in the production of low-silica zeolites.[41−45] The physicochemical conditions under which zeolites are obtained from metakaolin are very similar to those used in geopolymerization. Temperature and water content are generally higher in zeolite synthesis systems than in geopolymerization, but there is no clear distinction between the conditions under which each product is obtained. An indication of the products obtained under different conditions is given in Table 1. Approximate dividing lines between "low" and "high" temperature may be drawn at approximately 40−80 °C, and between "low" and "high" water content at H_2O/M_2O ratios of around 10−20. However, the distinctions between "low" and "high" values of each parameter are left intentionally vague as the exact nature of the products formed is subject to other synthesis variables, particularly Si/Al ratio and reaction time. In general, longer reaction times tend to give more crystalline products. Activation of metakaolin with alkali metal silicate rather than hydroxide solution tends to give geopolymeric rather than highly crystalline zeolitic products at high temperature and low water content, and in most cases gives a product of a higher compressive strength.

Suggestions of a correspondence between geopolymerization and zeolite synthesis have been strengthened by the use of high-resolution microscopic techniques to observe phase formation within geopolymeric binders. Transmission electron microscopy (TEM) has shown the geopolymer phase to be nanoparticulate, with many particles approximately 5 nm in diameter surrounded by what is either a secondary continuous phase or regions of nanoporosity, or a mixture of the two.[51,52] Electron diffraction studies of geopolymers show regions displaying varying degrees of crystallinity,

ranging from highly crystalline, nanocrystalline, or poly-crystalline through to fully amorphous,[51,53,54] but indexing of the diffraction patterns has never yet been carried out. High-resolution electron microscopy (HREM) shows that the particulate phase contains distinct regions of short- to midrange order, which are rapidly amorphized by beam damage.[51] The observed structures and behavior resemble the structures and amorphization process first noted by Bursill et al.[55] in their HREM investigation of zeolite A.

However, it is common that no newly formed crystalline phases are identifiable in X-ray diffraction (XRD) analysis of geopolymeric products. It can be deduced from these seemingly conflicting results that the crystallinity observed in the HREM and electron diffraction experiments is present on a length scale below the detection limit of XRD. Similar apparent discrepancies between XRD and electron diffraction results have been noted in studies of aluminosilicate zeolite precursor gels,[48] as well as in a variety of other inorganic systems.[56,57] In each case, crystallinity on a length scale of around 5 nm was detectable by electron diffraction experiments but not by XRD. This correlates very well with the observed presence of 5-nm particulates with varying degrees of crystallinity within the geopolymeric binder phase, and provides a plausible explanation for a series of apparently contradictory results present in the literature. Several studies of aluminosilicate crystallization kinetics have also quantitatively displayed the instrumental limitations of XRD crystallinity analysis by comparison of the development of the degree of crystallinity calculated from FTIR[42,58] or DTA[59] with corresponding XRD results.

Aiello et al.[60] carried out one of the first comprehensive microscopic studies of hydrothermal zeolite synthesis, and found that the initial particle morphology seen in the synthesis of zeolites in dilute solution is leaf-like, or "lamellar". The newly formed lamellae were initially amorphous to electron diffraction, but were seen by electron microscopy and diffraction to develop nanocrystalline regions within the general lamellar geometry as the reaction progressed. The research program led by Subotić[48,61] has since shown that the amorphous precursor gels from which zeolites are crystallized in fact contain many "quasicrystalline" regions, which act as sites for zeolite nucleation as the gel dissolves. Mintova et al.[62,63] have also shown that zeolite growth from gel precursors begins with the formation of nanosized crystallites within the amorphous gel particles. These crystallites resemble the ordered domains observed in HREM images of geopolymeric binders, adding further weight to the proposition that geopolymers contain a significant level of nanoscale crystallinity in the form of zeolitic nanocrystals.

Studies of the mechanism of zeolite formation have shown that the primary observable growth units in crystallization of silicalite-1 from clear solution are particles around 2−5 nm in size.[64−66] The exact structure of these particles remains a point of contention, with Ravishankar et al.[64] claiming to have observed a fully crystalline "nanoblock" structure, while Kragten et al.[65] have presented results showing the particles to be somewhat less constrained in structure and defect-filled, but still with some zeolitic
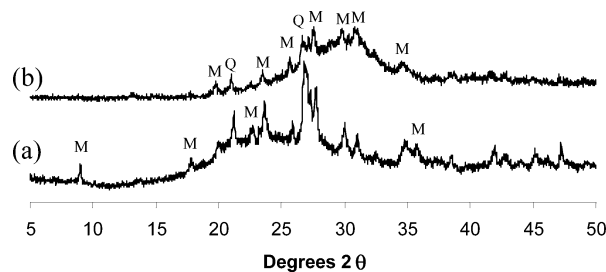
Figure 1. Cu Kα X-ray diffractograms of (a) metakaolin (MetaStar 501, Imerys, UK), and (b) a metakaolin/potassium silicate geopolymer with nominal composition $K_2O \cdot Al_2O_3 \cdot 2.65SiO_2$, cured at 70 °C for 24 h. All crystalline peaks are assigned to impurities in the metakaolin: muscovite (M) and quartz (Q).

character and pore networks. Viewing these results in the context of the current investigation, the nanoparticulate and at least partially zeolitic nature of the silicalite-1 growth units may be used as further confirmation of the significance of nanometer-level crystallinity in geopolymeric materials.

This information may then be used to provide an explanation for the observed properties of geopolymers: nanocrystalline regions within the circular particles observed under TEM will give electron diffraction patterns typical of crystalline structures, while being ordered on a length scale too short to provide the characteristic X-ray diffractograms of their actual crystal structure. As the crystalline state minimizes the free energy of a system, the formation of crystalline regions via the dissolution−reprecipitation process of geopolymerization is not unexpected, but identification of the chemical nature of these regions remains a point of some contention. Despite the complications inherent in analysis of diffractograms of "amorphous" materials, significant conclusions may still be reached by careful investigation and comparison of the existing published results in this field.

2.2 XRD Analysis of "Amorphous" Aluminosilicates and Some Comparisons. The major feature of XRD powder diffraction patterns of geopolymers is a largely featureless "hump" centered at approximately 27−29° 2θ. An example of a typical geopolymer X-ray diffractogram is provided in Figure 1. Numerous other examples may be found in the literature.[26,29,35,67,68] However, the most outstanding feature of all published diffractograms of geopolymers is that, regardless of the choice of solid aluminosilicate source (metakaolin with or without added calcium, fly ash, or blast furnace slag), activating solution (sodium or potassium hydroxide at different concentrations, with or without soluble silicate), and curing conditions (time, temperature, and humidity), the broad hump centered at around 27−29° 2θ is present in every case. This ubiquitous peak must therefore be considered the distinguishing feature of the diffractogram of any geopolymer, and so its identification becomes central to the determination of the microstructure of a geopolymer.

Sometimes described as a "diffuse halo peak",[2] this broad hump is generally attributed to the amorphous aluminosilicate gel assumed by most authors to be the primary binder phase present in geopolymeric systems.[9−11,69] However, high-resolution microscopy of geopolymeric systems has shown this gel phase to be present largely in the form of nanosized aluminosilicate particles,[7,51,54,70] as exemplified by Figure 2.
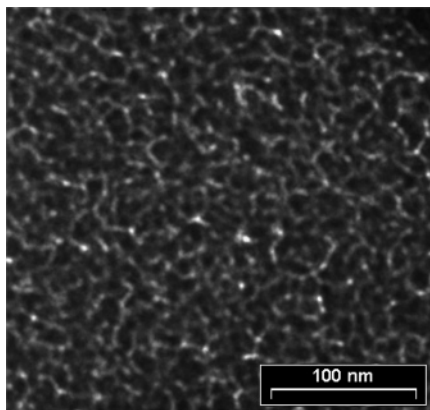
Figure 2. TEM micrograph of a section of a sodium silicate/metakaolin geopolymer of nominal composition $Na_2O\cdot Al_2O_3\cdot 4.3SiO_2$, cured at 40 °C for 24 h. Micrograph courtesy of Peter Duxson.

The fundamental theory of powder X-ray diffraction analysis of materials is that the angles at which diffraction occurs from a polycrystalline sample are characteristic of particular interlayer spacings in the crystal structure of the sample.[71] Therefore, materials with similar interlayer spacings, and thus similar crystal structures, will produce similar diffraction patterns. Reduction of the effective crystallite size of a sample causes broadening of the peaks observed in a diffractogram, with the diffractogram of a fully amorphous material displaying very broad, featureless peaks, or "humps". However, the exact boundary between "crystalline" and "amorphous" materials is very difficult to determine. The International Union of Crystallography defines a crystal as "any solid that gives a discrete X-ray diffraction diagram".[72] This means that a crystal is defined by its measurable properties. The definition is then clearly dependent on the measurement technique used because, as was demonstrated earlier in this report, X-ray amorphous materials can display crystallinity readily observable via electron diffraction. The importance of the vagueness of this definition in the context of characterization of geopolymeric systems is that even "X-ray amorphous" structures will produce a diffractogram that is to some extent characteristic of the particular structure present. These diffractograms are unlikely in themselves to provide positive identification of an unknown material as is the case with fully crystalline samples. However, comparison of the diffractogram of a sample of unknown structure with those of materials of similar chemical composition and known structure can at least show with which materials the unknown sample does or does not share significant structural features.

The geopolymeric binder phase is often assumed to be formed simply by the hardening of an amorphous aluminosilicate gel,[9,37,73] with no description or analysis of any potential crystallization pathways. Comparison of the XRD diffractogram of a truly amorphous aluminosilicate gel with that of a geopolymer can be used to comment on the validity of this assertion. Figure 3[74] shows X-ray diffractograms obtained from the solids present after heating a mixture of colloidal silica and sodium aluminate by 0.10 °C/min for different times as described by Table 2.

Diffractogram A in Figure 3 shows that the XRD pattern of an aluminosilicate gel formed by mixing colloidal silica
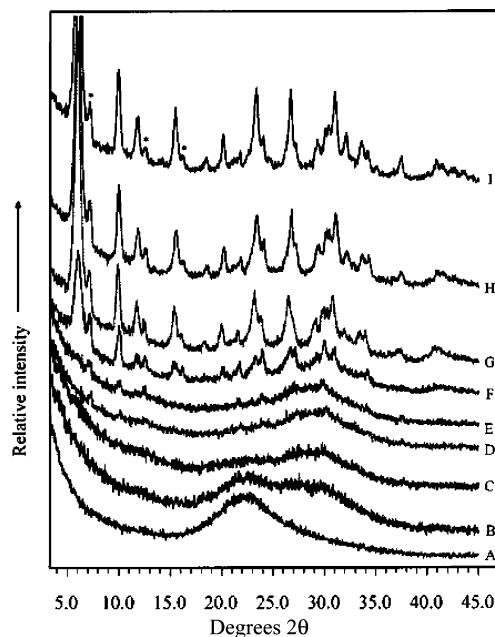

Figure 3. Cu Kα X-ray diffractograms of the solid phases present during heating of a mixture of colloidal silica and sodium aluminate as described in Table 2. From ref 74. Copyright 2000 American Chemical Society.

Table 2. Heating Times and Final Temperatures Corresponding to Diffractograms in Figure 3[74]

sample	time (h)	final temperature (°C)
A	1.64	34.4
B	4.52	51.5
C	6.09	60.8
D	7.11	66.8
E	8.28	73.8
F	9.42	80.5
G	9.99	83.9
H	10.9	89.0
I	13.7	97.2

with sodium aluminate solution displays a broad peak centered at approximately 22° 2θ. This is similar to the location of the broad peak observable for a dried layer of colloidal silica on a copper substrate.[75] From this similarity, it may be inferred that the initial gelation upon addition of sodium aluminate solution to colloidal silica resulted in only minor structural changes in the majority of the silica particles. The compositional analysis carried out in the same investigation[74] confirms this observation, with the solids giving diffractogram A in Figure 3 having a Si/Al ratio of approximately 14. Therefore, only a small amount of aluminate has been incorporated from the solution into the gel phase, which is comprised primarily of unreacted colloidal silica particles, at this early stage of the reaction.

However, as can be seen from diffractograms B–E in Figure 3,[74] the nature of the aluminosilicate gel changes rapidly on heating. The peak at 22° 2θ decreases in intensity as heating progresses, and is replaced by a new broad peak centered at ∼28° 2θ. As heating progresses further, this peak resolves into a number of sharp peaks identifiable as those produced by a mixture of FAU- and LTA-type zeolites.[74] The transition from the broad 28° peak of diffractogram D to the sharp peaks of diffractogram I in Figure 3 is observed to be a gradual process of peak sharpening rather than diminution of the existing peak and formation of new peaks.

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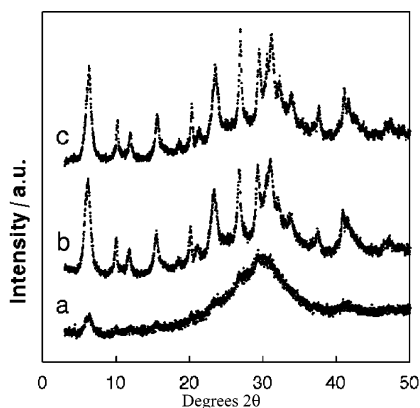
Figure 4. Cu Kα X-ray powder diffractograms of nanosized zeolite X crystals synthesized from sodium aluminate and sodium silicate solutions at 60 °C while shaking at 250 rpm for (a) 1 day, (b) 2 days, and (c) 4 days. From ref 76. Copyright 2002 American Chemical Society.

Taking into account also the peak-broadening effects of small crystal size as previously discussed, it is clear that the broad ∼28° peak is attributable to the initial development of crystalline zeolites on a length scale below the detection limits of XRD. The authors of the original study described this phase as "precrystallization", with zeolite structure present on a length scale of no more than 4 unit cells,[74] or approximately 8−10 nm. The identification of the corresponding peak in geopolymeric systems (Figure 2) as being due to the nanocrystalline phases identifiable by electron diffraction but amorphous to XRD[54] is therefore further supported.

A similar peak-sharpening effect was noted by Zhan et al.[76] during synthesis of nanometer-sized crystals of zeolite X, where a diffractogram showing a broad peak centered at ∼29° 2θ and attributed to nuclei of zeolite X is seen to sharpen in the diffractogram of the final product as the crystals grow above the detection limit of the instrument. These diffractograms, reproduced here as Figure 4, show that the broad peak due to crystallization on length scales below 10 nm (Diffractogram a) after 1 day of reaction resolves into the slightly sharper but still size-broadened peaks of diffractograms b and c. The mean crystallite size calculated by Scherrer's equation for the zeolite present after 4 days of reaction was 23 (±4) nm.[76]

The work of Dutta et al.[47] is also valuable in confirming the assignment of the broad "amorphous hump" centered at ∼28−29° 2θ to nanometer-sized zeolitic structures. These authors compared the XRD and Raman spectroscopic data shown in Figure 5, obtained under conditions as described in Table 3, and concluded that the change in XRD peak position and shape with heating from diffractograms a and b to diffractogram c in Figure 5 was due to zeolite nucleation. Diffractograms a and b in Figure 5 may be considered to represent vacuum-dried silica gel with slight (<8%) Al incorporation as impurities in the tetrahedral gel network. The peaks occur at a 2θ angle similar to those due to zeolitic nuclei, but the significant difference in composition between these high-silica gels and geopolymer-forming systems allows identification of diffractogram c in Figure 5 as the diffractogram most likely to be comparable to those of the nanocrystalline portion of geopolymeric materials.
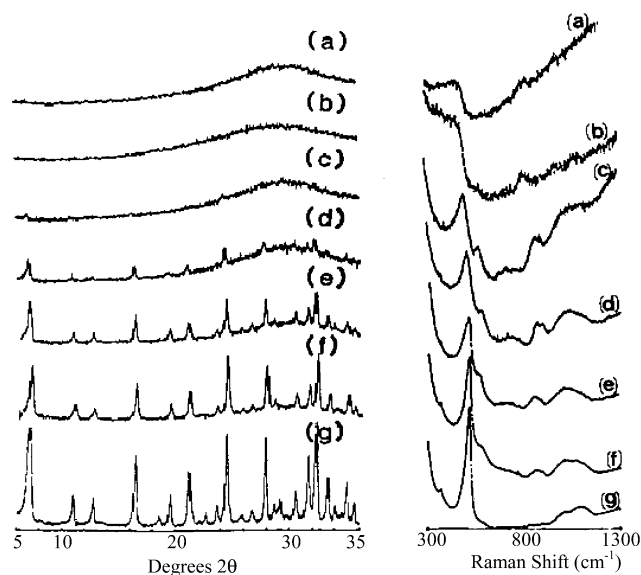

Figure 5. Cu Kα X-ray diffractograms and Raman spectra of the solid phase present at different times during aging and crystallization of a colloidal silica/sodium aluminate mixture, as described in Table 3. From ref 47. Copyright 1987 American Chemical Society.

Table 3. Preparation Regimes for Samples Used in Figure 5[47]

	preparation regime	Si/Al ratio in solids
a	mixing of reactants for 35 min	26
b	mixing + aging at room temperature for 24 h	15
c	mixing + aging + heating at 90 °C for 6 h	2.5
d	mixing + aging + heating at 90 °C for 12 h	1.7
e	mixing + aging + heating at 90 °C for 18 h	1.7
f	mixing + aging + heating at 90 °C for 25 h	1.8
g	mixing + aging + heating at 90 °C for 30 h	1.8

The coincidence of the XRD peak position of the aluminosilicate gels in Figure 5 with the peaks assignable to nanocrystalline zeolites throughout this investigation is a significant complication in the analysis of these diffractograms. However, it by no means invalidates the assignment of the peak to nanocrystalline structures, but rather shows that the superposition of peaks due to gel and nanocrystallite structures is possible. This corresponds to the observation that the phase surrounding the nanocrystallites is an aluminosilicate gel, and provides an explanation for the relatively small changes observed in XRD between geopolymers that are known to be highly nanocrystalline and those in which a much lower degree of crystalline phase formation is known to occur. In particular, crystallization has been observed to be less prevalent in geopolymeric systems containing higher levels of silica,[77] but XRD analysis shows only very slight differences between moderate- and high-silica geopolymers.[78] The coexistence of nanocrystalline and amorphous gel phases, both displaying diffraction peaks in approximately the same region, is consistent with experimental data, and allows a deeper level of analysis of these data than is possible by viewing the structure as a purely amorphous binder.

The onset of zeolite nucleation is also obvious in the Raman spectra presented in Figure 5, where several peaks attributable to a zeolitic structure can be seen to have developed after 6 h of heating despite the mainly featureless nature of the corresponding XRD diffractogram. The XRD diffractograms of Figure 5 show resolution of the sharp
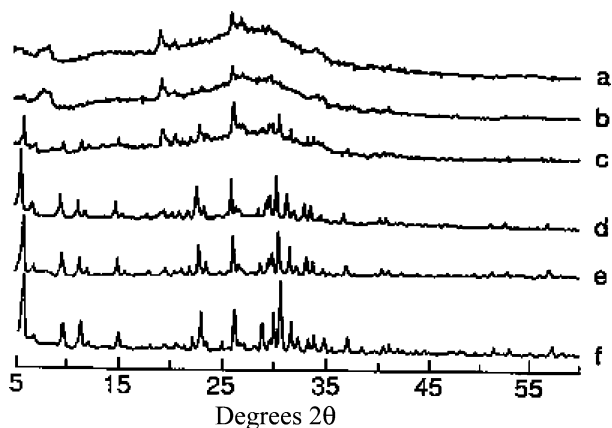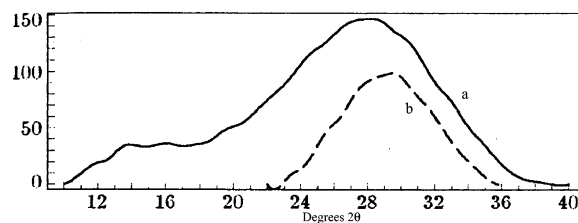
Figure 6. Cu Kα X-ray diffractograms of the products of the leaching of metakaolin extrudates with mixed NaOH/KOH solution at 51 °C for (a) 6 h, (b) 24 h, (c) 48 h, (d) 72 h, (e) 96 h, and (f) 240 h. Reprinted with permission from ref 42. Copyright 1997 Elsevier Science.

Figure 7. Cu Kα X-ray diffractogram of the aluminosilicate gels precipitated upon mixing alkali metal aluminate and silicate solutions with Si/Al ∼1.5, where the alkali metals used are (a) Na, and (b) K. Reprinted with permission from ref 48. Copyright 1994 Elsevier Science.

zeolite diffraction peaks from the broad peak with growth of the nanocrystals, as is also observed in Figure 3[74] and in Figure 6.[42] This therefore provides further confirmation of the assignment of the characteristic geopolymer "amorphous hump" centered at approximately 28° 2θ, at least in part, to diffraction from zeolite nanocrystals less than 10 nm in size, coexisting with an amorphous gel phase.

Figure 6[42] shows a time-resolved sequence of powder X-ray diffractograms detailing the transformation of metakaolin to zeolite X in mixed KOH/NaOH solution at 51 °C. As in the case of zeolite synthesis from colloidal silica and sodium aluminate as shown in Figure 3[74] and also in other investigations of zeolite formation by leaching of metakaolin,[43] a broad peak centered at approximately 28° 2θ is seen in diffractogram a in Figure 6 to replace the initial 22° peak early in the transformation of metakaolin to the zeolite product. Peaks characteristic of zeolite A, most notably at ∼7° 2θ, are observed in addition to the "amorphous hump" in the intermediate stages of the reaction (diffractograms b and c). However, these peaks decrease in intensity as zeolite X, the preferred product under the relatively low temperatures used,[79,80] is formed. This is in accordance with the accepted applicability of Ostwald's law of successive reactions to zeolite synthesis systems.[50] Davidovits[81] and Benharrats et al.[45] each obtained corresponding results in the reaction of kaolin or metakaolin with NaOH at 150 and 80 °C respectively, with zeolite A formed initially in each case and hydroxysodalite increasingly prominent as the reaction continued.

The presence of multiple zeolitic species in the reaction system of Akolekar et al.,[42] with conditions similar to those under which geopolymerization is carried out, suggests that a variety of zeolitic species will also be present in geopolymeric products. Authors identifying particular zeolites within a geopolymeric matrix have noted the presence of hydroxysodalite, faujasites (zeolites X and/or Y), and zeolite A,[9,29,38,40,77,82,83] with zeolite formation favored at lower activating solution Na₂O/SiO₂ ratio[77] and higher temperature.[9]

The XRD results of Subotić et al.[48] for two different aluminosilicate zeolite precursor gels (Figure 7) formed by mixing clear sodium aluminate and silicate solutions show broad peaks centered at ∼28−29° 2θ, matching the "amor-

phous hump" in the geopolymeric system. This may initially appear to suggest that an aluminosilicate gel structure could be solely responsible for the characteristic geopolymer peak. However, examination of the procedures by which these gel specimens were prepared for powder XRD analysis[84] reveals that after removal from the synthesis solution, the solid/gel material was rinsed in distilled water, then dried at 50 °C for 24 h and at 105 °C for 24 h. Electron diffraction studies of these solids[48] show the development of significant crystallinity on a nanometer scale, with *d* spacings matching selected *d* spacings of zeolite A. A recent study of Choy et al.[85] showed that heating of certain solid aluminosilicate precursor materials (a pillared montomorillonite clay) with solid NaOH under "ambient atmospheric conditions" at 80 °C for 60 min causes a solid-state transformation to give a zeolitic phase with significant crystallinity. It is therefore highly plausible that a similar phenomenon occurred during the drying of the aluminosilicate gel of Subotić et al.,[48] and that the observed broad peaks centered at ∼28−29° 2θ are at least in part due to the initial stages of the development of crystallinity within the amorphous gel, as was the case in the study of Yang et al.[74] as previously discussed. This further supports the proposal that the corresponding "amorphous hump" in the diffractogram of a geopolymer is also due to the products of nucleation in a hydrothermal synthesis process.

X-ray diffractograms of unreacted metakaolin, for example diffractogram a in Figure 1, display a broad "amorphous hump" at ∼22° 2θ. This peak may also be observed in geopolymeric systems in the work of Rowles and O'Connor,[29] where the quantity of activating solution used was only sufficient for partial activation of the metakaolin. Large amounts of unreacted metakaolin were present in the geopolymeric matrix, and the ∼22° peak is obviously superimposed on the characteristic ∼28° 2θ geopolymer peak in each case.

Phair et al.[86] stated that "crystallinity cannot yet be excluded as a means of strength development in geopolymeric systems." Far from excluding crystallinity as a means of strength development, information obtained by considering geopolymers as agglomerates of nanometer-scale crystal nuclei bound together by an amorphous gel phase may now be used to reinterpret and explain previously inexplicable experimental results. However, before this can be done these results must be reexamined with a view to reconciling various sets of seemingly contradictory data that have been published in the field of geopolymers and geopolymerization.

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2.3 Analysis of Mechanical Strength Results. The most commonly employed measure of the success or otherwise of a geopolymerization process is the compressive strength of the final product. This is primarily due to the low cost and simplicity of compressive strength testing, and the importance of strength development as a primary measure of the utility of materials in different applications in the construction industry. Due to the wide variety of product sizes, geometries, strength testing apparatus, and procedures used by different authors, strength results are generally not directly comparable between different research groups,[29] or even between different authors within a single research group.[12,36,87] Therefore, comparison of results or identification of trends by numerical comparison of data across different studies cannot be undertaken with any degree of accuracy.

Strength testing has primarily been carried out on Na^+-containing systems due to the high costs involved in production of K^+- or Cs^+-containing specimens sufficient in size and number for comprehensive strength testing investigations. However, recent work[30,78] shows identical trends in mechanical properties for K^+- and Na^+-containing systems, so in the absence of significant data to the contrary it may be assumed that any trends observed in mechanical strength testing of Na^+-containing geopolymers are applicable at least in a general sense to systems containing other alkali metal cations.

The investigation of Xu and van Deventer[88] tested a mixture of kaolinite, albite, and fly ash which, when activated with alkali silicate solution, gave a stronger geopolymeric product than any combination of any two of the three solid aluminosilicate sources used. This was attributed to the differing contributions of each of the source materials to the product: rapid solidification of highly soluble components leached from fly ash gave early strength,[53] albite dissolved relatively little but due to its high hardness acted as an aggregate in the cementitious product, and kaolinite reacted slowly to give high final strength.[89] The effect of the albite in increasing compressive strength on a macroscopic scale can be seen qualitatively in Figure 8,[88] where the progress of the crack in the center of the micrograph has clearly been prevented by the unreacted albite particle. Similar effects were observed by Phair et al.[16] by the addition of zirconia particles to geopolymeric systems.

However, the results of these investigations detailing the effects of inclusion of large crystalline particles on the compressive strength of geopolymeric systems must be interpreted very carefully when attempting to explain the effects of nanometer-scale crystallinity as proposed in the current work. These crystal nuclei are much too small to act effectively as aggregates, and so any data obtained from systems with significant aggregate effects will not necessarily be directly applicable. A prime example of this is seen in the data of Phair et al.,[16] where addition of 3% zirconia by mass to a fly ash-based geopolymer gave a significant improvement in compressive strength, but further zirconia addition to 5% or 7% by mass reduced strength to below that of the "pure" geopolymer. At low levels of zirconia addition, the unreactive particles were able to act as an aggregate in the geopolymeric binder to improve strength.
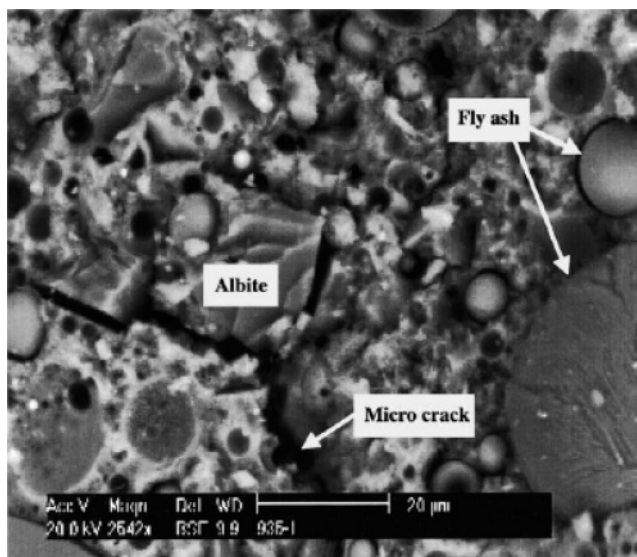

Figure 8. SEM micrograph of a geopolymer formed by activation of a 1:2:4 solid mixture of albite, kaolinite, and fly ash with potassium silicate solution. Reprinted with permission from ref 88. Copyright 2002 Elsevier Science.

However, when too much zirconia was added, the fact that the zirconia particles were bound only weakly to the aluminosilicate matrix and no $Zr-O-Si$ bonds were observed[16] meant that the binder network was disrupted to such an extent that strength was reduced.

These results may then be used in conjunction with further work of Phair et al.[86] on the interaction of sodium silicate with zirconia particles to further elucidate the chemical nature of geopolymers. Sodium silicate precipitates were found to bind chemically to the zirconia surface in the absence of dissolved aluminate species,[86] but the clear absence of such chemical binding in geopolymeric systems[16] shows that the number of regions of aluminate-free sodium silicate precipitate in a geopolymer will be small. This is in agreement with studies of incorporation of aluminate into dissolved silicate species, showing that silicate–aluminate exchange reactions are sufficiently labile to allow aluminate centers to be rapidly distributed throughout a silicate-dominated system.[90−93]

Having outlined the limitations of mechanical strength data in the analysis of geopolymerization, it must also be observed that several highly significant results regarding chemical structure may be obtained from these data. In particular, the importance of the charge-balancing role of cations within a geopolymeric structure is exemplified by Figure 9. This figure displays a sharp maximum in both compressive and tensile strength at a Na/Al ratio of exactly 1, corresponding to a single Na^+ cation balancing the charge on each tetrahedral Al center. Corresponding, but less detailed, results for sodium silicate activation of metakaolin have also been published by Rahier et al.[10]

Figure 10[29] appears to contradict this assertion, showing a peak in strength at Na/Al ∼1.25. However, the formation of crystalline Na_2CO_3 during geopolymerization was also noted, and consumed a significant proportion of the Na used. EDS analysis of the geopolymeric binder phase of "medium" and "high" strength products with nominal Na/Al ratios of
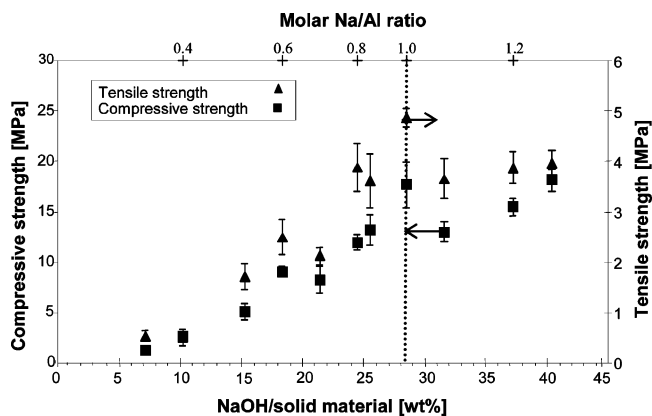
Figure 9. Influence of the Na/Al ratio on the mechanical properties of geopolymers formed by activation of metakaolin with NaOH solutions of differing concentrations, cured at 35 °C for 24 h. Data from ref 94.
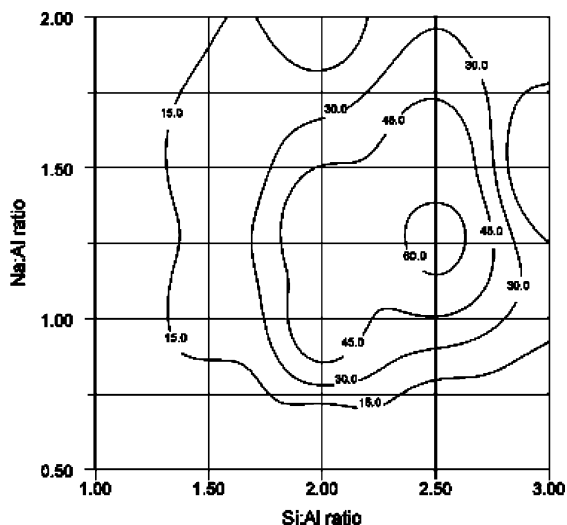
Figure 10. Contours of compressive strength variation with nominal composition for geopolymers formed by activation of metakaolin by sodium silicate, cured at 75 °C for 24 h then under ambient conditions for 7 days. The contours are in units of MPa, relative to the strength of the product with Na/Al = 0.5, Si/Al = 1.0. From ref 29. Reproduced by permission of the Royal Society of Chemistry.

1.29−1.5 showed actual Na/Al ratios of around 0.9 in the binder phase. It has been suggested that this figure may be a slight under-reporting of the actual Na content due to instrumental difficulties,[29] thereby confirming the charge-balancing requirement of Na/Al = 1 previously observed. In contrast, the "low" strength product in the same investigation, with nominal Na/Al = 0.7, showed negligible formation of Na_2CO_3 and a binder-phase Na/Al ratio matching the nominal ratio exactly. This shows that the charge-balancing requirement of the anionic tetrahedral Al centers is stronger than the propensity of the system to form Na_2CO_3, and therefore that the charge-balancing positions will be filled preferentially to the formation of carbonate crystals in the absence of excess alkali cations.

The work of Hos et al.[11] showed maximum strength was achieved at Na/Al ∼0.4, a strength approximately 2.5 times greater than achievable at any other Na/Al ratio tested by these authors. However, this investigation utilized melt-quenched glass as a solid aluminosilicate source, and much of this remained unreacted throughout geopolymerization. SEM micrographs of the product formed with Na/Al = 1
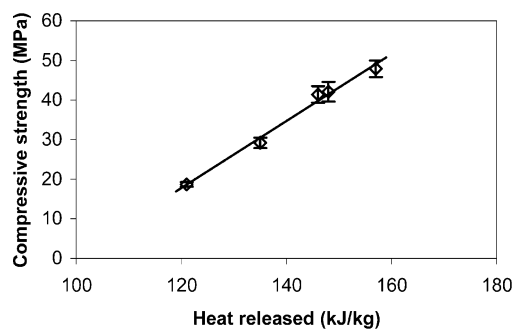
Figure 11. Relationship between total reaction enthalpy and product strength in geopolymers formed by activation of metakaolin with sodium silicate. Error bars represent one standard deviation. Data from ref 10.

clearly show large needlelike crystals of Na_2CO_3. EDS mapping of the actual binder phase of the strongest sample again showed a Na/Al ratio of 1 in this phase.[11]

The requirement for a particular stoichiometric M^+/Al ratio to achieve maximum strength in geopolymeric binders adds further support to the proposal presented in the current work that these binders display a significant degree of chemical ordering, and nanocrystallinity in particular. All the crystalline zeolitic structures previously mentioned as having been identified within geopolymeric binders require full charge-balancing by one alkali metal cation for each tetrahedral Al center. In contrast, amorphous structures do not show such strong charge-balancing requirements, as their less-ordered nature allows variation from strict tetrahedral geometry and therefore allows methods of charge compensation other than strict association of a single alkali metal cation with each Al center.

2.4 Analysis of Calorimetric Data. Another quantitative analytical method commonly used in the analysis of the geopolymerization process is calorimetry. A variety of data have been gathered by techniques including differential scanning calorimetry (DSC),[10,30,86] modulated DSC (MDSC),[31,32] and isothermal conduction calorimetry (ICC).[68,95] The most important results obtained to date from calorimetric experiments generally fall into one of two categories: (1) determination of the correspondence between degree of reaction and physical properties, and (2) elucidation of the mechanism of reaction. As the mechanism of geopolymerization is an area requiring considerably more study before definitive conclusions may be reached, the primary focus of this section will be the use of existing calorimetric data in conjunction with the nanocrystallinity hypothesis to describe the observed physical properties of geopolymers.

The data of Rahier et al.[10] presented in Figure 11 illustrate most clearly the relationship between degree of reaction and mechanical properties of a geopolymer. As all stages of the reaction between metakaolin and alkali silicate solution have been observed in ICC experiments to be exothermic,[68] reaction enthalpy may be used as a direct representation of the extent of the reaction.[83] Figure 11 shows a linear relationship, exact to within experimental error margins, between reaction enthalpy and product compressive strength. This corresponds with the absence of any observable aggregate effect in alkali-activated metakaolin systems due to the low hardness of metakaolin.

In contrast, fly-ash-based systems display no such clear general trend due to the compositional and physical differences between fly ashes from different sources[38,96,97] or even between different batches of ash from the same source.[98] This renders a detailed analysis of the general trends in these results extremely complex, so further discussion will primarily be focused on metakaolin-based systems.

A combination of calorimetric and IR data has been used to show that the degree of formation of crystalline materials generally increases with increasing alkali concentration in the NaOH activation of metakaolin/Ca(OH)$_2$ mixtures.[95] This high alkalinity also tends to give delayed setting, particularly in the absence of dissolved silicates in the initial activating solution.[68] A source of some confusion in the comparison of these data with those plotted in Figure 11[10] is the reversal of the strength/heat release relationship observed in Figure 11; with the investigation of Alonso and Palomo[68] instead showing the samples with the highest heat release had the lowest strength. However, the presence of high levels of calcium in the reaction mixtures used by Alonso and Palomo renders any direct comparisons with the data of Rahier et al.[10] impossible. Addition of significant levels of calcium to a geopolymer-forming system has been shown to give a phase-mixed CSH-amorphous aluminosilicate material rather than the zeolite-gel systems formed in the absence of calcium.[99] This will be expected to display very different synthesis pathways leading to its quite distinct microstructure, meaning that the heat release/strength relationships are not expected to be comparable to those of calcium-free systems.

3. Sources and Implications of Crystallinity

Nucleation in zeolitic systems has been shown to occur via replacement of water in the hydration shells of cations by small aluminate or silicate species.[100−102] The rate of nucleation occurring in a given system depends on many factors, primarily the degree of supersaturation of the solution and the presence or otherwise of nucleation triggers.[103,104] Nucleation triggers may include undissolved particles,[79,105] newly formed crystals[106] or amorphous aluminosilicate particles,[60,102,107] or any other solid−liquid interface.[104] In a geopolymerization system, the degree of supersaturation and the number of nucleation triggers present are very high, so the nucleation rate would be expected to be very high. Autocatalytic effects have been noted in the crystallization of zeolites,[49,105,108] and the possibility of similar effects in geopolymerization must be considered in any future mechanistic examination of this process.[39]

An early investigation of the formation of hydroxysodalite from quartz[79] found that very rapid nucleation due to very high local silicate concentration in the aluminate solution near the quartz particle surfaces led to formation of sub-micron-sized hydroxysodalite particles. Similar effects in geopolymerization would therefore be expected to be observed very close to the surfaces of metakaolin particles, where the release of high levels of Al(OH)$_4^-$ into the concentrated alkali silicate solution immediately surrounding the particles would likewise be expected to induce nucleation of solid phases. This effect will obviously be much more prevalent in activating solutions containing more soluble

silicate, whereas hydroxide-activated systems are less likely to generate rapid nucleation in these regions. Therefore, those nuclei that do develop during hydroxide activation will face less competition for the nutrients required for their growth into crystals, so they will potentially develop into larger crystals than are commonly observed in silicate-activated systems. This means that not only is the proposal of nanocrystallinity in geopolymeric binders highly plausible from a scientific standpoint, but it also has great potential importance in the prediction and explanation of the engineering properties of these materials.

The identification of nanocrystalline zeolitic materials as a significant component of geopolymeric materials, embedded in an amorphous aluminosilicate gel phase, is not unexpected. An explanation for the differences in crystallinity observed in geopolymers activated with different levels of soluble silicate is now possible, with the differing rates of nucleation and crystal growth in each scenario playing a large part in determining the physicochemical and engineering properties of the products in each case. The observation of Rahier et al.[77] that crystallinity decreases as more silicate is added to the activating solution in geopolymerization is justifiable from a theoretical standpoint. However, with nucleation not happening in such close proximity to the particle surfaces in hydroxide-activated as in silicate-activated geopolymers, the binding of the particles into the geopolymeric matrix is likely to be less strong, and so the mechanical strength of the product developed by activation with hydroxides is lower than that with silicates.[29]

The effects of temperature and alkalinity on geopolymerization can also be partially explained by the description of a geopolymer as an agglomerate of zeolite nuclei within a gel matrix. Increasing the temperature of a chemical reaction system will increase the rate of the reactions occurring according to the standard Arrhenius expression, which has been found to be applicable to nucleation and also to crystal growth in zeolite systems.[79,100] However, increases in either temperature or alkalinity of geopolymerization will also increase the solubility of aluminosilicate species in the aqueous phase, so a lower degree of supersaturation will be attained for any given aluminosilicate concentration. This will slow both nucleation and crystal growth, therefore giving variations in the crystallinity of the product. Presence of more nuclei will give a less crystalline product as the higher degree of competition for the nutrients required for crystal growth leads to a smaller average crystal size and therefore lower apparent crystallinity, while the presence of fewer nuclei will give larger crystals and slower solidification. Larger crystals will be less able to pack densely within the binder phase, so they will give a more porous geopolymer. Such a decrease in density with increasing curing temperature has been observed experimentally by Cioffi et al.[30] Depending on the exact nature and crystallite size of the product and the strength of the bonds between the crystalline nuclei and the surrounding material, the strength of the geopolymeric matrix could therefore either decrease or increase with increasing curing temperature, as has been previously observed.

The investigation of Xu and van Deventer[53] into the geopolymerization of kaolinite/stilbite mixtures confirms the

observation that the degree of binding of unreacted particles into the geopolymeric matrix plays a large part in determining the strength of a geopolymer. Xu and van Deventer showed under SEM that the majority of geopolymer samples fractured at the boundary between the binder phase and unreacted particles. The exception to this was a sample with a very low degree of binder formation due to the low levels of reactive solid aluminosilicate and soluble silicate used, which showed fracture in the partially formed binder phase. This may then be correlated with the previously discussed observation of Phair et al.[16] that addition of any more than 3% zirconia by mass weakens a geopolymeric matrix by disrupting the formation of the binder phase, because the binder phase is primarily responsible for the strength development of a geopolymeric system.

The effect of the presence of Ca^{2+} on geopolymerization has recently been the subject of a number of detailed investigations.[54,68,95,99] The conclusions of these investigations will not be repeated in detail here, other than to note that calcium silicate hydrate (CSH) compounds and $Ca(OH)_2$ precipitates have been observed in geopolymeric systems. The amount of Ca^{2+} added and the form in which it is added both play a significant role in determining the physical properties of the final geopolymer. The level of dissolved silicate in the activating solution will also play a highly significant role in determining the effects of calcium by controlling the pH of the activating solution and therefore influencing the relative stabilities of the different calcium-containing precipitates.

It has been observed[16,109] that CaO at levels above 3 wt % interferes with, but does not prevent, formation of fully crystalline zeolites. The formation of Ca-containing precipitates as observed by Yip and van Deventer[99] will provide a large number of potential nucleation sites at the solid−liquid boundaries thus formed. Nucleation at a proportion of these additional sites will then cause the total number of nuclei present to be higher than in the absence of calcium, leading to a smaller mean crystallite size and therefore lower observable aluminosilicate crystallinity. However, the formation of calcium silicate hydrates will also affect the formation of zeolite nuclei by the removal of a proportion of the excess silicate from solution,[109] thereby reducing the supersaturation levels. This reduces the primary driving force for nucleation and crystal growth,[103] and may therefore compete with the accelerating effects of added nucleation to further complicate description of the kinetic effects of calcium addition. The behavior of calcium is critical to the industrial and commercial application of geopolymeric materials, and so future work in the development of the theory of nanocrystallinity in these materials should pay significant attention to these issues.

4. Conclusions

From existing published experimental data and by comparison with related hydrothermal mineral synthesis systems, it is seen that a significant component of the binder phase formed in geopolymerization is likely to be comprised of nanometer-sized crystalline structures, resembling the nuclei around which zeolites crystallize. Agglomeration of these nanocrystallites by the remaining aluminosilicate material in the form of an amorphous gel forms a high-performance mineral binder, commonly referred to as a "geopolymer". Unreacted particles of the solid aluminosilicate source will be bound within this matrix by either chemical or physical means, as will any unreactive aggregate particles present. The physicochemical properties of the geopolymeric product are expected to be significantly determined by the degree of crystalline ordering within the binder phase, which is determined by the initial mix formulation and reaction conditions. The use of alkali silicate activating solutions gives a product with lower crystallinity than if alkali hydroxides are used, a phenomenon attributable to the rapid nucleation of solid products immediately surrounding the dissolving aluminosilicate source particles in the presence of soluble silicates.

Calorimetric data are potentially of great importance in the evaluation of geopolymerization, but the literature contains a number of apparently contradictory results. Identification of the effects of nanocrystallinity within a geopolymeric matrix provides a means for analysis of these data in conjunction with mechanical strength data and other measured properties of these materials, and a basis for reconciling conflicting data sets. The identification of zeolitic nanocrystals within the geopolymeric binder is potentially a highly significant observation, as it provides a link between the chemical composition and engineering properties of geopolymeric materials. In addition, the large body of existing knowledge regarding the chemistry and properties of aluminosilicate zeolites may now be applied to greatly further the understanding of geopolymers, particularly with regard to tailoring the geopolymer matrix properties to optimize performance in particular applications.

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