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ADVANCES IN GEOPOLYMER SCIENCE & TECHNOLOGY

Geopolymer technology: the current state of the art

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Abstract A brief history and review of geopolymer technology is presented with the aim of introducing the technology and the vast categories of materials that may be synthesized by alkali-activation of aluminosilicates. The fundamental chemical and structural characteristics of geopolymers derived from metakaolin, fly ash and slag are explored in terms of the effects of raw material selection on the properties of geopolymer composites. It is shown that the raw materials and processing conditions are critical in determining the setting behavior, workability and chemical and physical properties of geopolymeric products. The structural and chemical characteristics that are common to all geopolymeric materials are presented, as well as those that are determined by the specific interactions occurring in different systems, providing the ability for tailored design of geopolymers to specific applications in terms of both technical and commercial requirements.

Introduction

The reaction of a solid aluminosilicate with a highly concentrated aqueous alkali hydroxide or silicate solution produces a synthetic alkali aluminosilicate material generically called a 'geopolymer', after Davidovits [1], but probably more appropriately referred to as an example of what is more broadly termed an 'inorganic polymer' [2]. These materials can provide comparable performance to traditional cementitious binders in a range of applications, but with the added advantage of significantly reduced Greenhouse emissions [3]. Depending on the raw material selection and processing conditions, geopolymers can exhibit a wide variety of properties and characteristics, including high compressive strength, low shrinkage, fast or slow setting, acid resistance, fire resistance and low thermal conductivity. Despite this wide variety of commonly boasted attributes, these properties are not necessarily inherent to all geopolymeric formulations. Inorganic polymers should not be considered a universal panacea for all material selection problems, but rather a solution that may be tailored by correct mix and processing design to optimize properties and/or reduce cost for a given application. This article explicates some aspects of the intrinsic structure and properties of inorganic polymers, as well as some of the extrinsic properties that may be imparted by appropriate raw material selection and mix design.

Although the term 'geopolymer' is generically used to describe the amorphous to crystalline reaction products from synthesis of alkali aluminosilicates from reaction with alkali hydroxide/alkali silicate solution, geopolymeric gels and composites are also commonly referred to as 'low-temperature aluminosilicate glass'

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[4], 'alkali-activated cement' [5], 'geocement' [6], 'alkali-bonded ceramic' [7], 'inorganic polymer concrete' [8], and 'hydroceramic' [9]. Despite this variety of nomenclature, these terms all describe materials synthesized utilizing the same chemistry, which can be described as a complex system of coupled alkali mediated dissolution and precipitation reactions in an aqueous reaction substrate. Discussion of the suitability of these nomenclatures will be left aside in this article, as this has no real scientific purpose or meritorious goal, other than to note that some of the different 'brand names' mentioned above arise from either (1) the (often significantly) different appearance, properties and characteristics of materials synthesized using different solid aluminosilicate sources; or (2) the presence or absence of filler materials [10]. Here, the term geopolymeric gel will be used to describe the material generically, and geopolymeric composite to describe the material with gel and filler.

In order to show how the nature of selected raw materials can affect the progress and development of chemical reaction, this review will simultaneously discuss the current state of understanding of both metakaolin-based and fly ash-based materials. Other aluminosilicate precursors, in particular synthetic aluminosilicate powders [11] and natural minerals [12] have also been the subject of some investigation. Alkali-activation of blast-furnace slags has been used as an alternative means of cement production for over 65 years [13, 14], and slags are often used as a component of geopolymeric systems. However, the complexity of slag chemistry as it relates to geopolymer formation places detailed discussion of the role of slags in geopolymers beyond the scope of this review. Similarly, cementitious binder systems other than alkali aluminosilicates have also been broadly categorized as 'geopolymers' due mainly to similarities in processing [15, 16], but will also not be reviewed in detail here.

Though many macroscopic characteristics of geopolymers prepared from different aluminosilicate sources may appear similar, their microstructure and physical, mechanical, chemical and thermal properties vary to a large extent depending predominantly on the raw material from which they are derived. Typical images illustrating the microstructures of geopolymers synthesized from metakaolin and Class F fly ash are presented in Fig. 1. Large differences can be observed between the microstructures of these geopolymers. The microstructure of metakaolin derived geopolymers, for example, has been investigated by systematic variation of activator composition and related to mechanical strength [17–19]. It was observed that the microstructure changed from containing large pores to being more homogenous with small pores as the Si/Al ratio was increased. This observation was linked to a strong correlation with the Young's modulus and large increases in mechanical strength [17]. Any effect on the microstructure of changing the alkali cations from Na to K was not readily observed [18].

Despite similarities in the molecular structure and nanostructure, the differences in the properties of geopolymers derived from different raw materials are clearly evident. Fly ash-based geopolymers are generally more durable and stronger. These traits often lead to the belief that the binder phase and reaction mechanism of fly ash systems are inherently different to that of metakaolin-based geopolymers. Although the inherent differences in the dissolution properties and phase composition of fly ash result in geopolymers that exhibit different properties, it is observed both in molecular structure and in microstructure that the same silicon and aluminum bonding and the same gel-phase binder are present in both systems. Therefore, the differences in the setting behavior, bulk microstructure and property development observed in the literature must be reconciled within the conceptual geopolymer reaction model presented in Fig. 2.

A conceptual model for geopolymerization

In the 1950s Glukhovsky [20] proposed a general mechanism for the alkali activation of materials

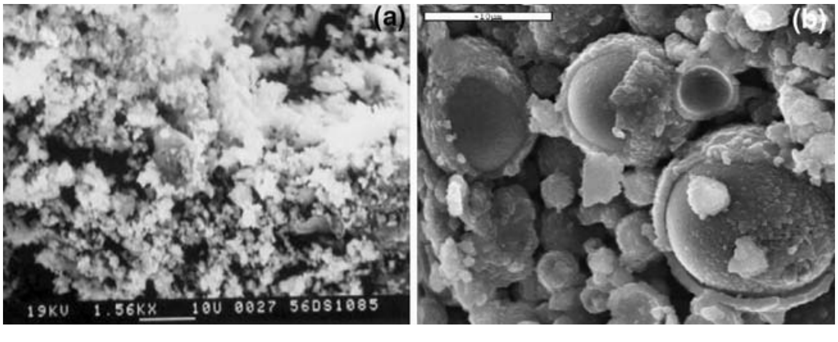


Fig. 1 (**a**) Metakaolin activated with 8 M NaOH, (**b**) Fly ash activated with 8 M NaOH

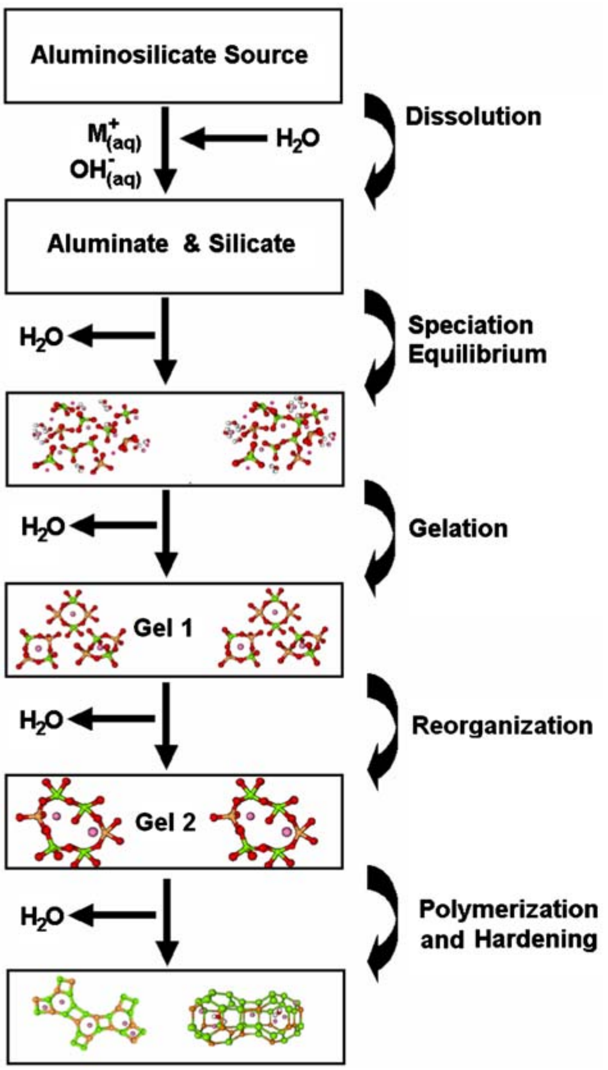


Fig. 2 Conceptual model for geopolymerization

primarily comprising silica and reactive alumina. The Gluhhovsky model divides the process into three stages: (a) destruction–coagulation; (b) coagulation–condensation; (c) condensation–crystallization. More recently, different authors have elaborated on and extended the Glukhovsky theories and applied the accumulated knowledge about zeolite synthesis in order to explain the geopolymerization process as a whole [21–25].

Figure 2 presents a highly simplified reaction mechanism for geopolymerization. The reaction mechanism shown in Fig. 2 outlines the key processes occurring in the transformation of a solid aluminosilicate source into a synthetic alkali aluminosilicate. It should be noted that the potential requirement for processing of raw materials by fine grinding, heat treatment etc. to vary the reactivity of aluminum in the system is not shown for the sake of simplicity. Though presented linearly, these processes are largely coupled and occur concurrently. Dissolution of the solid aluminosilicate source by alkaline hydrolysis (consuming water) produces aluminate and silicate species. The volume of data available in the field of aluminosilicate dissolution and weathering represents a whole field of scientific endeavor in itself [26–29], and will not be reviewed in detail here. It is important to note that the dissolution of solid particles at the surface resulting in the liberation of aluminate and silicate (most likely in monomeric form) into solution has always been assumed to be the mechanism responsible for conversion of the solid particles during geopolymerization. This assumption does have almost overwhelming scientific merit based on the literature describing alkaline dissolution, and so is shown in Fig. 2. Despite this, the actual process of particle-to-gel conversion has never been confirmed in the highly alkaline and poorly solvated conditions prevailing during geopolymer synthesis. Without the benefit of conclusive mechanistic understanding of solid particle conversion, surface dissolution will be assumed in the simplistic mechanistic model described here.

Once in solution the species released by dissolution are incorporated into the aqueous phase, which may already contain silicate present in the activating solution. A complex mixture of silicate, aluminate and aluminosilicate species is thereby formed, and the speciation equilibria within these solutions have been studied extensively [30, 31]. Dissolution of amorphous aluminosilicates is rapid at high pH, and this quickly creates a supersaturated aluminosilicate solution. In concentrated solutions this results in the formation of a gel, as the oligomers in the aqueous phase form large networks by condensation. This process releases the water that was nominally consumed during dissolution. As such, water plays the role of a reaction medium, but resides within pores in the gel. This type of gel structure is commonly referred to as bi-phasic, with the aluminosilicate binder and water forming the two phases.

The time for the supersaturated aluminosilicate solution to form a continuous gel varies considerably with raw material processing conditions and solution composition and synthesis conditions [32, 33]. Despite this, some systems never gel. These are typically dilute, and the concentration of dissolved silicon and aluminum is observed to oscillate due to the slow response of the system far from equilibrium [34]. After gelation the system continues to rearrange and reorganize, as the connectivity of the gel network increases, resulting in the three-dimensional aluminosilicate network commonly attributed to geopolymers. This is depicted in Fig. 2 by the presence of multiple ‘gel’ stages, consistent with recent experimental observations [22, 35] and numerical modeling for both metakaolin- and fly ash-based geopolymers [36]. Figure 2 describes the activation reaction as an outcome of two successive and controlling stages. Nucleation, or the dissolution of the aluminosilicate material and formation of polymeric species, is highly dependent on thermodynamic and kinetic parameters and encompasses the two first steps proposed by Glukhovsky. Growth is the stage during which the nuclei reach a critical size and crystals begin to develop. These processes of structural reorganization determine the microstructure and pore distribution of the material, which are critical in determining many physical properties [17, 37].

Structural characterization

The Si^{4+} and Al^{3+} cations in the framework of aluminosilicate geopolymeric gels (often referred to as “T atoms”) are tetrahedrally coordinated and linked by oxygen bridges. The negative charge on the AlO_4^- group is charge-balanced by alkali cations (typically Na^+ and/or K^+). Geopolymers derived from different combinations of raw materials can easily be synthesized containing multivalent cations [38–42], and the location and structure of these cations are discussed later in this article. The cross-link density of the AlO_4^- and SiO_4 groups is effectively four, with no significant non-bridging oxygen signal observable in ^{17}O MAS or MQMAS spectra [43]. Some terminal hydroxyl groups will doubtless be present at the surface of the gel [37], although this is largely insignificant in the context of the structure of the material.

Davidovits was the first to investigate the structure of metakaolin-based geopolymers using NMR in the 1980s [44]. ^{27}Al MAS NMR investigations of metakaolin-based products determined that reacted samples contain predominantly Al(IV) (~60 ppm) with trace amounts of Al(VI) (~0 ppm) [1]. A ^{27}Al MAS NMR spectrum of typical metakaolin-based reaction products is presented in Fig. 3 (spectrum B). Metakaolin is known to contain approximately equal populations of Al(IV), Al(V) (~30 ppm) and Al(VI) [45]. A ^{27}Al MAS NMR spectrum of a typical metakaolin is presented in Fig. 3 (spectrum A). The broad peaks are a result of the highly disrupted geometry of all three aluminum sites. Therefore, it was observed that during the course of alkali-mediated reaction, Al(V) and Al(VI) were converted to tetrahedral sites with an associated alkali cation to maintain electroneutrality [1]. The speciation of aluminum in alkaline solutions is

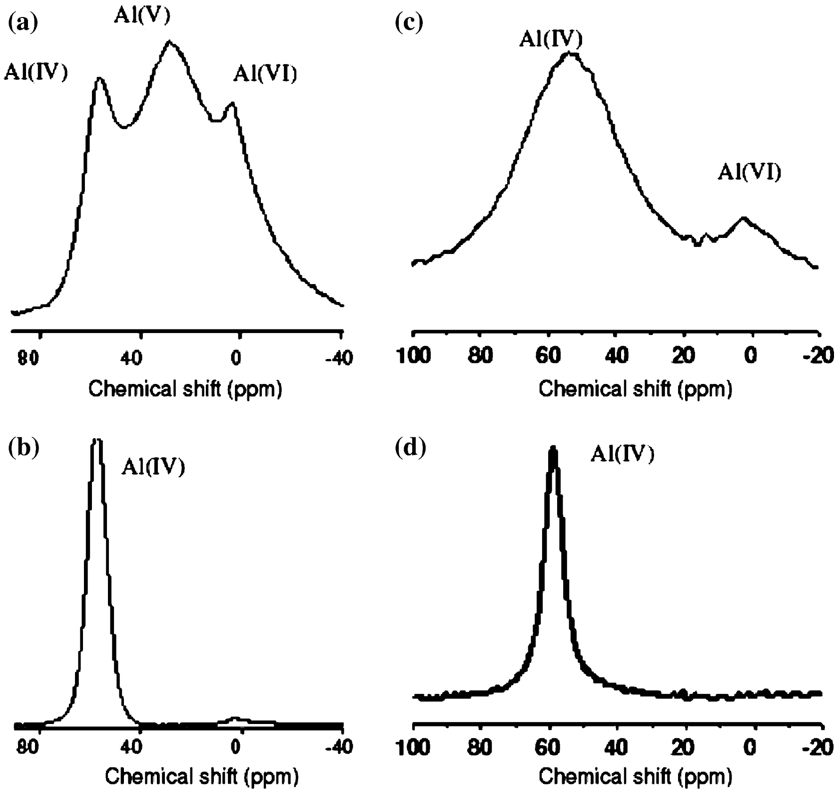


Fig. 3 ^{27}Al MAS-NMR spectra of (**a**) typical metakaolin, (**b**) metakaolin-based Na-geopolymer from metakaolin with Si/Al ratio of 2.15, (**c**) typical fly ash, and (**d**) Na-geopolymer from NaOH activation of fly ash (20 h, 85 °C)

restricted to Al(OH)$_4^-$(aq) in all but the most concentrated aluminate solutions, where some dimerization is observed [30]. Therefore, any remnant Al(VI) observed in the ^{27}Al spectra of inorganic polymers (Fig. 3b, d) is the result of unreacted raw material and not the formation of Al(VI) as part of the reaction products. Indeed, the appearance of Al(VI) in the spectra of reacted specimens has been utilized as a quantitative measure of the amount of unreacted metakaolin in geopolymers [45]. A similar situation has been described in fly ash based geopolymers. The main difference in aluminum coordination between metakaolin and fly ashes is that fly ashes have a higher content of Al (IV) than metakaolin (see Fig. 3c). When the reaction takes place this wide (disordered) signal becomes sharper, showing a higher degree of structural order similar to the peak that is characteristic of tetrahedral aluminum in zeolites (see Fig. 3d) [22, 45, 46].

^{29}Si MAS-NMR spectroscopy of fully cured geopolymers reveals a broad resonance located around –85 to 95 ppm from TMS depending on the Si/Al ratio [47], which can be linked to the resonance of tetrahedral silicon in zeolite gels prior to crystallization [1]. Davidovits [1] speculated that this broad peak comprised all five possible silicon Q^4(mAl) species, as seen in previous investigations of aluminosilicate systems [48]. This relatively limited conceptual understanding of the structure of amorphous silicate materials remained for several years, due to the poor resolution of these individual sites in geopolymers compared to the more easily resolved peaks from crystalline aluminosilicate minerals and zeolites [48, 49]. However, investigation of amorphous glasses showed that it is in fact possible to deconvolute reliably an apparently featureless silicon resonance into the Q^4(mAl) centers that comprise the aluminosilicate framework [50]. Similar approaches have since been adopted for geopolymers derived from metakaolin [47] and fly ashes [22] as shown in Fig. 4. It was found from deconvolution of ^{29}Si MAS NMR spectra that the chemical ordering of silicon and aluminum in geopolymers and the relative extent of incorporation of each type of T-atom into the geopolymer gel framework were significantly affected by the raw material and reaction conditions [22], as well as by the nature of the alkali cation(s) present [47]. Subsequent statistical thermodynamic modeling [51] of the Q^4(mAl) distribution expected in metakaolin-based geopolymers has found that the basis for the variation in chemical ordering lies in an energetic preference for bonding between unlike atoms within an aluminosilicate framework, meaning that Si–O–Al bonds are generally preferred. The extent to which this preference is expressed is determined by the alkali cation type, with Na$^+$ giving a stronger preference (i.e. a more ordered framework) than K$^+$.

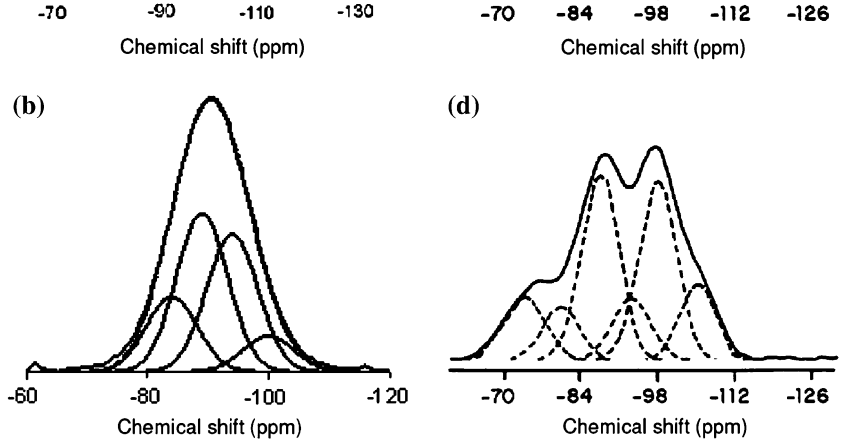


Fig. 4 ^{29}Si MAS-NMR spectra of (**a**) typical metakaolin, (**b**) metakaolin-based Na-geopolymer with Si/Al ratio of 1.65, (**c**) typical fly ash, and (**d**) fly ash-based Na-geopolymer (20 h, 85 °C)

Figure 4 depicts the ^{29}Si MAS-NMR spectra of metakaolin and fly ash (spectra A and C) and the reaction products after activation of metakaolin with sodium silicate solution (spectrum B) and fly ash with sodium hydroxide (spectrum D). The broad peak observed in the spectra for the initial materials shows the range of Si sites in these materials. The differences between spectra A and B, and between C and D, show the chemical and microstructural transformations taking place during the alkali activation process in both cases. These spectral changes are associated with the formation of an alkaline aluminosilicate gel (i.e. inorganic polymer) exhibiting a certain degree of structural order.

Comparison between the ^{29}Si NMR spectra of geopolymers derived from fly ash and metakaolin has recently been published [25]. It was shown that both spectra of all amorphous geopolymers exhibit similar broad resonances between 80 and 100 ppm, typical of tetrahedral silicate centers with highly variable bond angle distributions surrounded by varying numbers of aluminum atoms. However, the presence of silicon-containing crystalline phases in fly ash, such as quartz and mullite, causes sharp peaks to appear in the spectrum of the fly ash-based specimen. The resonances from non-reactive materials may be subtracted or accounted for from the overall spectrum to yield the spectrum approximating that of the gel phase, similar to what has been done for metakaolin-based geopolymers. Deconvolution of ^{29}Si MAS NMR spectra has been shown to be an effective method for analysis of fly ash [46]. The broad resonance remaining after spectral deconvolution and subtraction appears similar to that of high gel-phase-containing geopolymers derived from metakaolin. This implies that the chemical distribution of silicon and aluminum in geopolymers based on different raw materials is similar. Analysis of ^{29}Si MAS NMR spectra has shown that the resonance position and shape can be predicted by knowledge of the Si/Al ratio of the specimen [47, 51]. More recently an accurate quantification of all of the whole phases (crystalline, vitreous and amorphous) taking part in geopolymerization of fly ash has been carried out with Rietveld XRD analysis together with NMR data [52, 53].

The microstructure of the gel phase present in metakaolin-based geopolymers as observed by TEM has recently been presented [17, 54]. The microstructure of geopolymer on a nanometer scale is reproduced in Fig. 5, alongside a similar micrograph of the gel from a fly ash-based geopolymer (Fig. 5). The structure of the metakaolin-based gel specimen comprises small clusters of precipitates with pores dispersed throughout the structure in the interstices (Fig. 5a). The size and packing of these clusters is likely to be greatly affected by the processing conditions discussed above, and may explain the changes in long-range ordering that appear in specimens formed at high temperature, high dilution rates and low soluble silicon concentrations. These factors each increase the lability of the gel and allow for structural reorganization and densification. The concentration of soluble silicon has been shown to be intimately linked with the distribution of porosity in metakaolin-based geopolymers [17], with low concentrations resulting in dense gel. High concentrations of soluble silicon hinder reorganization and result in reduced skeletal densities of the gel [17]. Further microstructural and porosimetry studies of metakaolin-based systems synthesized at different temperatures and silicate concentrations would be valuable to elucidate the effect of these parameters on the gel and how this relates to structural stability and reorganization with aging. The TEM microstructure of the fly ash-based geopolymer in Fig. 5b appears remarkably similar to that of the metakaolin-based specimen in Fig. 5a. Combined with the similarity in the chemical distribution of silicon and aluminum observed by NMR [25] and SEM microstructure (Fig. 1), there is strong

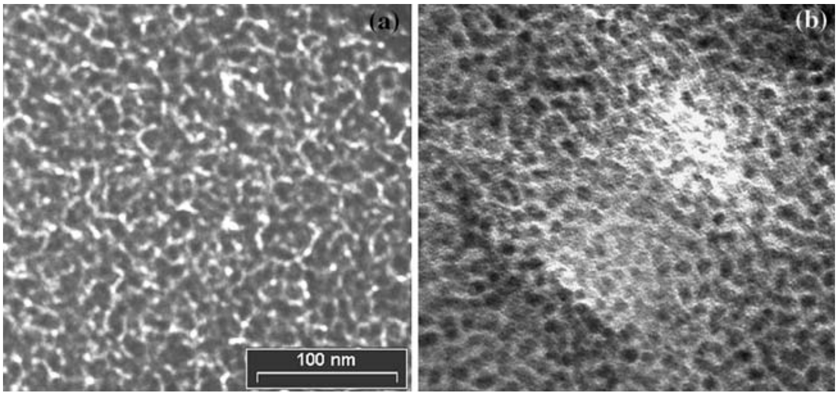


Fig. 5 TEM bright field micrographs of geopolymers synthesized by alkali-silicate activation of (**a**) metakaolin, and (**b**) fly ash

evidence to suggest that the reaction products of geopolymers synthesized from different raw materials are structurally analogous.

The effect of processing conditions on short-range ordering

Time and temperature

Geopolymers are often described as 'X-ray amorphous' [42, 55, 56], since the major feature of powder X-ray diffraction (XRD) patterns is a 'featureless hump' centered at approximately 27–29° 2*θ*. Typical XRD diffractograms of geopolymers derived from metakaolin and from fly ashes are shown in Fig. 6. Indeed, the XRD diffractograms of many predominantly amorphous materials appear almost identical to those of geopolymers, including some silicate gels [57] and aluminosilicate zeolite gel precursors prior to crystallization [58]. The similarity of these XRD diffractograms is linked to characteristic bonding distances of inorganic oxide frameworks and is not specific to geopolymers. However, authors have also noted formation of phases described as either semi-crystalline or polycrystalline on several occasions [1, 19, 59, 60], particularly where little or no soluble silicon is present in the alkali activating solution. These crystalline phases are generally zeolitic, and are more predominant when synthesis is carried out under hydrothermal conditions in alkaline solutions with high dilution rates, in excess of 50 wt%. Hydrothermal alkaline reaction of kaolin clay, metakaolin, fly ashes, and some different aluminosilicate materials results in the formation of zeolites with various frameworks depending on the reaction conditions (temperature, alkali cation, Si/Al ratio etc.) [61–64]. A comparatively high water content allows for the species in solution to be fully hydrated, with little to no influence of ion-pairing interactions, which impact greatly on the speciation and energetics in highly concentrated ionic solutions [31, 65]. Although the speciation of silicate and aluminate is largely determined by the concentration of alkali and the Si/Al ratio in the solution, dilution allows for improved solution phase transport and reorganization [31]. Nucleation centers in solution are readily supplied with aluminosilicate nutrients for growth by diffusion of dissolved components molecules. Under these conditions the growth of precipitates occurs without steric hindrance and fully crystalline precipitates form. A recent review of geopolymer science provides a detailed discussion of the role played by crystallite formation in these materials [23].

In highly concentrated solutions, which typically produce amorphous materials (and are called geopolymers here), the ionic species are not fully hydrated. Indeed, in 10 M NaOH solutions the H_2O/Na^+ ratio is approximately 5.5. Given that the coordination number of the first hydration shell of Na^+ (aq) is significantly greater than this [66], some of the positions in the hydration shells of the alkali cations instead will be filled by silicate anions, leading to ion pairing. The effects of ion pairing in concentrated alkaline silicate solutions result in speciation that is affected by alkali cation type [31, 65]. The interaction of ionic species and steric hindrance of precipitate growth combine to result in a material that lacks long-range ordering, appearing amorphous to XRD, as observed in Fig. 6.

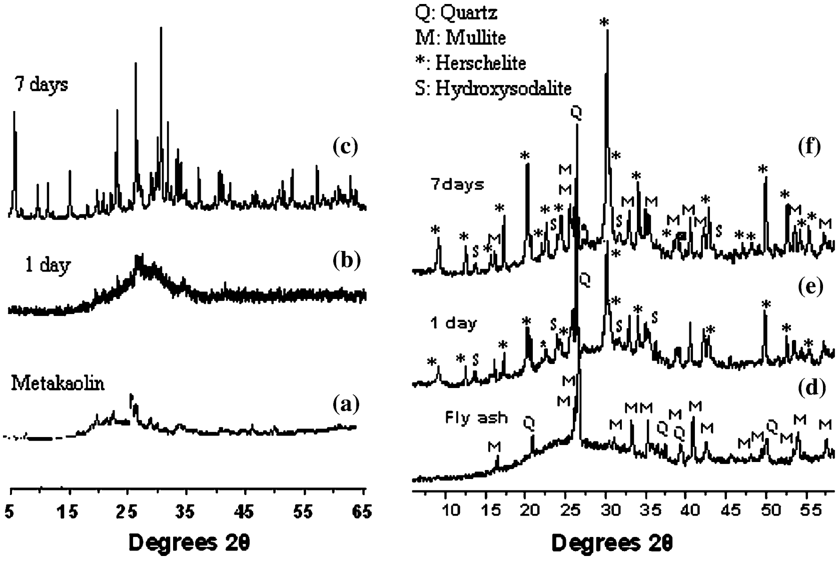


Fig. 6 XRD diffractograms of (**a**) typical metakaolin (with slight muscovite impurity), (**b**) geopolymer with nominal composition $NaAlSiO_4$ obtained after 1 day and (**c**) 7 days after synthesis, showing peaks corresponding to zeolite X, (**d**) typical fly ash, (**e**) inorganic polymer from fly ash at 20 h, 85 °C and (**f**) 7 days at 85 °C

The XRD diffractogram labeled B in Fig. 6 is of a geopolymeric gel with nominal composition $NaAlSiO_4$, synthesized from metakaolin (diffractogram A) in a 35 wt% water activating solution at 40 °C, 1 day after synthesis. Although this material appears amorphous to XRD initially, evidence of the same reaction mechanism being responsible for the formation of geopolymer and crystalline zeolite can be observed, with the formation of zeolite observed within 7 days of synthesis (diffractogram C). Similar results are obtained when fly ash (diffractogram D) is used as reactive material, as seen in Fig. 6 diffractograms E & F. The alkali activation of the ash also gave rise (by increasing the time of thermal treatment) to the formation of crystalline phases identified as herschelite (Na-chabazite) and hydroxysodalite-type zeolites [53].

Indeed, transition of these materials from apparently amorphous to partially crystalline has been observed numerous times, and the concept of even 'X-ray amorphous' specimens containing some level of short-range ordering has been recently considered with supporting evidence from the literature [23]. The continuation of geopolymerization significantly past the time at which the specimen is observed to set has also previously been observed by calorimetric methods [67].

The transition of amorphous geopolymers to a well-defined zeolite structure has also been observed through ^{29}Si MAS NMR, FTIR spectroscopy, SEM, etc, as shown in Figs. 7 and 8 [22, 68]. The ^{29}Si spectrum of the aged metakaolin-derived geopolymer closely resembles that of a crystalline zeolite, and the spectrum of the aged fly ash geopolymer is identical to the one belonging to Na-chabazite [22]. In both cases the $Q^4(m\mathrm{Al})$ sites that form the structure of zeolite are clearly observable as is the narrowing of the spectra in comparison to those shown in Fig. 4. The transformation of typically X-ray amorphous geopolymer synthesized in a concentrated slurry and at mild temperature into a well-defined zeolite structure provides a very simple yet powerful example of the similarity of the two reaction mechanisms.

The structural transition from amorphous to crystalline of geopolymers synthesized at low to mild temperatures in concentrated slurries also implies that the synthesis temperature and aging are critical in determining the structure of the reaction products. Figure 9 shows the XRD diffractograms of metakaolin-derived geopolymers with nominal composition $KAlSiO_4$ cured at temperatures of 70, 90 and 120 °C for 24 h. It can be observed that no new crystalline phases can be observed in the diffractograms of the specimens cured at 70 or 90 °C. However, a new phase can be observed in the specimen cured at 120 °C, demonstrating that even mild increases in synthesis temperature result in a readily observable increase in

Fig. 7 ^{29}Si MAS-NMR spectrum of (**a**) of Na-geopolymer with Si/Al ratio of 1.15 after 6 months of aging from alkali activated metakaolin (spectrum resembles faujasite); (**b**) alkaline aluminosilicate from alkali activated fly ash. 3 months at 85 °C (spectrum resembles Na-Chabazite)

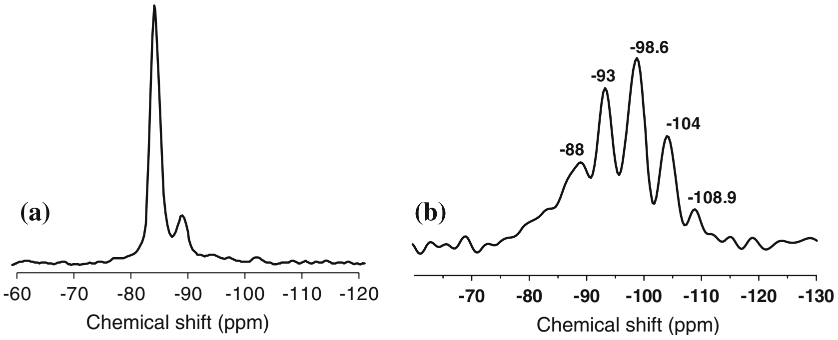
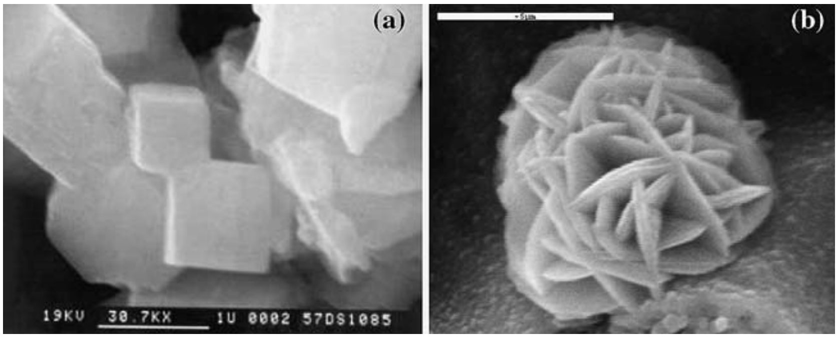


Fig. 8 (**a**) Linde zeolite crystals detected in alkali-activated metakaolin, (**b**) Na-chabazite detected in alkali-activated fly ash



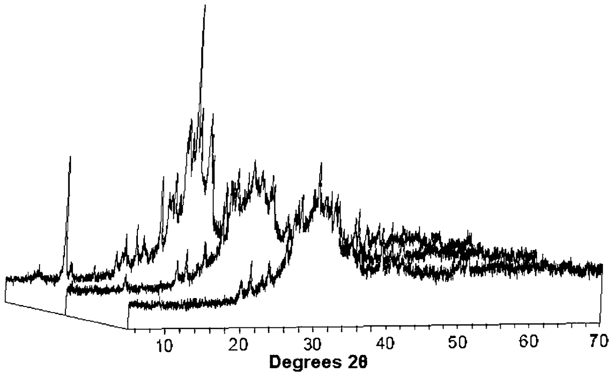


Fig. 9 XRD diffractograms of geopolymer with nominal composition $KAlSiO_4$ synthesized at (from front to back) 70, 90 and 120 °C, Diffraction peaks in the diffractogram of the specimen synthesized at 120 °C correlate with zeolite K-I

crystallinity. Similar results have been observed many times in the literature [62], but this observation confirms that mere increase in synthesis temperature is sufficient to increase the level of long-range ordering in geopolymeric binders. Furthermore, recent work carried out with fly ashes [46] has demonstrated that time and temperature highly affect the mechanical development of geopolymer materials. As the temperature of reaction increases, the mechanical strength development increases also. However, there is a threshold value for mechanical strength development, above which the strength-gaining rate is slow.

This begs the question as to what level of structural ordering is present in specimens cured at lower temperature, which appear amorphous to XRD [23]. In this light, the assertion that geopolymeric materials that appear amorphous to XRD are indeed totally amorphous appears to be bolder than prudence would commend. It is more likely that new techniques and methods for determining the extent of order existing in seemingly amorphous materials will be developed, rather than some demarcation point where 'true amorphicity' begins being found. The exact definition of crystallinity as applied to organic polymeric materials has been the subject of some discussion recently [69, 70], and the situation for inorganic polymers is likely to be almost as complex.

Influence of the alkaline activator

The apparent structural stability of geopolymers is known to increase with addition of soluble silicon to the activating solution [46, 71]. Specimens synthesized at mild temperatures (40 °C) with high concentrations of silicon in the activating solution do not transform into X-ray crystalline phases even after long periods of time at 40 °C, and probably need a very long time for such a transformation to take place. The X-ray amorphous structure of specimens synthesized with soluble silicon in the activating solution does not, however, result from a fundamental change in reaction mechanism or reaction product. Figure 10 shows the XRD diffractograms of metakaolin-based geopolymers synthesized with differing amounts of soluble silicon in their activating solutions after curing at 120 °C for 24 h. It can be observed that although the specimens synthesized using the highest levels of soluble silicon appear amorphous to XRD, specimens synthesized with small amounts of soluble silicon ($Si/Al \leq 1.25$) exhibit peaks due to crystalline phases. Addition of soluble silicon to the activating solutions used in the synthesis of geopolymers can be observed to substantially reduce the level of long-range structural ordering with increasing concentration, but does not appear to fundamentally change the reaction mechanism. Rather, a gradual reduction in the level of ordering in these specimens is observed with increase in the soluble silicon concentration. Indeed, the short-range chemical ordering of specimens with Si/Al ratio controlled by addition of soluble silicon is well described both experimentally [47] and theoretically [72] as a continuum that can be predicted by knowledge of nominal chemical composition alone.

However it is very important to remark that the aluminosilicate gel formed depends not only on the concentration of the added soluble silica; it also depends on its polymerization degree, which is also

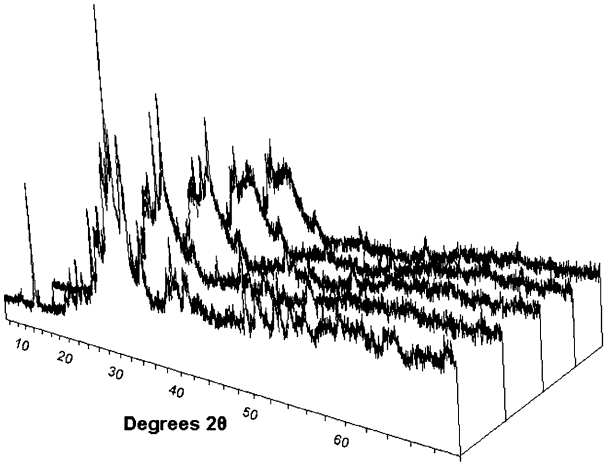


Fig. 10 XRD diffractograms of metakaolin-based geopolymer synthesized at 120 °C with nominal composition $KAlO_2(SiO_2)_z$, where $1 \leq z \leq 1.5$. The Si/Al ratios of specimens are (from front to back) 1.000, 1.125, 1.250, 1.375 and 1.50, respectively. Diffraction peaks in specimens with $1 \leq z \leq 1.250$ correlate with zeolite K-I

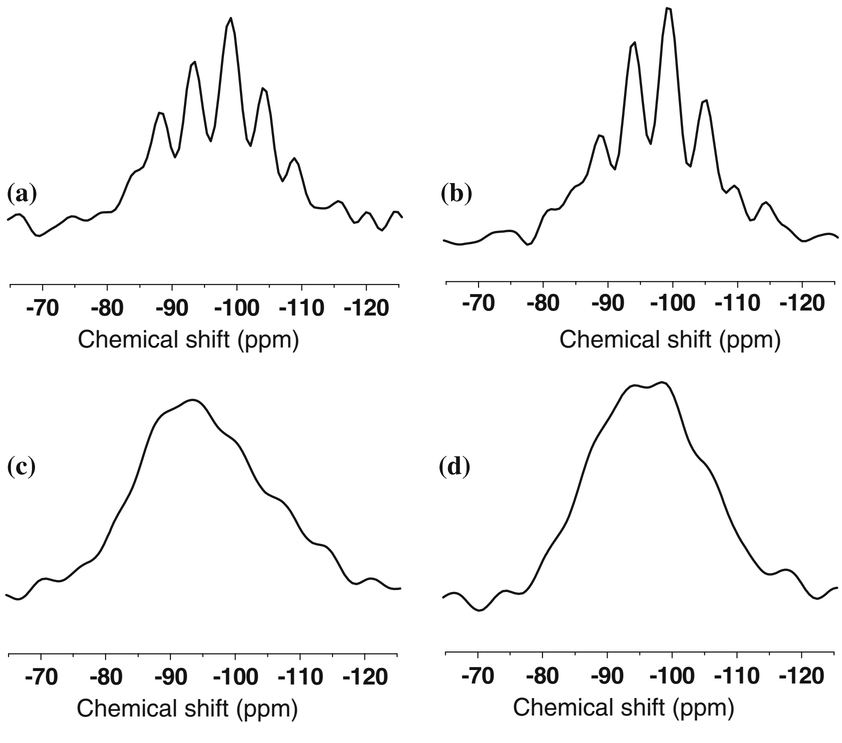
dependent on the alkalinity of the solution [73, 74]. In some investigations carried out by Palomo and Fernández-Jiménez [74] with fly ashes it has been observed that the incorporation of low amounts of soluble silicate to the system favors the tendency of the tectosilicate structure to achieve a high level of ordering in a short time. The kinetics of the transformation of the zeolitic precursor to crystalline phases (aluminosilicates) is notably accelerated. However, when the polymerization degree of soluble silica is increased, the gels formed are apparently more amorphous, and have broader, more featureless peaks in ^{29}Si MAS NMR (see Fig. 11) [74].

It is well known that variation in the ratio SiO_2/Na_2O significantly modifies the degree of polymerization of the dissolved species in an alkaline silicate solution [31, 65, 75], and that this plays a significant role in determining the structure and properties of geopolymer gels synthesized using these solutions [17, 59, 76, 77]. Figure 12 shows ^{29}Si NMR spectra of the activating solutions used in synthesis of the samples shown in Fig. 11 [74, 78]. These results are in accordance with the known behavior of alkali silicate solutions, showing that the connectivity distribution of the silicate anions is significantly influenced by the SiO_2/Na_2O ratio. McCormick et al. [79] showed that aluminate anions react preferentially with silicate anions of low connectivity (Q^0 and Q^1), and this leads to significantly different microstructures in geopolymer gels of different SiO_2/Al_2O_3 ratios, as well as differing effects of processes such as syneresis [17]. The speciation of the activating solution is therefore probably more critical than the absolute silicate concentration in determining geopolymer microstructure, although the water content of the activator is also significant [76].

On the other hand, the requirement of a large concentration of silicon in the activating solution to form amorphous geopolymer with high mechanical strengths and microstructures comprised of small pores has been known for some time in fly ash systems [71, 80]. It can be clearly observed in the microstructure of alkali-activated Class F fly ash in Fig. 13b that there is a far greater level of unreacted phase present, compared to the metakaolin geopolymer specimen in Fig. 13a. While the microstructure of metakaolin-based geopolymers comprises almost entirely the gel phase, the fly ash geopolymer microstructure is best described as a gel-bonded ash composite. Microstructural analysis has shown that the unreacted phase in fly ash specimens is not only the crystalline impurities, but also glassy phases that are either insoluble in alkaline media due to their chemical composition, or alternatively some potentially soluble phases that have not been able to react due to hindered mass transport [21].

The microstructures of geopolymer specimens derived from fly ash and metakaolin and synthesized with small concentrations of soluble silicon in the activating solution have been compared elsewhere

Fig. 11 ^{29}Si MAS NMR of alkali aluminosilicate gel from fly ash activated 7 days with (**a**) 8 M NaOH, and with sodium silicate solutions, SiO_2/Na_2O = (**b**) 0.19, (**c**) 0.69, and (**d**) 1.17



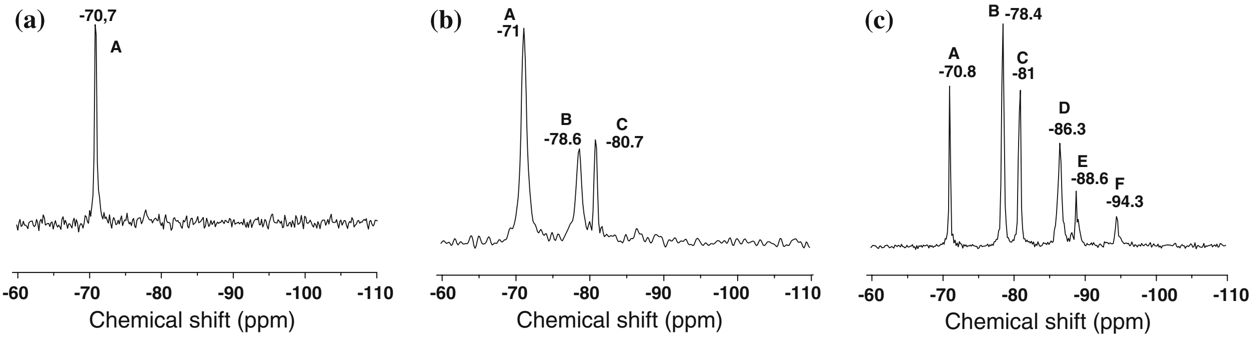
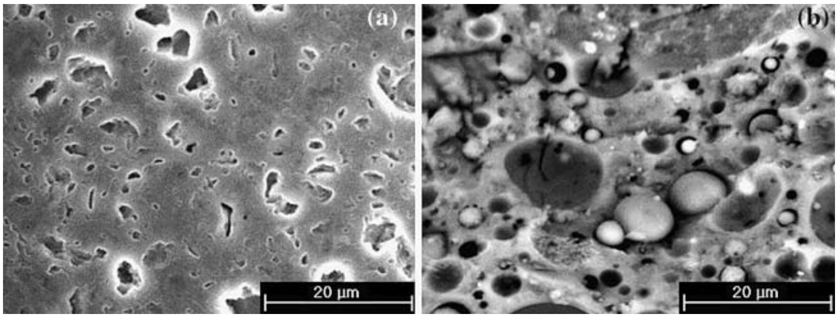


Fig. 12 ^{29}Si NMR spectra of sodium silicate solutions, SiO_2/Na_2O ratio equal to (**a**) 0.19, (**b**) 0.69 and (**c**) 1.17

Fig. 13 SEM micrographs of inorganic polymers synthesized from (**a**) metakaolin, (**b**) F class fly-ash



[25]. The specimens both contained large pores compared to specimens synthesized with high soluble silicon as shown in Fig. 13, signifying analogous effects of system parameters on the microstructural development and properties of both systems. This implies that the structural reorganization of the gel is constrained by the same chemistry and physical processes. Furthermore, the extent of raw material reaction is known to decrease with increasing soluble silicon content in the activating solution at constant Na_2O/H_2O ratio, due to reduction in pH and increase in solution viscosity [45]. This has been linked with the reduction in mechanical performance at high soluble silicon content observed in numerous studies [47, 81] as a result of the unreacted particles providing defect locations. Even more poorly reacted systems contain insufficient binder to provide appreciable mechanical properties [82], which is especially observed in fly ash derived specimens or with largely insoluble mineral phases [12, 71]. Despite this, unreacted particles can serve as a microaggregate and can improve some engineering properties [83]. Therefore, being able to increase or decrease the extent of raw material dissolution during geopolymerization (i.e., release of Si and Al species into the geopolymer gel), whether by use of multiple raw materials or processing raw materials prior to alkali activation, is an important consideration.

It is clear from the experimental data presented here and the discussion above that the alkali-mediated reaction mechanism is able to describe the continuum of zeolitic and geopolymeric materials ranging from those that are highly crystalline to those that appear totally amorphous. Variation in the reaction conditions alone results in different levels of structural ordering. As such, the actual reaction mechanisms underlying geopolymerization are in fact quite well understood, albeit from the point of view of reaction conditions that tend towards formation of crystalline products. The process of dissolution of aluminosilicate and multi-oxide minerals and glasses in highly alkaline solutions in the presence of aluminum and silicon is also well understood in the literature [28, 84, 85]. Therefore, investigation of geopolymerization should be focused on understanding the phenomena that are characteristic of and unique to the reaction conditions utilized in systems that generate amorphous products, such as low temperature synthesis, highly concentrated slurries and utilization of different raw materials.

Influence of alkali cations

It is well known that the type of cation involved in the activation reaction also affects the microstructural development of the systems as well as the Si/Al ratio of the prezeolitic gel. In general it can be affirmed that the OH^- ion acts as a reaction catalyst, and the alkaline metal cation acts as a structure-forming element, balancing the negative framework charge carried by tetrahedral aluminum. In this respect and given that the first stage of the reaction is controlled by the aptitude of the alkaline compound to dissolve the solid fly ash network and to produce small reactive species of silicates and aluminates, it would be reasonable to think that in the case of sodium and potassium hydroxides, KOH should show a greater extent of dissolution due to its higher level of alkalinity. Nevertheless, reality demonstrates that it is NaOH that possesses a greater capacity to liberate silicate and aluminate monomers [18, 45, 86, 87]. It is likely that the ion size difference is a determining factor in the kinetics of the reactions due to the tendency of K^+ to favor formation of larger silicate oligomers [79], and this will play an increasingly significant role when higher-silicate activating solutions are used [36]. It is also observed that the sodium cations have better zeolitization capabilities in geopolymer-forming systems [18, 88], possibly because they are smaller than potassium cations and therefore more able to migrate through the moist gel network, or possibly due to their higher charge density. This corresponds to the greater tendency of sodium to form zeolites in a regular hydrothermal synthesis compared to other alkali cations—either the larger K^+, Rb^+ or Cs^+ [89–91], or the smaller but more strongly hydrated (and therefore effectively bulkier) Li^+ [92].

Comparison between metakaolin and fly ash

There are several critical differences between the structures of metakaolin and fly ash, which are primarily determined by their respective methods of derivation and manufacture. Metakaolin is ideally synthesized by dehydroxylation of phase pure kaolin. While the temperature and calcination time of kaolin affect the ultimate surface area, degree of dehydroxylation and reactivity, the base structure is that of a highly disrupted phyllosilicate structure containing silicon and aluminum only. Although most commercial metakaolin contains levels of impurities, primarily muscovite and titanium dioxide, the effect of these impurities is limited by both their low dissolution and the inability of the products of their dissolution to affect the formation mechanism. In general, the knowledge gained by investigation of metakaolin-based geopolymers may be applied to all metakaolin supplies in the world. Metakaolin-based geopolymers can be manufactured consistently, with predictable properties both during preparation and in property development. The particle size of metakaolin varies to some degree, but is generally smaller than 5 μm, with the intrinsic size of the clay being in the order of 20 nm. Although the dispersion of particles during mixing will affect the rheological behavior and degree of reaction somewhat, it has been shown that there is little difference in the reaction of metakaolin-based geopolymer with variation in raw material surface area [93], although the amount of soluble silicate and alkali cation in the activating solution affects the extent of reaction [45].

In contrast, fly ash is an industrial waste that is not derived from a well-defined starting material. The bulk of the ash is made up of silicon, aluminum and iron oxides, as well as significant amounts of calcium in Class C ashes [94]. The particles in fly ash are generally spherical, but inhomogeneous, and comprise glassy as well as crystalline (often mullite and quartz) phases. The particle size distribution can be very broad, and different size fractions will differ in elemental and phase composition. This degree of inhomogeneity means that more care is required when working with fly ash to ensure that the optimal mix design is obtained for a given ash if a consistent product is to be obtained, and this area is the subject of much ongoing work worldwide [22, 52, 53, 95, 96]. In any case in a pioneering investigation the main characteristics of fly ashes were ranged in order to establish their potential to be alkali activated [97].

Importance of aluminum incorporation

Before the effects of mineralogy and impurities on geopolymerization can be fully explored, it is important to elucidate the mechanism of chemical triggering of hardening during geopolymerization. Highly concentrated alkali silicate solutions are generally at least metastable. Therefore, the presence of soluble silicate alone is not sufficient to create a chemically hardened material. Silicate bonded composites constitute a class of materials that are formed by the removal of water from silicate glass slurries, but dissolve again when in contact with water. However, the solubility of alkali aluminosilicates is extremely low, even when present in very low concentrations (in the order of mmol/L) [98, 99]. For instance, even when stable silicate and aluminate solutions are brought into contact, the resulting aluminosilicate solution gels or precipitates to form geopolymer or zeolite [99–101]. Therefore, in the instance of pure alkali aluminosilicate slurries, it must be the presence of aluminum that provides the chemical trigger to irreversible chemical hardening, though the exact reason for this is not yet wholly understood. Weng et al. [102] applied the Partial Charge Model to attempt to describe this phenomenon. However, this is a highly simplified approach with potentially limited application, and provides results that appear to contradict trends in partial charges obtained experimentally or at higher levels of theory [103, 104].

Regardless, it is clear that the release of aluminum into solution from the solid aluminosilicate source controls the rate, stoichiometry and extent of solution phase reactions. This has been shown for the model case by controlled calcination of kaolin to form metakaolin [105–107] and manipulation of activator composition [45]. Despite the absence of definitive studies on how to enhance or reduce aluminum availability during geopolymerization from industrial wastes, the potential for selection of activator and raw materials to control aluminum release has been proven in principle.

The rates of amorphous aluminosilicate dissolution and precipitation are known to be dependent on several factors, including temperature, pH, concentration and soluble Si/Al ratio [32, 34, 79, 108, 109]. Therefore, it is of little surprise that these same factors have been identified earlier in this article as being critical in determining the synthesis characteristics and products of geopolymerization. Knowing this, the effects of raw material selection and pre-processing, temperature of reaction, transient solution phase Si/Al ratio (i.e. related to the independent rates of silicon and aluminum release from dissolution and the initial soluble silicon concentration in the activator), and dilution rate can be incorporated into the rates of exchange, lability and speciation of the silicate, aluminate and aluminosilicate species in the solution phase, with the solubility of the supersaturated solution as a function of dissolution and precipitation kinetics based on published literature [24, 36]. With a more rigorous conceptual understanding of the importance of aluminum in the formation of geopolymers, the importance of raw material chemical composition and mineralogy in the kinetics and products of geopolymerization can be elucidated. Therefore, determination of the amount of available aluminum is critical in successful formulation of fly ash-based geopolymers [22, 52, 53].

It is clear from the above discussion that the challenge of producing consistent geopolymer products from heterogeneous industrial wastes sources such as fly ash requires a greater degree of characterization than is provided by an elemental composition analysis [97]. The extent of raw material dissolution, the rate of aluminum release, activator pH, soluble silicon concentration and water demand are all critical components in formulation of consistent, user friendly, cost competitive geopolymer products. Since it is more likely for product requirements and cost to drive product development, rather than raw material suitability, it is critical to be able to manipulate the Al and Si dissolution behavior of existing raw material sources to achieve product specifications. This may then require pre-processing of raw materials (eg. fine grinding etc.) and/or use of combinations of raw materials of differing reactivity in a geopolymer system.

Recently, Fernandez-Jimenez and Palomo [22], by interpreting FTIR and NMR results, showed how important the role of the reactive aluminum is in the kinetics of gel formation and in the mechanical strength behavior when working with fly ashes. They analyzed the relationship between mechanical strengths and the relative amount of $Q^4(4Al)$ versus $Q^4(3Al) + Q^4(2Al)$ units in gels. From these results, it was concluded that the mechanical strength of the geopolymer increases during formation of an Al-rich aluminosilicate gel (*Gel 1*) in the first stage of the alkaline activation of ash particles, but increases further as a result of the Si enrichment of the material (formation of *Gel 2* Si enriched aluminosilicate gel) (see Fig. 14).

The effect of contaminants in fly ash on geopolymerization

The discussion of material structure and characteristics above is predicated by the composition comprising alkali metals, silica and alumina. The inclusion of impurities in the chemical composition of geopolymer raw materials, such as calcium and iron in fly ash and blast furnace slag, has the effect of adding reaction pathways during geopolymerization. These side reactions are known to cause large changes in material properties during synthesis and in the final product, as a result of changes in setting times, slump, strength and shrinkage. Despite this, the predominant network forming cations in these specimens remain silicon and aluminum. Therefore, it is clear that impurity cations play an important role in altering the products of geopolymerization, which requires to be fully understood. Calcium is known to react strongly with silicon in the presence of water to form various calcium silicate hydrate phases, as well as with aluminum to form calcium aluminate hydrates. Indeed, these reactions form the basis of

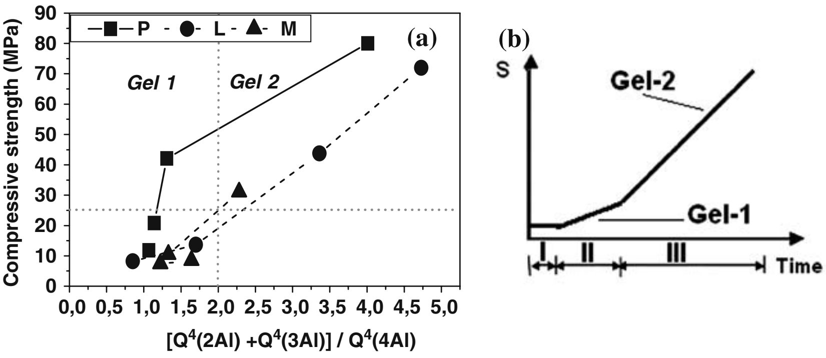


Fig. 14 (**a**) Mechanical strength versus $Q^4(2Al) + Q^4(3Al)/Q^4(4Al)$ ratios deduced by NMR spectroscopy for three fly ashes with different reactive alumina content ($P \approx 18.0\%$; $L \approx 22.5\%$; $M \approx 12.6\%$) (see Ref. [22]); (**b**) Schematic description of mechanical properties evolution with reaction time as function of chemical composition of gel

ordinary Portland cement (OPC) and calcium aluminate cement (CAC) respectively [110]. The reactions of calcium with silicon and aluminum to form hydrates occur quickly in the presence of large amounts of soluble species, such as those provided by dissolution during geopolymerization.

The effect of calcium on geopolymerization has recently been the subject of a number of detailed investigations [40–42]. The amount of calcium in the raw materials and the form in which it is present both play significant roles in determining the reaction pathway and the physical properties of the final geopolymer. Similarly, the level of soluble silicate in the activating solution effects the incorporation of calcium in the final reaction product by affecting the pH of the activating solution and the Ca/Si ratio of any CSH phases formed. In particular, the pH influences the relative stabilities of the different calcium-containing precipitates [41]. The physical effects of this were identified by Lee and van Deventer [38], who found that small additions of soluble calcium to a Class F fly ash-based geopolymer reduced the setting time as measured by the yield stress.

Understanding the structure and dissolution properties of the calcium compounds initially present, even at the relatively low levels (<10%) present in Class F fly ash but more critically in the case of Class C fly ash or blast furnace slag, is central to the industrial and commercial application of geopolymeric materials. Currently there is no fundamental understanding of the location of calcium in the structure of geopolymers, which needs to be elucidated. Recently, ^{43}Ca 3Q and 5QMAS NMR studies of isotopically enriched synthetic slags have yielded new information on the importance of processing conditions in determining the structure of calcium sites [111]. Initial Ca L-edge XANES studies of Ca-containing geopolymers have also been carried out [112], but much further work is required in this area. This information is required before a definitive mechanism for the incorporation of calcium in geopolymers can be proposed. Despite this, the microstructure of calcium-containing geopolymers has been widely investigated. SEM micrographs displaying the microstructures of metakaolin/slag and fly ash/slag geopolymers are presented in Fig. 15. These microstructures are clearly different to the slag-free systems shown in Fig. 13, with a much greater extent of heterogeneity introduced by the precipitation of high-Ca phases throughout the geopolymer gel matrix. It is now well understood that the formation of calcium compounds in geopolymers is greatly dependent on the pH and Si/Al ratio [40, 41].

Fly ashes generally contain appreciable levels of iron in various forms, either as a network former or network modifier in the glassy phases, and as crystalline oxide phases such as maghemite or magnetite [25]. Similar to calcium, there is no structural information on the role of iron in geopolymers. Determining this is experimentally complicated by NMR, since iron inter-

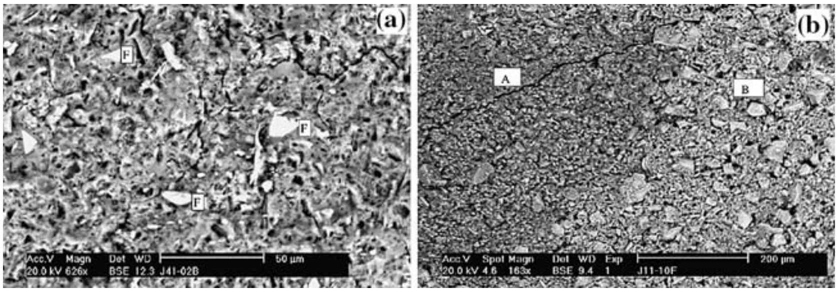


Fig. 15 SEM micrographs of inorganic polymers synthesized from (**a**) metakaolin/slag, (**b**)class F fly-ash/slag

feres with acquisition. Despite this, precipitation of Fe dissolved from basaltic glasses containing significant levels of network-forming Fe^{3+} under slightly alkaline conditions is known to be much faster than for Si and Al [113]. Therefore it is expected that any reactive iron present during geopolymerization would behave similarly, and precipitate rapidly in hydroxide or oxyhydroxide phases. This is a similar effect to that of calcium discussed above with regard to precipitation of calcium hydroxide, which removes hydroxide ions from the solution phase, and will affect the setting behavior and material properties. Finally, in a previous paper [114], it has been observed that the Fe present in the original fly ash can play and important role in the capacity of immobilize arsenic in alkaline activated fly ash matrices.

Applications

Materials generated by the alkaline activation of metakaolin and/or fly ashes constitute a unique family of materials of a mixed nature, with properties varying from those characteristic of cements, ceramics and zeolites (depending on formulation). These characteristics arise from a number of beneficial features, including rapid development of mechanical strength, fire resistance, dimensional stability, acid resistance, excellent adherence to aggregates and reinforcements, etc. Also, for the case of geopolymer concrete derived from fly ash, the cost of the material is generally lower than OPC by a factor of about 10–30%. Further, when compared to the properties of traditional Portland cement concrete, the technological characteristics of geopolymer concrete show promising improvements. However, in general, geopolymers derived from metakaolin require too much water (which increases porosity) and are too soft to be of much practical importance in construction applications. Metakaolin or other synthetically derived aluminosilicate raw material sources are important for use in making geopolymers for applications as adhesives, coatings and hydroceramics.

Because of the traditional use of fly ashes in the cement and concrete industry, engineering and durability properties of geopolymer concrete are being studied in detail [115–120]. Geopolymer concrete derived from fly ash may develop high compressive strength in the first few hours after alkali activation (60–70 MPa after 24 h) [119]. The interfaces formed between the binder phase and aggregate are characterized by the same dense and compact microstructure as found in the bulk of the material. Finally, attention should also be drawn to the high dimensional stability of fly ash derived binder [115], as well as to its capacity for protecting the steel reinforcement [120]. This allows for use of geopolymer concrete with enhanced design for shrinkage cuts and controlled cracking. From the standpoint of the future application of geopolymer as a cementitious material, attention should be drawn to the compatibility, under certain working conditions, between the C–S–H gel (generated during the hydration of the OPC) and the geopolymer gel [121, 122]. Such compatibility may be the key to the future development of more environment-friendly, economical, durable and higher performing cement materials than today's Portland cement.

Conclusions

The current state of the art in geopolymer technology may be succinctly summarized as follows: much work has been done, yet much work remains to be done. Research in this field has historically been applications-focused, and the mechanisms and processes underlying geopolymer formation, and controlling the structures of the products of these reactions, have only relatively recently become the subject of detailed attention. However, progress is being made in this area, and the understanding that has been developed to date provides indications that geopolymer technology does in fact have the potential for wide-scale utilization in the construction industry, as well as in other niche applications. The more knowledge is built on this foundation, the closer the eventual goal of tailored geopolymer design becomes, which will allow exploitation of the full technological potential of these materials. This review has provided a relatively brief overview of the progress in geopolymer science and technology over the past two or more decades, and it is hoped that future research progress in this field will drive the commercial and industrial success of these materials as an environmentally friendly solution to some of the materials selection problems faced by the construction industry.

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References

1. Davidovits J (1991) J Therm Anal 37:1633
2. Van Wazer JR (1970) Inorg Macromol Rev 1:89
3. Gartner E (2004) Cem Conc Res 34:1489
4. Rahier H, Van Mele B, Biesemans M, Wastiels J, Wu X (1996) J Mater Sci 31:71
5. Palomo A, De La Fuente JIL (2003) Cem Conc Res 33:281
6. Krivenko PV (1994) In: Krivenko PV (ed) Proceedings of the first international conference on alkaline cements, concretes. VIPOL Stock Company, Kiev, Ukraine, pp 11–129
7. Mallicoat S, Sarin P, Kriven WM (2005) Ceram Eng Sci Proc 26:37
8. Sofi M, Van Deventer JSJ, Mendis PA, Lukey GC (2006) J Mater Sci (this issue)
9. Bao Y, Grutzeck MW, Jantzen CM (2005) J Am Ceram Soc 88:3287
10. Phair JW, Smith JD, Van Deventer JSJ (2003) Mater Lett 57:4356
11. Gordon M, Bell JL, Kriven WM (2005) Ceram Trans 165:95
12. Xu H, Van Deventer JSJ (2000) Int J Miner Proc 59:247
13. Purdon AO (1940) J Soc Chem Ind Trans Commun 59:191
14. Roy D (1999) Cem Conc Res 29:249
15. Iwahiro T, Nakamura Y, Komatsu R, Ikeda K (2001) J Eur Ceram Soc 21:2515
16. Wagh AS (2005) Ceram Trans 165:107
17. Duxson P, Provis JL, Lukey GC, Mallicoat SW, Kriven WM, Van Deventer JSJ (2005) Colloid Surf A 269:47
18. Duxson P, Mallicoat SW, Lukey GC, Kriven WM, Van Deventer JSJ (2006) Coll Surf A (in press), DOI: 10.1016/j.colsurfa.2006.05.044
19. Rowles M, O'connor B (2003) J Mater Chem 13:1161
20. Glukhovsky VD (1959) Soil silicates. Gosstroyizdat, Kiev, 154pp
21. Fernández-Jiménez A, Palomo A, Criado M (2005) Cem Conc Res 35:1204
22. Fernández-Jiménez A, Palomo A, Sobrados I, Sanz J (2006) Micropor Mesopor Mater 91:111
23. Provis JL, Lukey GC, Van Deventer JSJ (2005) Chem Mater 17:3075
24. Provis JL, Duxson P, Van Deventer JSJ, Lukey GC (2005) Chem Eng Res Des 83:853
25. Van Deventer JSJ, Provis JL, Duxson P, Lukey GC (2006) J Hazard Mater (in press), DOI 10.1016/j.jhazmat.2006.02.044
26. Blum AE, Lasaga AC (1988) Nature 331:431
27. Walther JV (1996) Am J Sci 296:693
28. Oelkers EH (2001) Geochim Cosmochim Acta 65:3703
29. Smith JV (1998) Proc Natl Acad Sci USA 95:3366
30. Swaddle TW Salerno J, Tregloan PA (1994) Chem Soc Rev 23:319
31. Swaddle TW (2001) Coord Chem Rev 219:221–665
32. Aiello R, Crea F, Nastro A, Subotić B, Testa F (1991) Zeolites 11:767
33. Ivanova II, Aiello R, Nagy JB, Crea F, Derouane EG, Dumont N, Nastro A, Subotić B, Testa F (1994) Micropor Mater 3:245
34. Faimon J (1996) Geochim Cosmochim Acta 60:2901
35. Provis JL, Van Deventer JSJ (2006) J Mater Sci (this issue)
36. Provis JL (2006) PhD Thesis, University Of Melbourne, 310pp
37. Duxson P, Lukey GC, Van Deventer JSJ (2006) J Mater Sci (this issue)
38. Lee WKW, Van Deventer JSJ (2002) Cem Conc Res 32:577
39. Alonso S, Palomo A (2001) Mater Lett 47:55
40. Yip CK, Lukey GC, Van Deventer JSJ (2003) Ceram Trans 153:187
41. Yip CK, Van Deventer JSJ (2003) J Mater Sci 38:3851
42. Granizo ML, Alonso S, Blanco-Varela MT, Palomo A (2002) J Am Ceram Soc 85:225
43. Duxson P (2006) PhD Thesis, University Of Melbourne, 287pp
44. Davidovits J (1988) In: Davidovits J, Orlinski J (eds) Proceedings of geopolymer '88—first European conference on soft mineralurgy. Universite De Technologie De Compeigne, Compeigne, France, pp 149–166
45. Duxson P, Lukey GC, Separovic F, Van Deventer JSJ (2005) Ind Eng Chem Res 44:832
46. Palomo A, Alonso S, Fernández-Jiménez A, Sobrados I, Sanz J (2004) J Am Ceram Soc 87:1141
47. Duxson P, Provis JL, Lukey GC, Separovic F, Van Deventer JSJ (2005) Langmuir 21:3028
48. Klinowski J (1984) Prog NMR Spec 16:237
49. Engelhardt G, Michel D (1987) High-resolution solid-state NMR of silicates and zeolites. Wiley, New York, 485pp
50. Lee SK, Stebbins JF (1999) Am Miner 84:937
51. Provis JL, Duxson P, Lukey GC, Van Deventer JSJ (2005) Chem Mater 17:2976
52. Fernández-Jiménez A, De La Torre AG, Palomo A, López-Olmo G, Alonso MM, Aranda MAG (2006) Fuel 85:625
53. Fernández-Jiménez A, De La Torre AG, Palomo A, López-Olmo G, Alonso MM, Aranda MAG (2006) Fuel 85: 1960
54. Kriven WM, Bell JL, Gordon M (2003) Ceram Trans 153:227
55. Barbosa VFF, Mackenzie KJD, Thaumaturgo C (2000) Int J Inorg Mater 2:309
56. Alonso S, Palomo A (2001) Cem Conc Res 31:25
57. Brinker CJ, Scherer GW (1990) Sol-Gel science: the chemistry and physics of Sol-Gel processing. Academic, London, 980pp
58. Yang S, Navrotsky A, Phillips BL (2000) J Phys Chem B 104:6071
59. Palomo A, Glasser FP (1992) Br Ceram Trans J 91:107
60. Van Jaarsveld JGS, Van Deventer JSJ (1999) Cem Conc Res 29:1189
61. Barrer RM, Mainwaring DE (1972) J Chem Soc Dalton Trans 1254
62. Barrer RM, Mainwaring DE (1972) J Chem Soc Dalton Trans 2534
63. Barrer RM (1982) Hydrothermal chemistry of zeolites. Academic, London, 360pp
64. Baerlocher C, Meier WM, Olson DH (2001) Atlas of zeolite framework types, 5th revised edition. Elsevier, Amsterdam, 308pp
65. Provis JL, Duxson P, Lukey GC, Separovic F, Kriven WM, Van Deventer JSJ (2005) Ind Eng Chem Res 44:8899
66. Kollman PA, Kuntz ID (1972) J Am Chem Soc 94:9236
67. Swier S, Van Assche G, Van Hemelrijck A, Rahier H, Verdonck E, Van Mele B (1998) J Therm Anal 54:585
68. Palomo A, Fernández-Jiménez A, Criado M (2004) Mater Construc 54:77
69. Desiraju GR (2003) Nature 423: 485
70. Corradini P, Auriemma F, De Rosa C (2006) Acc Chem Res 39:314

71. Lee WKW, Van Deventer JSJ (2002) Colloid Surf A 211:49
72. Provis JL, P, Duxson, Lukey GC, Van Deventer JSJ (2005) Chem Mater 17:2976
73. Criado M, Fernández-Jiménez A, Palomo A (2007) Micropor Mesopor Mater (submitted)
74. Criado M, Fernández-Jiménez A, Palomo A, Sobrados I, J Sanz (2007) Micropor Mesopor Mater (submitted)
75. Svensson IL, Sjöberg S, Öhman LO (1986) J Chem Soc Faraday Trans I 82:3635
76. Rahier H, Simons W, Van Mele B, Biesemans M (1997) J Mater Sci 32:2237
77. Sindhunata, Van Deventer JSJ, Lukey GC, Xu H (2006) Ind Eng Chem Res 45:3559–73
78. Criado M (2007) PhD Thesis, Eduardo Torroja Institute (in progress)
79. Mccormick AV, Bell AT, Radke CJ (1989) J Phys Chem 93:1741
80. Lee WKW, Van Deventer JSJ (2003) Langmuir 19:8726
81. Fernández-Jiménez A, Palomo A (2005) Cem Concr Res 35:1984
82. Hos JP, Mccormick PG, Byrne LT (2002) J Mater Sci 37:2311
83. Xu H, Van Deventer JSJ (2002) Miner Eng 15:1131
84. Oelkers EH, Gislason SR (2001) Geochim Cosmochim Acta 65:3671
85. Oelkers EH, Schott J, Devidal JL (1994) Geochim Cosmochim Acta 58:2011
86. Xu H, Van Deventer JSJ (2003) Colloid Surf A 216:27
87. Van Jaarsveld JGS, Van Deventer JSJ (1999) Ind Eng Chem Res 38:3932
88. Fernández-Jiménez A, Palomo A, Criado M (2006) Mater Construc 56:51
89. Barrer RM, White EAD (1952) J Chem Soc 1561
90. Barrer RM, Baynham JW (1956) J Chem Soc 2882
91. Barrer RM, Mccallum N (1953) J Chem Soc 4029
92. Barrer RM, White EAD (1951) J Chem Soc 1267
93. Rahier H, Denayer JF, Van Mele B (2003) J Mater Sci 38:3131
94. Cockrell CF, Muter RB, Leonard JW, Anderson RE (1970) Potential for recovering unreacted lime from limestone-modified fly ash by agglomerate. Coal Res. Bur.,West Virginia Univ., Morgantown, 267 pp
95. Fernández-Jiménez A, Palomo A (2005) Micropor Mesopor Mater 86:207
96. Keyte LM, Lukey GC, Van Deventer JSJ (2005) In: Nzihou A (ed) Wasteeng 2005. Albi, France. CD-ROM Proceedings
97. Fernández-Jiménez A, Palomo A (2003) Fuel 82:2259
98. Ejaz T, Jones AG, Graham P (1999) J Chem Eng Data 44:574
99. Gasteiger HA, Frederick WJ, Streisel RC (1992) Ind Eng Chem Res 31:1183
100. Dent LS Glasser, Harvey G (1984) J Chem Soc Chem Commun 1250
101. Patra A, Ganguli D (1994) Bull Mater Sci 17:999
102. Weng L, Sagoe-Crentsil K, Brown T, Song S (2005) Mater Sci Eng B 117:163
103. Henry M (2002) Chem Phys Chem 3:561
104. Xu H, Van Deventer JSJ, Roszak S, Leszczynski J (2004) Int J Quant Chem 96:365
105. Granizo ML, Blanco-Varela MT, Palomo A (2000) J Mater Sci 35:6309
106. Madani A, Aznar A, Sanz J, Serratosa JM (1990) J Phys Chem 94:760
107. Rahier H, Wullaert B, Van Mele B (2000) J Therm Anal Calor 62:417
108. Azizi N, Harris RK, Samadi-Maybodi A (2002) Magn Reson Chem 40:635
109. Antonić T, Čižmek A, Subotić B (1994) J Chem Soc Faraday Trans 90:3725
110. Taylor HFW (1964) The chemistry of cements. Academic, London
111. Shimoda K, Tobu Y, Kanehashi K, Nemoto T, Shimoikeda Y, Saito K (2005) In: Naito A (ed) 1st Asia Pacific Nmr Symposium, Yokohama, Ap130
112. Vance ER, Perera DS, Hanna JV, Pike KJ, Aly Z, Blackford MG, Zhang Y, Zhang Z, Rowles M, Davis J, Uchida O, Yee P, Ly L (2005) International workshop on geopolymers and geopolymer concrete, Perth, Australia. CD-ROM Proceedings
113. Daux V, Guy C, Advocat T, Crovisier J-L, Stille P (1997) Chem Geol 142:109
114. Fernández-Jiménez A, Palomo A, Macphee DE, Lachowski E (2005) J Am Ceram Soc 88:1122
115. Fernández-Jiménez AM, Palomo A, López-Hombrados C (2006) ACI Mater J 103:106
116. Hardjito D, Wallah SE, Rangan BV (2002) In: Lukey GC (ed) Geopolymers 2002—turn potential into profit, Melbourne, Australia. CD-ROM Proceedings
117. Fernández-Jiménez A, Garcia-Lodeiro I, Palomo A (2006) J Mater Sci (this issue)
118. Bakharev T (2005) Cem Concr Res 35:1233
119. Fernández-Jiménez A, Palomo A (2007) Mater Construc (in press)
120. Miranda JM, Fernández-Jiménez A, Gonzalez JA, Palomo A (2005) Cem Concr Res 35:1210
121. Yip CK, Lukey GC, Van Deventer JSJ (2005) Cem Conc Res 35:1688
122. Palomo A, Fernández-Jiménez A, Kovalchuk G, Ordóñez LM, Naranjo MC (2006) J Mater Sci (this issue)