JOURNAL OF MATERIALS SCIENCE **39** (2004) 571–580

Ultrasound enhanced geopolymerisation

D. FENG, H. TAN, J. S. J. VAN DEVENTER*
Department of Chemical and Biomolecular Engineering, The University of Melbourne, Victoria 3010, Australia
E-mail: jannie@unimelb.edu.au

The feasibility of using ultrasound to enhance the geopolymerisation of metakaolinite/sand and fly ash/metakaolinite mixtures was investigated. The introduction of ultrasonication into the geopolymerisation systems increased the compressive strength of the formed geopolymers and the strength increased with increased ultrasonication up to a certain time. The dissolution of metakaolinite and fly ash in alkaline solutions was enhanced by ultrasonication, hence releasing more Al and Si into the gel phase for polycondensation. SEM analysis demonstrated that ultrasonication improved the distribution of the gel phase in the geopolymeric matrices and strengthened the binding between the particle surfaces and the gel phases. XRD patterns showed that ultrasonication enhanced the formation of semi-crystalline to crystalline phases in the formed geopolymers. The ^{27}Al MAS-NMR spectra showed ^{27}Al chemical shifts at around 55 ppm for the geopolymers synthesised with and without ultrasonication, indicating that Al was tetrahedrally coordinated in the form of Al(4Si). ^{29}Si MAS-NMR studies showed that ultrasonication largely improved the interlinkage between Si and Al species, increased the concentrations of polysialate species and enhanced the ordering of the Si and Al tetrahedra in the gel phase in geopolymerisation. Both ^{27}Al and ^{29}Si MAS-NMR spectra indicated an increased extent of polymerisation between Al and Si species in the presence of ultrasonication. The thermal analysis indicated that ultrasonication improved the thermal stability of the formed geopolymers. The improved performance of the ultrasonically formed geopolymers in terms of compressive strength and thermal stability could be attributed to the accelerated dissolution of the Al—Si source materials, the strengthened bonds at the solid particle/gel phase interfaces, the enhanced polycondensation process and the increased semi-crystalline and crystalline phases. *© 2004 Kluwer Academic Publishers*

1. Introduction

A geopolymer is a three-dimensional aluminosilicate mineral polymer that contains a variety of amorphous to semi-crystalline phases. Geopolymerisation can transfer aluminium and silicon containing materials into a monolithic geopolymer with a high mechanical strength and high fire, acid, water and bacterial resistance. In the past two decades, aluminosilicate minerals, such as kaolinite and metakaolinite have been applied in geopolymerisation to form products used as bricks, high strength tools, high acid-resistance moulds, ultrahigh efficiency filters, high temperature-resistance composite materials, protective coating materials, water and fire resistance construction materials and lightweight thermal insulation materials [1–5].

Alkali-activated alumino-silicate binders are formed by reacting silica-rich and aluminium-rich solids with a solution of alkali or alkali salts resulting in a mixture of gels and crystalline compounds that eventually harden into a new strong matrix. According to Davidovits [6], geopolymeric binders are the synthetic analogues of natural zeolitic materials and require much the same hydrothermal conditions for synthesis. Reaction times, however, are substantially faster than that of the comparable zeolite resulting in an amorphous to semi-crystalline product with some zeolite properties. Ideally geopolymers consist of aluminium and silica tetrahedra interlinked alternately by sharing all the oxygen atoms. A polymeric structure of Al—O—Si—bonds is thus formed that constitutes the main building blocks of the geopolymeric structure. Because of aluminium's four-fold coordination, other cations must be present in the structure in order to keep structure neutrality and this is usually done by Na^+, K^+, Ca^{2+} as well as other metallic cations. The exact mechanism by which geopolymers harden is still not fully understood and most proposals in this regard involve dissolution of Al—Si oxides from solid surfaces, diffusion of dissolved Al—Si complex from the solid surface into the gel phase, condensation of gel phase and hardening of the gel phase [7]. The overall rate of this polycondensation reaction, i.e., the setting or curing time of

---

*Author to whom all correspondence should be addressed.

the geopolymer, is determined by all factors affecting the individual steps, and will affect the final structure and strength. Therefore, whatever factors affect those steps mentioned above will affect the final mechanical strength of the geopolymers. As the first step, dissolution has two major roles in geopolymerisation. First, it is the necessary process whereby polysialate-forming species are liberated from the starting materials similarly to zeolite precursors [8, 9]. Second, it prepares or "activates" the surface for surface binding reactions which are hypothesised to significantly contribute to the final strength of the structure. Depending upon the quantities and nature of starting aluminium and silicate sources, the extent of dissolution will vary and therefore determine the chemical composition of the gel phase, which controls the resultant bulk physical and chemical properties of the final product [10]. In general, minerals with a higher extent of dissolution exhibited higher ultimate compressive strengths [11].

Through the micro-structural studies of the cracking surfaces of geopolymers, it has been shown that fractures occasionally occur in the gel phase. Despite its importance, little work has been focused on tailoring the gel phase strength. The polycondensation step is actually a sol-gel process, starting from molecular precursors in solution, to making a condensed phase [12, 13]. Referring to the polymerisation of aluminosilicates in the synthesis of zeolite, suitably designed aluminosilicate crystals could be obtained through the nucleation and growth of the precursors such as $Al(OH)_4^-$ and silicate monomer, dimer and larger oligomer anions. The ordered arrays of the aluminosilicates may form an important sub-structure of the gel phase, which could significantly contribute to the improvement of the gel phase strength, and hence the overall geopolymer strength. In conventional geopolymerisation, the reaction conditions are, however, not manipulated to yield ordered crystals evenly distributed in the gel phase. The growth of the microscale crystals could become macroscale aggregates without control.

Cavitation as a source of energy input for chemical processes is increasingly being studied in various areas such as synthesis and materials processing, chemical and biological engineering, and waste disposal due to its ability to generate localised high temperatures and pressures (hot spots) under nearly ambient conditions as well as high speed microjets [14, 15]. In a heterogeneous solid-liquid system, the collapse of the cavitation bubble will have significant mechanical effects. This effect can increase mass and heat transfer to the surface by disruption of the interfacial boundary layers. Ultrasound has been successfully coupled with the sol-gel process in the synthesis of a wide range of nano- and micro- particles [15]. During geopolymerisation, dissolution and diffusion occur in the mixing process. Effective Al—Si particle contact and dissolution in solution in a short time could result in efficient geopolymerisation. Mechanical mixing cannot satisfy this key step. The present work therefore introduces ultrasonication into geopolymerisation, in an attempt to tailor the dissolution and the polycondensation processes for possible improvement in the microstructure of the final products. The qualitative relationship between the microstructure and the performance of geopolymers will also be discussed.

2. Experimental work

2.1. Materials

Metakaolinite (MetaStar 402) was purchased from Commercial Minerals, Australia and had a particle size of 50% less than 0.5 μm and 1% greater than 38 μm. The metakaolinite sample contained SiO_2 (54.78%), Al_2O_3 (40.42%), K_2O (2.72%) and trace amounts of Fe, Ca and Mg. Fly ash (Gladstone) was obtained from Pozzolanic Enterprises Pty. Ltd., Queensland, Australia and had a particle size of 50% less than 8.47 μm and 1% greater than 110 μm. The composition for the fly ash was 46.2% SiO_2, 30.3% Al_2O_3, 12.6% Fe_2O_3, 4.31% CaO, 1.66% TiO_2, 1.52% MgO, 0.92% P_2O_5 and trace amounts of K, Na and Mn. Fine washed beach sand (<2 mm) was used as a filler in the geopolymerisation of metakaolinite. Sodium silicate (Vitrosol N40) and potassium silicate (Kasil 2236) solutions were supplied by PQ Australia Pty. Ltd., Victoria, Australia. The sodium silicate sample contained 8.7–9.1% Na_2O and 28.4–28.9% SiO_2 and the potassium silicate sample contained 10.8–11.2% K_2O and 24.2–24.8% SiO_2. Analytical grade chemicals and distilled water were used throughout the geopolymerisation and chemical analyses.

2.2. Leaching and geopolymerisation tests

Leaching was conducted with NaOH or KOH solution in a 150 mL polypropylene beaker at a room temperature of 20°C for a certain time using a magnetic stirrer. 100 mL of leaching solution was added to 50 g of the solid samples. Leaching tests with ultrasonication were conducted in a water bath of 20°C using an ultrasonic probe (UP200S ultrasonic processor, Sonotool S7, Dr. Hielscher GmbH, 24 kHz, maximum power intensity 300 W/cm^2). Samples were taken at certain intervals. The samples were centrifuged, filtered and neutralised by condensed HCl for the determination of the elemental concentrations of Al, Si, Fe and Ca in solutions by ICP-OES (Perkin-Elmer Optima 3000). For geopolymerisation, Al—Si minerals were dry mixed at specified mass ratios for 5 min in a container by hand prior to the addition of MOH and M_2SiO_3 solution (where $M =$ Na and/or K). After another 3 min of mixing with hand, the slurry was subjected to ultrasonication with the ultrasonic probe for a desired amount of time. The slurry was cooled in icy water to keep the slurry temperature relatively constant during ultrasonication. For comparison, a FRITSCH Vibratory Shaker was employed to conduct the mixing of the slurry for the same amount of time. The resulting paste was then transferred to a mould (PVC cylinder mould of 28 mm in diameter × 55 mm in height) and left in an oven for setting at 40°C for 24 h. After being removed from the mould, the sample was left at a room temperature of 20°C for 10 days. The compressive strength of each sample was tested using a Tinus Tolsen Compressive Strength testing machine.

Two or three samples of each condition were tested, with average compressive strength values reported.

2.3. Analytical techniques

The elemental concentrations of Al—Si materials were determined by XRF (Siemens SRS 3000 sequential X-ray fluorescence spectrophotometer). XRD (Phillips PW1800) was used to identify the mineralogy of the geopolymers synthesized with or without ultrasound. The ^{29}Si and ^{27}Al MAS NMR responses were used to detect the structural environment for Al and Si sited in the geopolymers. The ^{29}Si and ^{27}Al spectra were recorded at 59.61 and 18.18 MHz on a Varian 300/solid-state spectrometer employing magic angle spinning at 6.9 kHz. The obtained NMR peaks were fitted using Gaussian lines. Geopolymer samples were pulverised and densely packed into a 7 mm zirconium rotor. SEM/EDX analysis was the key tool for the investigation of fractured surfaces of geopolymers and for the determination of elemental concentrations in gel phases. A Phillips XL30 SEM coupled with an Oxford energy dispersive spectrometer was employed for this purpose. The particle size distribution of raw materials was analysed by a Coulter LS 130 optical particle size analyser. Modulated Differential Scanning Calorimetry (MDSC 2920, Thermal Analyst 3000, TA Instruments) was used to characterise the glass phase transformation in geopolymers. Heat flow was recorded from 0 to 750°C at a temperature rate of 10°C/min.

3. Results and discussion

3.1. Al—Si mineral dissolution in the presence of ultrasound

As stated above, the process of geopolymerisation starts with the dissolution of Al and Si from Al—Si source materials in alkaline solutions as hydrated reaction products, forming the $[M_x(AlO_2)_y(SiO_2)_z \cdot n\text{MOH} \cdot m\text{H}_2\text{O}]$ gel. Metakaolinite was used as main or secondary sources of soluble Si and Al in most previous studies on geopolymerisation [16–19]. As an important industrial by-product, fly ash was also used as a source of soluble Si and Al in geopolymerisation [17–19]. The leaching behaviour of these two Al—Si materials in alkaline solutions was investigated by Xu and Van Deventer [20]. However, the leaching of Al—Si materials with ultrasonication has never been reported in the literature. The leaching of metakaolinite and fly ash was conducted at different alkaline concentrations in the presence and absence of ultrasonication. For comparison, leaching was also conducted with magnetic stirring at two different speeds of 400 and 800 min^{-1}. The ultrasonic probe was operated at a power intensity of 150 W/cm^2. Fig. 1 shows the leaching result for metakaolinite. Metakaolinite had a higher extent of dissolution with an increase of NaOH concentration from 7.5 M to 10 M and Si had higher concentrations in solutions than the corresponding Al, in accordance with the observation of Xu and Van Deventer [11]. The leaching curves for Al and Si showed the same patterns (Fig. 1), indicating that Al followed Si to dissolve and re-precipitate simultaneously. Ultrasonication largely increased the leaching of metakaolinite (Fig. 1). In the presence of ultrasonication, the Al and Si concentrations in solutions reached a maximum at the first hour, then decreased with time and gradually increased with a further increase in the leaching time (Fig. 1). In the absence of ultrasonication, the Al and Si concentrations in solutions reached a maximum at around 4 h, and afterwards slowly decreased (Fig. 1). The maximum Al and Si concentrations were lower in the absence of ultrasonication. In terms of the very short time scale for the dissolution of metakaolinite in geopolymerisation, it is expected that ultrasonication could largely enhance the dissolution of metakaolinite to release more Al and Si into the gel phase. Despite being low in all the leaching systems, the Ca concentrations were increased in the presence of ultrasonication. The stirring speed did not show much effect on the dissolution of metakaolinite. This indicates that effective mixing was not the only factor attributable to the enhanced dissolution of metakaolinite by ultrasonication.

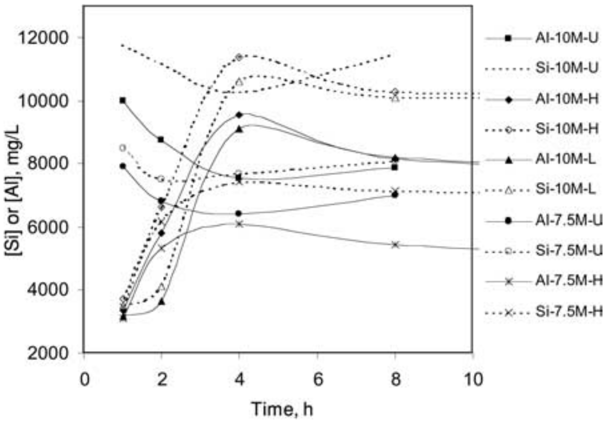


Figure 1 Leaching of metakaolinite in the presence of ultrasonication. Solution: 7.5 M or 10 M NaOH. U–with ultrasound; H–high speed mixing (800 min^{-1}); L–low speed mixing (400 min^{-1}).

The dissolution of metakaolinite followed chemical hydration reactions, where the OH$^-$ anion reacted with the Al—Si solid surfaces to form Al(OH)_4^-, —OSi(OH)_3, divalent orthosilicic acid and trivalent orthosilicic acid ions [21, 22]. The hydration reactions were followed by cation-anion pair condensation interactions based on Coulombic electrostatic attraction, where the M$^+$ cations reacted with Al(OH)_4^- and orthosilicic acid ion species to form ion pairs of the MAl(OH)_4 monomer and silicate monomer, dimmer and trimer ions [21–23]. At high concentrations, the silicate tetramer, pentamer, hexamer, octamer, nonamer, and their compounds would appear [24]. Therefore, Al and Si concentrations in solutions decreased after reaching certain levels, due to the formation of the MAl(OH)_4 monomer and silicate monomer, dimmer and trimer species. The aluminate and silicate species could precipitate on the particle surfaces, hindering the further leaching of metakaolinite, as observed in the leaching without ultrasonication. However, in the presence of ultrasonication the dissolution appeared to continue after the decline of the Al and Si concentrations due to the formation of aluminate and silicate species (Fig. 1). This indicates that ultrasonication likely cleaned the particle surfaces for further leaching.

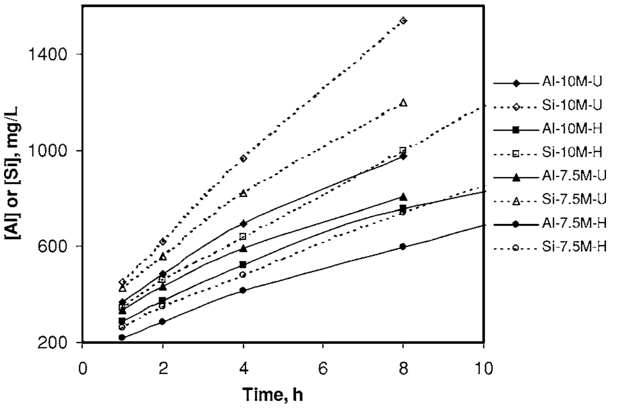


Figure 2 Leaching of fly ash in the presence of ultrasonication. Solution: 7.5 M or 10 M KOH. U–with ultrasound; H–high speed stirring (800 min^{-1}).

Ultrasonication also increased the leaching of fly ash, as shown in Fig. 2. However, the extent of increase was much smaller in comparison with the metakaolinite system. The fly ash contained a substantial amount of Ca and Fe, which were difficult to leach in alkaline solutions. KOH was used instead of NaOH, and the latter was shown to give a better leaching performance [11]. Similarly, a higher alkaline concentration favoured the dissolution of fly ash.

It is well established that ultrasound driven cavitation events cause chemical and physical effects in a liquid medium [15]. Ultrasonic cavitation induces ‘hot spot’ effect, which generates localised high temperatures and pressures. The ‘hot effect’ could directly occur at the mineral surfaces, weakening the physical and chemical bonds. In addition to the ‘hot spot’ effect, ultrasonication also causes mechanical effects, which can be either ‘macroscopic’ induced by the acoustic streaming or ‘microscopic’ induced by microjets [25]. The mechanical effects could clean the solid particle surfaces and enhance the mass transfer at the solid/liquid interfaces. As a consequence, ultrasonication enhanced the leaching of the Al—Si minerals in alkaline solutions.

3.2. Ultrasonication enhanced geopolymerisation

Two geopolymerisation systems were investigated with metakaolinite and fly ash as the main Al—Si source materials. One employed metakaolinite as the main Al—Si source and fine sand as the filler, and the other employed fly ash as the main Al—Si source and metakaolinite as the secondary Al—Si source. A solid/liquid ratio of 2.84 was used in all the geopolymerisation systems, and an ultrasonic power intensity of 300 W/cm^2 was employed. The compressive strength was tested after 10 days of curing at a room temperature of 20°C and an atmosphere pressure. Table I shows the compressive strength of the geopolymers synthesised in the presence of ultrasonication. The geopolymers synthesised with varied times of shaking in the absence of ultrasonication did not show any differences in compressive strength. Therefore, only one strength value was reported for the geopolymers synthesised without ultrasonication.

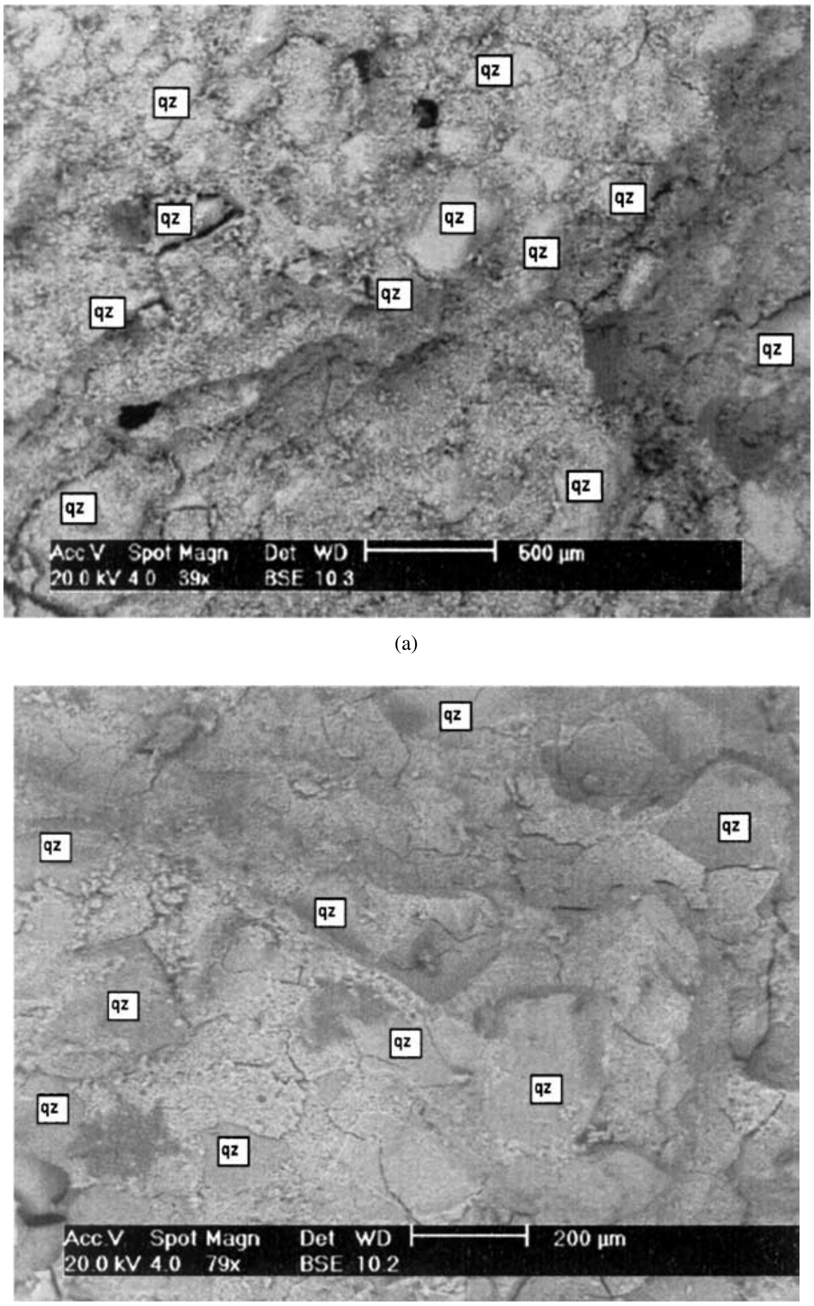
TABLE I Compressive strength of geopolymers synthesised with ultrasonication

Condition		Compressive strength (MPa)
60 g metakaolinite, 160 g sand 0.5 M Na_2SiO_3, 10 M NaOH	Without ultrasonication	7.6
	Ultrasonication time (min)	
	4	10.0
	8	12.5
	14	15.0
	20	15.5
60 g metakaolinite, 160 g sand 2.5 M K_2SiO_3, 8 M KOH	Without ultrasonication	15.8
	Ultrasonication time (min)	
	1	22.0
	3	24.3
	5	24.5
225 g fly ash, 25 g metakaolinite 2.5 M K_2SiO_3, 8 M KOH	Without ultrasonication	11.8
	Ultrasonication time (min)	
	1	13.4
	3	18.5
	5	19.1
200 g fly ash, 50 g metakaolinite 2.5 M Na_2SiO_3, 8 M KOH	Without ultrasonication	14.8
	3 min ultrasonication	23.2

As can be seen from Table I, the introduction of ultrasonication into the geopolymerisation systems increased the compressive strength of the geopolymers and the strength increased with an increase of ultrasonication up to a certain time. However, a prolonged ultrasonication no longer increased the compressive strength of the formed geopolymers (Table I). This is likely because the geopolymer paste became more viscous after a prolonged ultrasonication, due to the polycondensation and hardening occurring simultaneously. The condensed paste would hence hinder ultrasonic cavitation. A higher sodium silicate concentration was beneficial to the geopolymerisation of the metakaolinite/sand mixture. As the secondary Al—Si source, metakaolinite enhanced the geopolymerisation of fly ash, as a higher metakaolinite content gave a better compressive strength of the formed geopolymer (Table I). This could be explained by the fact that metakaolinite tended to dissolve to a larger extent than fly ash.

It should be noted that the geopolymerisation and ultrasonication were conducted under preset conditions without optimisation for the specific systems. The solid/liquid ratio, ultrasonic power and intensity, and Al/Si ratio could affect the effect of ultrasonication on geopolymerisation. The use of ultrasonication for the enhancement of geopolymerisation appeared to be promising, with regard to improved performance of formed geopolymers after a very short time of ultrasonication.

Ultrasonication enhanced the dissolution of Al—Si source materials to release more Al and Si into the gel phases, and hence improving the extent of geopolymerisation. It was shown that a larger extent of the dissolution of source Al—Si materials improved the compressive strength of the formed geopolymers [11]. However, dissolution alone could not have such a significant effect on geopolymerisation within a short period of ultrasonication. In general, the compressive strength of



(a)

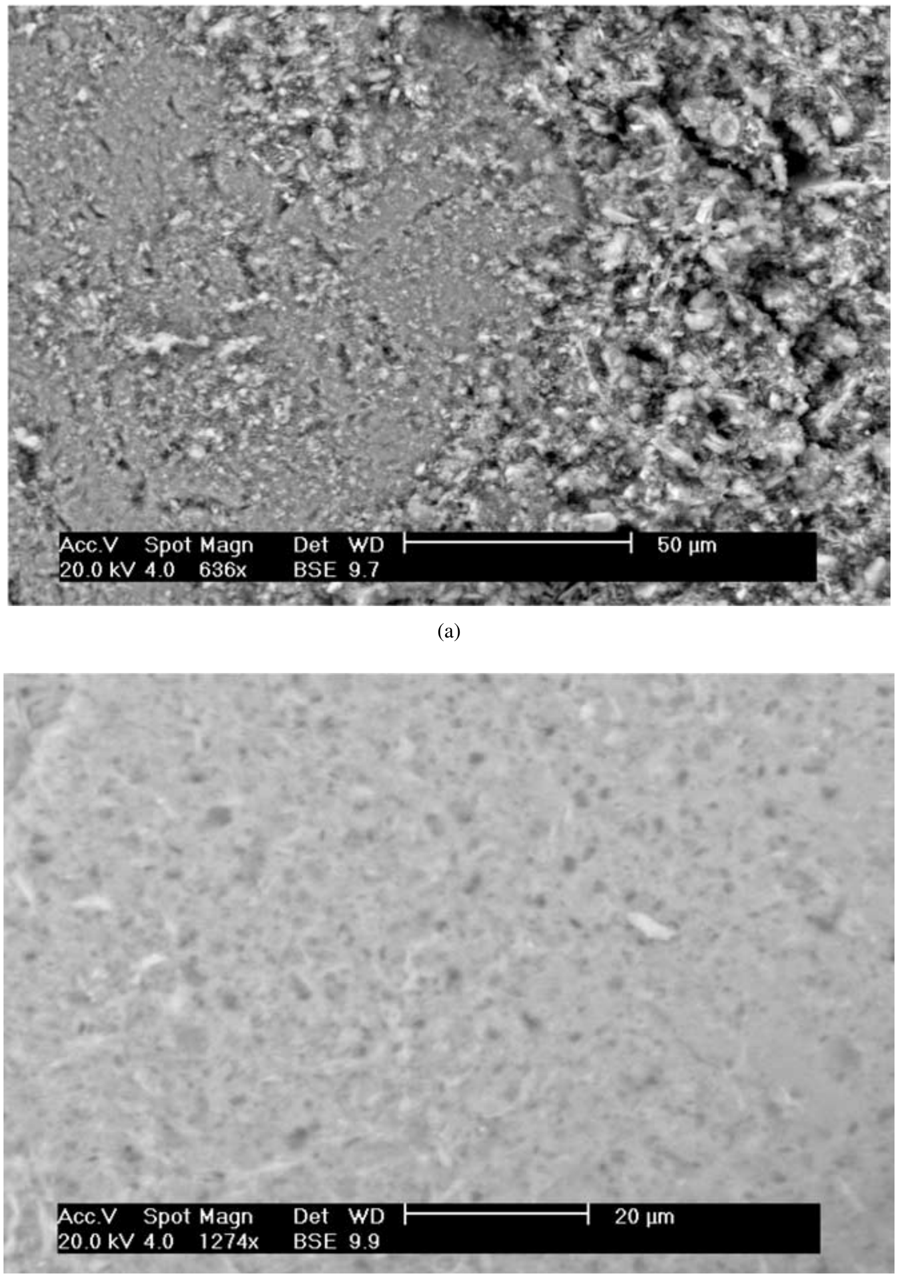
(b)

Figure 3 Typical SEM images of the fractures of the geopolymers synthesised (a) without ultrasonication and (b) with ultrasonication. Geopolymerisation condition: 160 g sand, 60 g metakaolinite, 10 M NaOH, 0.5 M Na_2SiO_3. qz–quartz.

geopolymers is determined by the filler particles (or remaining Al—Si particles), the gel phase and their boundaries. It is expected that the mechanical effects induced by ultrasonication could clean the remaining particle surfaces, favouring the formation of a strong bond between the particles and the gel. On the hand, ultrasonication could modify the microstructure of the gel phase in the formed geopolymers, as discussed below.

3.3. Morphological studies of geopolymers

After compressive strength tests, the cracked geopolymer samples were collected for SEM/EDX analysis. The morphological studies were focused on the fractured surfaces of the geopolymers. Typical SEM images of the fractured surfaces are shown in Fig. 3. Clear boundaries appeared between the quartz particles and the gel phase in the geopolymers synthesised without ultrasonication, showing gaps or cracks between these two phases (Fig. 3a). However, the interfaces appeared to be blurred between the quartz particles and the gel phase in the geopolymers formed with ultrasonication, and no gaps or cracks were present at the interfaces (Fig. 3b). The improved binding between the quartz particles and the gel phase could be one of the important factors attributable to the increase in the compressive strength of the geopolymers synthesised with ultrasonication. The mechanical effects induced by ultrasonication could clean the sand particle surfaces, enhancing the binding between the particle surfaces and the gel phase. In addition, less cracks were present in the gel



(a)

(b)

Figure 4 Typical SEM images of the gel phase in the geopolymers synthesised (a) without ultrasonication and (b) with ultrasonication. Geopolymerisation condition: 160 g sand, 60 g metakaolinite, 10 M NaOH, 0.5 M Na_2SiO_3.

phases in the geopolymers synthesised with ultrasonication, indicating that the strength of the formed gel phases was improved.

The gel phase appeared to be unevenly distributed in the geopolymers synthesised without ultrasonication, as shown in Fig. 4a. This could induce unbalanced stress in the gel phase, causing the decrease in the compressive strength of the geopolymers. In contrast, the gel phase was evenly structured for the geopolymers formed with ultrasonication (Fig. 4b). This could be achieved by the molecular-scale mixing in ultrasonication, due to the microjets and microstreams induced by cavitation. EDX also indicated that the Al and Si concentrations in the gel phases increased with ultrasonication in the geopolymers synthesised with metakaolinite. At 0.5 M Na_2SiO_3 and 10 M NaOH, the Al, Si and Ca concentrations in the gel phase were respectively 13.58, 26.37 and 0.13% in the metakaolinite geopolymer synthesised with 8 min ultrasonication, compared to 10.03, 22.92 and 0.02% in that without ultrasonication. This further demonstrates that ultrasonically enhanced dissolution of the Al—Si minerals played a significant role in the improved performance of the formed geopolymers. In the fly ash system, the SEM images showed that remaining fly ash particles became smaller in the geopolymers synthesised with ultrasonication. In the 225 g fly ash/25 g metakaolinite system, the remaining fly ash particles were about 6.8 μm in size in the geopolymer synthesised with 3 min ultrasonication, compared to 8.0 μm in that synthesised without ultrasonication, based on the average size of 30 particles with <10 μm. This also reveals that ultrasonication enhanced the dissolution of fly ash in the geopolymerisation. Similarly, ultrasonication improved the distribution of the gel phase in the geopolymers as well as the binding at the particle/gel phase interfaces.

3.4. XRD patterns of geopolymers

The geopolymer samples were crushed and milled in a ring mill to fine powders for XRD analysis. The polysialates resulting from the polycondensation of various alkali-alumino-silicates present in the gel phase were actually X-ray amorphous materials. The XRD patterns suggested however that polysialates consisted of disordered frameworks of short-range order materials with structures similar to those of feldspatic glass or crystalline zeolites [6]. In the metakaolinite/sand geopolymerisation system, quartz showed clear characteristic peaks in the amorphous and semi-crystalline phases dominated matrix in the XRD patterns of the formed geopolymers. In comparison, the relative intensities for the semi-crystalline phases increased to a large extent in the XRD patterns of the metakaolinite/sand geopolymers synthesised with ultrasonication. This indicates that polysialate species tended to be more regularly ordered in the geopolymerisation with ultrasonication. The presence of the short-range ordered semi-crystalline phases could improve the strength of the gel phases, and hence the overall strength of the geopolymers.

Fig. 5 shows the XRD patterns of the geopolymers synthesised with the fly ash/metakaolinite mixture in the presence and absence of ultrasonication. In the synthesised geopolymers, the quartz peaks became higher in the relative intensities, and the mullite peaks almost remained unchanged. Quartz and mullite were relatively stable in alkaline solutions, while the other crystalline phases in the fly ash dissolved readily and formed amorphous and semi-crystalline phases after geopolymerisation. As indicated in Fig. 5, the peak intensities for the identified crystalline aluminosilicate increased for the geopolymers synthesised with ultrasonication. Similarly, the peak intensities for the unidentified semi-crystalline phases also increased for the geopolymers synthesised with ultrasonication (Fig. 5). This suggests that ultrasonication could enhance the ordering of the polysialate species for the formation of semi-crystalline to crystalline phases in the gel phases, which likely contributed to the improvement of the compressive strength of the geopolymers synthesised with ultrasonication. The high-speed microjets and microstreams induced by ultrasonic cavitation could increase the collision of Al and Si species for the formation of polysialate species and enhance the ordering of the polysialate species for the formation of small-scale ordered semi-crystalline and highly regularly ordered crystalline materials. On the other hand, the 'hot spot' effect could generate localised high temperatures and pressures, which likely favoured the forming and ordering of the polysialate species as well.

3.5. MAS-NMR spectra of geopolymers

The geopolymer samples for NMR analysis were subjected to crushing and ring milling to fine powders. ^{29}Si and ^{27}Al MAS-NMR studies present a powerful tool for the structural analysis of aluminosilicate species [26]. It was shown that in aluminate anions, four-coordinated aluminium (with respect to oxygen) resonated at 60–80 ppm, and that in silico-aluminates, four-coordinated aluminium resonated at approximately 50 ± 20 ppm while six-coordinated aluminium resonated at approximately at about 0 ± 10 ppm from $[Al(H_2O)_6]^{3+}$ [27]. According to the Loewenstein aluminium avoidance principle, the environment of every Al atom was Al(4Si) in alumino-silicate anions [28]. ^{27}Al MAS-NMR spectroscopy of all polysialates showed ^{27}Al chemical shifts in the range of 55 ppm from $[Al(H_2O)_6]^{3+}$, which indicated that the aluminium was of the AlQ4(4Si) type and was tetrahedrally coordinated [6]. The ^{27}Al MAS-NMR spectra showed ^{27}Al chemical shifts at around 55 ppm for the metakaolinite/sand geopolymers synthesised with and without ultrasonication, as shown in Fig. 6. This means that ultrasonication did not change the environment of every Al atom, which was tetrahedrally coordinated in the form of Al(4Si). However, the relative intensity for the aluminium peak in the ^{27}Al MAS-NMR spectrum was much higher for the geopolymers synthesised with ultrasonication than those without ultrasonication (Fig. 6). This indicates that the concentrations of the

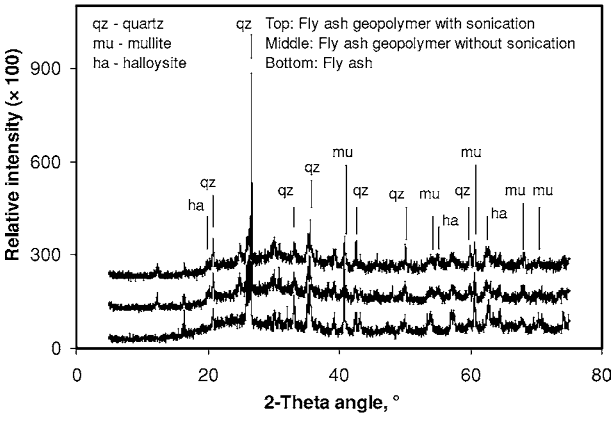


Figure 5 XRD patterns for the geopolymers synthesised with or without ultrasonication. Geopolymerisation condition: 200 g fly ash, 50 g metakaolinite, 8 M NaOH, 2.5 M Na_2SiO_3.

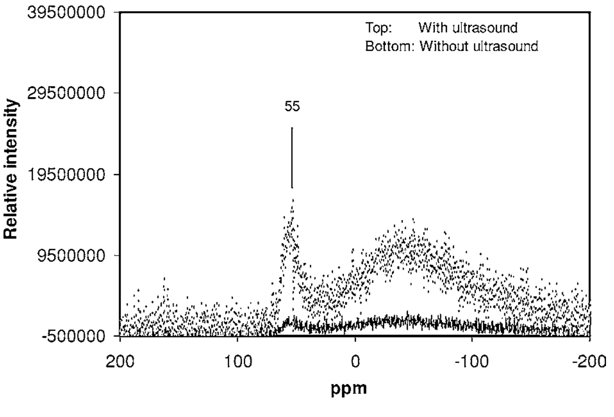


Figure 6 ^{27}Al MAS-NMR spectra for the geopolymers synthesised with and without ultrasonication. Synthesis condition: 160 g sand, 60 g metakaolinite, 10 M NaOH, 0.5 M Na_2SiO_3, 8 min ultrasonication.

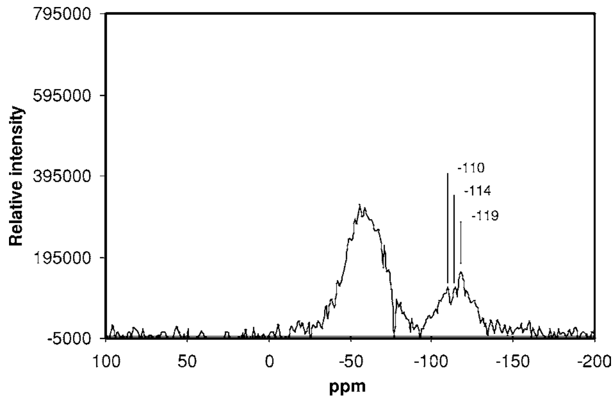


Figure 7 ^{29}Si MAS-NMR spectra for the geopolymers synthesised without ultrasonication. Synthesis condition: 160 g sand, 60 g metakaolinite, 10 M NaOH, 0.5 M Na_2SiO_3.

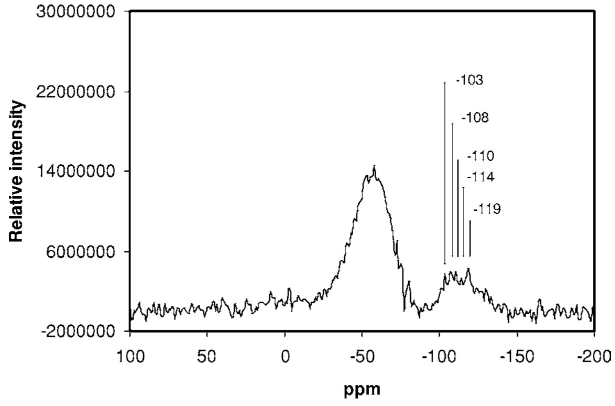


Figure 8 ^{29}Si MAS-NMR spectra for the geopolymers synthesised with ultrasonication. Synthesis condition: 160 g sand, 60 g metakaolinite, 10 M NaOH, 0.5 M Na_2SiO_3, 8 min ultrasonication.

polysialate species were increased by ultrasonication. In other words, the extent of polymerisation increased in the presence of ultrasonication.

^{29}Si resonated at −119, −114 and −110 ppm for the geopolymers synthesised without ultrasonication (Fig. 7), while a much broader resonance of ^{29}Si appeared in the MAS-NMR spectrum for the geopolymers synthesised with ultrasonication, showing resonance peaks at −119, −114, −110, −108 and −103 ppm (Fig. 8). A previous study showed that the chemical shift ^{29}Si in an amorphous or highly disordered environment was increased by approximately 5 ppm [28]. The resonances found for 'disordered' ^{29}Si in polysialates, namely −81.5, −87 and −94.5 ppm, related to 'ordered' ^{29}Si chemical shifts of −86.6, −92, −99.5 ppm which were assigned to Q(4Al), Q(3Al) and Q(2Al), respectively [6]. In the present studies, the ^{29}Si resonances systematically shifted by about −10 ppm. Therefore, the resonances of −119, −114, −110, −108 and −103 ppm for ^{29}Si could be assigned to Q(0Al), Q(1Al), Q(2Al), Q(3Al) and Q(4Al), respectively. As a result, Si presented in the forms of Q(0Al), Q(1Al) and Q(2Al) in the gel phase in the geopolymers synthesised without ultrasonication, while appeared in the more 'ordered' forms of Q(3Al) and Q(4Al) besides the forms of Q(0Al), Q(1Al) and Q(2Al). This indicates that the interlinks between Al and Si atoms increased, and that the Si and Al tetrahedra were more regularly ordered along the polymeric chains in the gel phases in the geopolymers synthesised with ultrasonication. By comparing Figs 7 and 8, it is clear that the relative intensities for the ^{29}Si resonances were much higher in the geopolymers synthesised with ultrasonication than those without ultrasonication, which suggests the presence of higher concentrations of the polysialate species in the former ones, in agreement with the ^{27}Al MAS-NMR spectra (Fig. 6).

^{29}Si and ^{27}Al MAS-NMR studies showed that ultrasonication largely improved the interlinkage between Al and Si species, increased the concentrations of the polysialate species and enhanced the ordering of the Si and Al tetrahedra in geopolymerisation. In other words, the polycondensation of Al and Si species was improved with ultrasonication. This is in accordance with the above XRD studies, where more semi-crystalline to crystalline phases were produced by ultrasonication. The improvement of the polycondensation step would play a dominant role in the enhancement of geopolymerisation with ultrasonication. The mixing at molecular levels due to high-speed microjets and microstreams and localised high temperatures and pressures due to the 'hot spot' effect could be the two major factors improving the polycondensation of Al and Si species in the geopolymerisation with ultrasonication.

3.6. MDSC studies of geopolymers

The geopolymer samples were pulverised for MDSC analysis. A clear understanding of the glass phase transformation in geopolymers would be fairly hard, due to the complexity of the gel phase ranging from highly disordered amorphous phase, to short-range ordered and regularly ordered semi-crystalline and crystalline phases. Fig. 9 shows the thermal analysis results with MDSC for the kaolinite/sand geopolymers synthesised with and without ultrasonication. The maximum glass phase transformation point occurred at 661°C for the geopolymer synthesised with ultrasonication, compared with 665°C for the geopolymer formed without ultrasonication (Fig. 9). The slight decrease in the maximum glass phase transformation point could indicate the increase in the concentrations of Ca and Mg silicates in the gel phase [29]. This is in agreement

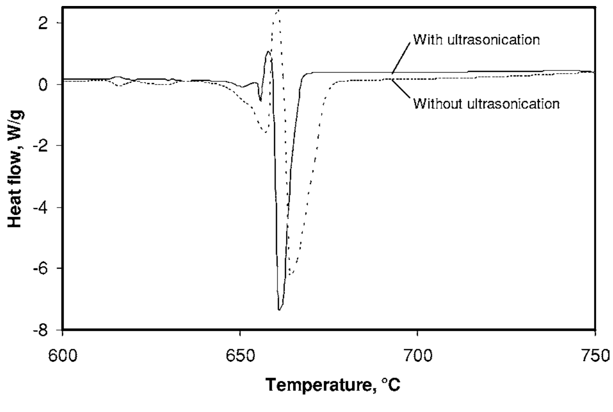


Figure 9 Thermal analysis for the geopolymers synthesised with and without ultrasonication. Synthesis condition: 160 g sand, 60 g metakaolinite, 10 M NaOH, 0.5 M Na_2SiO_3, 8 min ultrasonication.

with the leaching and SEM/EDX results, which showed higher Ca and Mg concentrations in the gel phase in the geopolymers synthesised with ultrasonication. According to the energy integral results between 550 and 720°C, the energy involved in the glass phase transformation was 168 J/g for the geopolymers synthesised with ultrasonication, compared to 145 J/g for those synthesised without ultrasonication (Fig. 9). This indicates that ultrasonication improved the thermal stability of the formed geopolymers.

4. Conclusions

- The dissolution of metakaolin and fly ash in alkaline solutions was enhanced by ultrasonication, releasing more Al and Si for polycondensation.
- The introduction of ultrasonication into the geopolymerisation systems of the metakaolinite/sand and fly ash/metakaolinite mixtures increased the compressive strength of the formed geopolymers and the strength increased with an increase in ultrasonication up to a certain time.
- SEM analysis demonstrated that ultrasonication improved the distribution of the gel phase in the geopolymer matrices and strengthened the binding at the particle/gel phase interfaces. EDX results indicated higher Al, Si and Ca concentrations in the gel phases in the geopolymers synthesised with ultrasonication, in accordance with leaching results.
- XRD patterns showed that ultrasonication enhanced the formation of semi-crystalline to crystalline phases in the geopolymers, which likely contributed to the improvement of the compressive strength of the geopolymers synthesised with ultrasonication. Ultrasonication could improve the ordering of the polysialates to form semi-crystalline to crystalline phases.
- The ^{27}Al MAS-NMR spectra showed ^{27}Al chemical shifts at around 55 ppm for the geopolymers synthesised with and without ultrasonication, indicating that Al was tetrahedrally coordinated in the form of Al(4Si). The ^{27}Al MAS-NMR spectra demonstrated that the concentrations of polysialates were increased by ultrasonication. ^{29}Si MAS-NMR studies showed that ultrasonication largely improved the interlinkage between Si and Al species, increased the concentrations of the polysialate species and enhanced the ordering of the Si and Al tetrahedra in geopolymerisation. In other words, the polycondensation of Al and Si species was improved with ultrasonication, in accordance with the XRD results.
- The thermal analysis of the formed geopolymers indicated an increase in the ion concentrations such as Ca and Mg in the gel phase in the geopolymers synthesised with ultrasonication, in agreement with the leaching and SEM/EDX results. As a higher energy was required for the glass phase transformation, the thermal stability of the formed geopolymers was improved by ultrasonication.
- Ultrasonication increased the compressive strength and thermal stability of the formed geopolymers through accelerating the dissolution of the Al—Si materials, strengthening the bonds at the solid particle/gel phase interfaces, enhancing the polycondensation process and improving the formation of semi-crystalline to crystalline phases.
- The localised high temperatures and pressures due to the 'hot spot' effect and mechanical effects due to acoustic streaming or microjets could contribute to the accelerated dissolution of the source materials, the strengthened bonds at the solid/gel phase and the improved polycondensation process.

Acknowledgements

The financial support from the Melbourne Research Grant Scheme is gratefully acknowledged. Appreciation is also expressed to Dr. H. Xu for assistance with the NMR analysis and valuable discussions.

References

1. J. DAVIDOVITS and M. DAVIDOVICS, *Ceram. Eng. Sc. Proc.* **9** (1988) 835.
2. J. DAVIDOVITS, "Geopolymer'88, 1st European Conference on Soft Mineralurgy" (Compiegne, France, 1988) Vol. 1, p. 49.
3. A. PALOMO, A. MACIAS, M. T. BLANCO and F. PUERTAS, in Proceedings of the 9th International Congress on the Chemistry of Cement (1992) p. 505.
4. B. E. LANEY, US Patent, No. 5194091 (1993).
5. J. DAVIDOVITS, M. DAVIDOVICS and N. DAVIDOVITS, US Patent, No. 5342595 (1994).
6. J. DAVIDOVITS, J. Thermal Anal. **37** (1991) 1633.
7. *Idem.*, in Geopolymer'88, 1st European Conference on Soft Mineralurgy, Compiegne (France, 1988) Vol. 1, p. 25.
8. T. ANTONIC, A. CIZMEK and B. SUBOTIC, *J. Chem. Soc., Faraday Trans.* **90** (1994) 1973.
9. M. W. GRUTZECK and D. D. SIEMER, *J. Amer. Ceram. Soc.* **80** (1997) 2449.
10. H. RAHIER, W. SIMONS, B. V. MELE and M. BIESEMANS, *J. Mater. Sci.* **32** (1997) 2237.
11. H. XU and J. S. J. VAN DEVENTER, *Int. J. Miner. Process.* **59** (2000) 247.
12. C. J. BRINKER and G. W. SCHERER, "Sol-Gel Science" (Academic Press Inc., New York, 1990).
13. M. HENRY, J. P. JOLIVET and J. LIVAGE, "Aqueous Chemistry of Metals Cations, Hydrolysis, Condensation and Complexation in Structure and Bonding," Vol. 77 (Springer-Verlag, Berlin, 1992) p. 155.
14. O. V. ABRAMOV, "Ultrasound in Liquid and Solid Metals" (CRC Press, London, 1994).
15. T. J. MASON and J .P. LORIMER, "Sonochemistry—Theory, Applications and Uses of Ultrasound in Chemistry" (Ellis Horwood, Chichester, 1988).
16. D. C. COMRIE and J. DAVIDOVITS, "Geopolymer'88, 1st European Conference on Soft Mineralurgy" (Compiegne, France, 1988), Vol. 1, p. 125.
17. J. G. S. VAN JAARSVELD, J. S. J. VAN DEVENTER and L. LORENZEN, *Miner. Eng.* **10** (7) (1997) 659.
18. *Idem.*, *Metall. Mater. Trans.* B **29B** (1998) 283.
19. J. G. S. VAN JAARSVELD, J. S. J. VAN DEVENTER and A. SCHWARTZMAN, *Miner. Eng.* **12**(1) (1999) 75.
20. H. XU and J. S. J. VAN DEVENTER, *Ind. Eng. Chem. Res.* **40** (2001) 3749.
21. V. I. BABUSHKIN, G. M. MATVEYEV and O. P. MCHEDLOV-PETROSSYAN, "Thermodynamics of Silicates" (Springer Verlag, Berlin, 1985) p. 276.
22. A. V. MCCORMICK, A. T. BELL and C. J. RADKE, *J. Phys. Chem.* **93**(5) (1989) 1733.
23. *Idem.*, *ibid.* **93**(5) (1989) 1741.
24. W. M. HENDRICKS, A. T. BELL and C. J. RAFKE, *ibid.* **95**(1991) 9513.

25. T. LEIGHTON, "The acoustic Bubble" (Academic Press, London, 1994).
26. E. LIPPMAA, M. MÄGI, A. SAMOSON, M. TARMAK and G. ENGELHARDT, *J. Amer. Chem. Soc.* **103** (1981) 4992.
27. D. MULLER, D. HOEBBEL and W. GESSNER, *Chem. Phys. Lett*. **84**(1) (1981) 25.
28. W. LOEWENSTEIN, *Amer. Mineral*. **39** (1954) 92.
29. V. A. BERSHTEIN and V. M. EGOROV, "Differential Scanning Calorimetry of Polymers: Physics, Chemistry, Analysis, Technology," Translation edited by, T. J. Kemp (Ellis Horwood, New York, 1994).

Received 3 October 2002
and accepted 20 August 2003