

Mechanochemical synthesis of one-part alkali aluminosilicate hydraulic cement

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Abstract A novel approach was devised to synthesize a sustainable hydraulic cement based on alkali aluminosilicate chemistry via mechanochemical activation. This approach builds upon past work on activation of aluminosilicate precursors using alkaline solutions to produce inorganic binders for concrete construction. Recent efforts to develop one-part hydraulic cements based on the chemistry of alkali-activated aluminosilicates have resorted to high-temperature processing techniques which compromise the sustainability advantages of the system, and also

require curing at elevated temperatures. The mechanochemical process developed here takes place at room temperature, and yields a hydraulic cement that does not require addition of caustic solutions to render binding effects via room-temperature curing. Processing of this hydraulic cement takes place at room temperature; this advantage together with extensive use of recycled raw materials yield significant sustainability benefits. The (dry) raw materials used for mechanochemical processing of hydraulic cement included coal fly ash, quick lime, sodium hydroxide and Magnesium oxide. The mechanochemically processed hydraulic cement was evaluated through performance of tests concerned with their pH, heat of hydration, chemical composition, crystallinity and microstructure. The hydraulic cement was used to produce concrete materials cured at room temperature. The resulting concrete materials were found to provide desired levels of workability in fresh state and compressive strength after curing, which were comparable to those of Portland cement concrete. Investigations were also conducted on the hydration kinetics of the hydraulic cement and the microstructure of its hydrates in order to gain insight into its hydration process and the nature of hydration products.

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1 Introduction

An alternative cementitious binder, occasionally referred to as (two-part) “geopolymer”, obtained by alkali-activation of an aluminosilicate precursor (e.g., metakaolin or ground granulated blast furnace slag), has been considered as a substitute for the hydrated Portland cement binder. Geopolymers are conventionally produced via activation of a solid aluminosilicate powder using alkali hydroxide/alkali silicate solutions [1–3]. Geopolymerization involves polycondensation reaction of aluminosilicate oxide (geopolymer precursor) with alkalis, yielding inorganic polymers (alkali aluminosilicate hydrates) with 3D crosslinked chain structures [4]. The complex mineralogy of by-product precursors (e.g., slag or fly ash) could prompt simultaneous hydration reactions, which incorporate calcium silicate hydrate (C–S–H) and calcium hydroxide into the core geopolymer structure. Despite the superior mechanical and durability properties of geopolymers, there are some drawbacks with the two-part nature of their formulation [5]. The use of alkaline solutions limits the commercial prospects of this technology due to the corrosive (and viscous) nature of the required alkaline solutions [6]. Fresh geopolymer mixtures could also experience rapid stiffening (e.g., in the presence of high-calcium fly ash as an aluminosilicate precursor) [7], which is not compatible with mainstream construction practices. The one-part hydraulic cement developed in this project seeks to overcome these drawbacks of two-part geopolymers while providing (or even enhancing) their sustainability and performance advantages.

Several investigations have been undertaken for developing methods of synthesizing one-part alkali aluminosilicate-based hydraulic cements. The more elaborate methods of synthesizing one-part geopolymer cements involve thermal activation of raw materials (including aluminosilicate precursors and alkalis). For example, albite has been activated thermally in the presence of solid alkalis (sodium hydroxide or sodium carbonate) at about 1000 °C [8]. The resulting one-part hydraulic cements provide viable rates of compressive strength development and final compressive strengths. Another investigation prepared one-part geopolymer cement via calcination of low-quality aluminosilicates in the presence of alkali hydroxides, which led to almost complete conversion of all aluminum sites into tetrahedral coordination and extensive chemical

linking between Si–O₄ and Al–O₄ tetrahedra. The resulting powder could, upon addition of water, undergo polycondensation and formation of an amorphous geopolymer matrix. Although the resulting geopolymer paste exhibited spectroscopic parameters similar to conventional geopolymers, its compressive strength was relatively low [9]. Another example involved thermal treatment of low-quality kaolinite in the presence of alkalis [10]. It was found that nepheline and glassy phase sodium aluminosilicate are generated during heat treatment of blends of kaolinite and alkalis; hydration of this cement (at curing temperature of 80 °C) yielded P-zeolite. These particular one-part geopolymer cements yielded reasonable levels of dry compressive strength; their moisture resistant, however, was a concern. The methods used so far for production of one-part geopolymer cements employ relatively high alkali contents and also high processing temperatures, which compromise their economics and sustainability. A recent work in this field synthesized on-part geopolymer cement through thermal activation of red mud blended with silica fume at about 25 wt% to improve the long-term strength of the binder by optimizing the Al/Si ratio to enhance the stability of the geopolymer structure [11]. Eventhough the resulting geopolymer binder reached viable compressive strengths, use of high-temperature processing and relatively high concentrations of silica fume compromised the sustainability and economics of this approach. Another approach followed for production of one-part geopolymer cement involves simple blending of the dry caustic activator and the aluminosilicate precursor. A recent example involves blending of rice husk ash with sodium aluminate [12]. The resulting cement required curing at elevated temperature to yield viable levels of early-age compressive strength. At later ages, however, a drop in compressive strength was observed. The high cost of sodium aluminate is another drawback of this approach. More recent investigations have synthesized one-part formulations by blending either coal fly ash and sodium silicate or rice hull ash and sodium aluminate to reliably develop compressive strength with room-temperature curing [13].

Effects of mechanical activation on coal fly ash and geopolymers incorporating the ash have been investigated [14]. It was found that mechanical activation reduces the particle size, changes the particle shape, and increases the reactivity of coal fly ash. The two-



part geopolymer prepared using the mechanically activated fly ash cured at room temperature showed up to 80% increase in compressive strength when compared with that prepared with as-received fly ash. Work has also been reported on mechanochemical activation of natural pozzolans for use as precursors in geopolymer [15]. Ball milling of volcanic ash of relatively low reactivity induced some changes in the mineralogical composition of ash by reducing its degree of crystallinity. The rate of geopolymerization was found to increase with increasing duration of ball milling. Both these investigations view mechanical activation as a way of improving the source materials (precursors) for production of two-part geopolymer. The work reported here focuses on production of a one-part geopolymer cement via mechanochemical processing of blends of raw materials.

A novel approach was developed in this investigation in order to produce economically viable and sustainable one part geopolymer cements (with relatively low carbon footprint and energy content). This approach employed mechanochemical processing at room temperature in order to transform the raw materials into hydraulic (geopolymer) cement. The raw materials comprised aluminosilicate precursors and sources of alkaline earth and alkali metal cations; mechanochemical processing of these raw materials was accomplished via simple ball-milling of their blends. The milling action incorporates alkali and alkaline earth metal cations into the aluminosilicate structure by disrupting the aluminosilicate bonds. Through this process, the presence of alkalis facilitates mechanochemical activation of the aluminosilicate precursor. In addition, incorporation of the alkali metal cations into the aluminosilicate structure makes the resultant hydraulic cement less caustic. Mechanochemical processing of raw materials yields hydraulic cement particles which embody soluble sources of aluminum, silicon, alkali and alkaline earth metals, which can undergo through-solution reactions to yield alkali aluminosilicate hydrate binders with viable performance characteristics.

2 Mechanochemical processing

Mechanochemistry describes the chemical and physicochemical transformation of substance induced by mechanical energy [16]. This phenomenon is

generally caused by simple milling operations (in ball mills, planetary mills, etc.) at room temperature and atmospheric pressure [17]. In particular, mechanochemistry deals with the physico-chemical transformations and chemical reactions affecting substances following the administration of mechanical energy. As mills represent typical energy suppliers, grinding and co-grinding are the common processes inducing mechanochemical transformations [18].

The mechanochemical processing approach adopted in this work seeks to activate aluminosilicate precursors such as coal fly ash (in the presence of alkaline compounds) to produce one-part alkali aluminosilicate hydraulic cements. This approach emphasizes compounding and activation of the blend of coal fly ash and supplementary materials by input of mechanical energy. The supplementary materials primarily introduce additional alkaline earth and/or alkali metal cations to destabilize the aluminosilicate constituent of the coal fly ash, facilitating their mechanochemical disordering/depolymerization and compounding to form a reactive alkaline earth/alkali metal aluminosilicate with desired hydraulic qualities. The resulting hydraulic cement can be processed into concrete using equipment and practices commonly applied to Portland cement, which is a major advantage for large-scale transition of the technology to construction markets.

The mechanochemical activation process is schematically depicted in Fig. 1. Control of the dissolution rates of the glassy phases present in coal fly ash can be achieved by optimizing the addition of readily available network-breaking cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) during mechanochemical synthesis. The presence of alkaline earth cations in a glassy phase also produces an increased tendency toward framework disordering, including the formation of a small concentration of (weak, reactive) Al–O–Al bonds [19]. Divalent alkaline earth cations enhance dissolution when compared with monovalent alkali cations, enabling glasses to show different dissolution rates according to composition [5].

Four initial steps in hydration of an aluminosilicate-based hydraulic cement can be identified as: (a) ion-exchange; (b) hydrolysis; (c) network breakdown; and (d) release of Si and Al. These dissolution and breakdown phenomena, which occur with simple addition of water, prompt subsequent speciation, gelation, reorganization and polymerization processes which yield the solid alkali aluminosilicate hydrate-



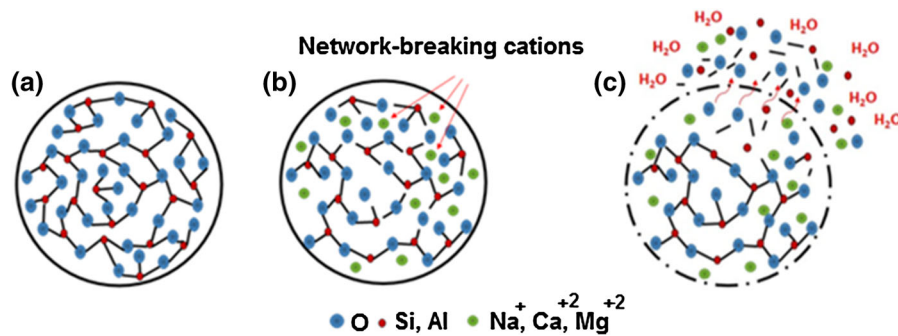


Fig. 1 Schematics of mechanochemical transformation and hydration of aluminosilicate precursors and alkaline activators into hydraulic cement: **a** ordered aluminosilicate precursor;

based binder [20]. The hydraulic cement particle has an amorphous aluminosilicate structure containing both monovalent and divalent network-modifying cations. Dissolution of this glassy structure occurs at the moderately high pH generated upon partial release of alkali cations to the solution; this step resembles that observed under acidic conditions as it is initiated by ion exchange of H^+ for Na^+ or Ca^{2+} . The difference between Na^+ and Ca^{2+} largely derives from the greater damage to glass structure induced by removal of a divalent versus a monovalent cation. The network breakdown process during glass transition is largely controlled by the surface-charging behavior. Some glasses show synchronous release of Si and Al while others leach one component preferentially—this is strongly dependent on the specific glassy phase used and also the leaching environment. The presence of alkaline earth cations in a glass also gives an increased tendency toward framework disorder, including the formation of a small concentration of (weak, reactive) Al–O–Al bonds, as well as a non-bridging oxygen atom content higher than is strictly required by stoichiometry. An optimal glassy phase, or combination of glassy phases, would allow for tailored control of alkali activation, including workability, set time, strength development profile and durability [5].

3 Materials and methods

3.1 Materials

The coal fly ash used in this study is a dry fly ash obtained from a power plant operated by the Lansing Board of Water & Light in Lansing, Michigan. The

b disordered and reactive alkali earth/alkali metals aluminosilicate cement; **c** dissolution of an aluminosilicate glass during the early stages of hydration

chemical composition of the fly ash, determined by X-ray fluorescence (XRF) spectroscopy, comprised 43.1% SiO_2 , 14.3% CaO , 23.3% Al_2O_3 , 1.7% K_2O and 0.9% N_2O and with LOI of 1.7%. Figure 2 shows the XRD spectrum for the as-received coal fly ash used in this study. The coal fly ash was found to be highly amorphous. Three main crystalline mineral phases were detected in the fly ash, namely quartz (SiO_2), mullite ($3Al_2O_3 \cdot 2SiO_2$), and calcite ($CaCO_3$). Laboratory grade sodium hydroxide, reactive MgO and quick lime (CaO) were purchased in powder form with 97–98% purity from Sigma Aldrich.

Granite aggregate with 8.5 mm maximum particle size was used as coarse aggregate. Natural sand was used as fine aggregate with 0.15–4.75 mm size range.

3.2 Methods

The hydraulic cements considered in this investigation were formulated around coal fly ash. The formulation comprised coal fly ash:quick lime:MgO:NaOH at 75:14:5:6 weight ratios. This blend was selected, via trial experimental studies, to produce a desired balance of strength, set time and moisture stability. The blends of raw materials were mechanochemically processed through ball-milling in a ceramic jar (5.6 L) with solid-to-steel ball ratio of 1:10. Five different steel ball sizes were used as shown in Table 1. The speed of rotation was chosen to be in the range where milling media experiences “cascade” action, that is, the balls gain enough energy to get up to a certain height and fall down, hitting other balls and the particles of powder at an angle of 45° – 60° above the horizontal. The critical speed (rpm) was calculated as: $n_c = 42.29/\sqrt{d}$, where d is the internal diameter

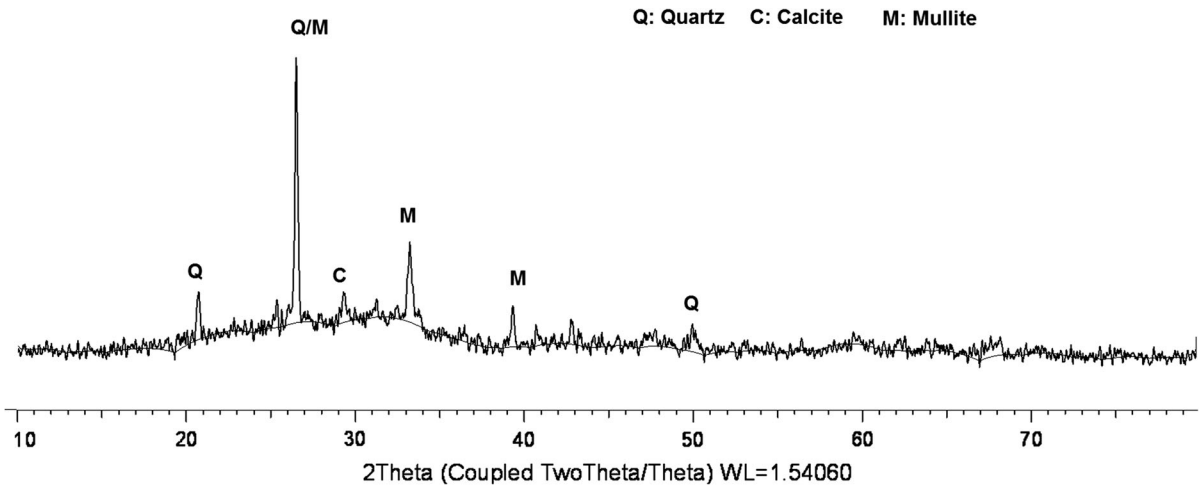


Fig. 2 XRD patterns of the coal fly ash used in this investigation

of the milling jar (in meters) [21]. Dry grinding was performed at about 75% of the critical speed. The mill was filled with balls and materials to 40–60% of its volume. Ball-milling was carried out over a 2-h period.

The resulting hydraulic cements were evaluated through experimental investigation of concrete materials incorporating them. The base concrete mix design considered in this experimental work is presented in Table 2.

A 20 Quart planetary mixer (Hobart A-200) was used to prepare the geopolymer concrete mix. The hydraulic cement was added first to the mixer, and mixed for about 1 min at medium speed. Water was then added to the dry cement, and mixing was continued for 30 s. Fine and coarse aggregates were added subsequently, followed by 3 min of mixing to produce a homogeneous fresh concrete mix.

The fresh mix workability was measured per ASTM C230 flow table test method. Initial and final set times were measured per ASTM C191 using the Vicat needle apparatus. The amount of water mixed with cement in the set time test was selected to produce the normal consistency per ASTM C187.

Table 1 Steel ball sizes and mass percentages

	Ball size (mm)				
	50	25	20	9.5	5
Mass (%)	20	20	30	20	10

Q: Quartz C: Calcite M: Mullite

Table 2 Mix design of hydraulic cement concrete materials

Material	Quantity (Kg/m ³)
Hydraulic cement	320
Fine aggregate	750
Coarse aggregate	1070
Water-to -cement ratio	0.4

The specimens prepared for compressive strength testing were 50 mm cubes. The fresh mix was placed inside molds, and consolidated via external vibration at medium speed for 3 min. The molded specimens were kept in sealed condition, and were demolded after 24 h. They were then subjected to room-temperature curing which was accomplished by simply sealing the specimens and storing them at room temperature until different test ages.

Another set of specimens was prepared with the same raw materials and proportions, which were milled separately and then blended during mixing of concrete. This separate milling was performed to demonstrate that the mechanochemical effects induced by combined milling of raw materials is key to successful processing of hydraulic cement.

The Particle size distribution was evaluated using a HORIBA LA-920 laser particle size analyzer. This test was performed on 0.5 g of powder dispersed in a water-based solution of sodium hexametaphosphate ((NaPO₃)₁₃·Na₂O) in a glass vial by gently shaking the vial for 1 h. The Blaine fineness of the hydraulic cement powder as well as that of the raw materials

milled separately were measured using the air-permeability apparatus per ASTM C204. The pH of hydraulic cement in solution was evaluated by adding the cement to deionized water at 1 wt% concentration in a vial. A pH meter (Extech pH 110) was used to determine the pH of solutions versus time.

The heat of hydration of hydraulic cement was measured using the calorimetry test method (I-cal 2000 HPC). For this purpose, the cementitious material was mixed with sufficient amount of water (defined by a w/c ratio that gives the normal consistency) by hand for 1 min. The fresh paste was then placed inside the calorimeter, and heat release was monitored over 20 h. The microstructure of hydrates was evaluated via scanning electron microscopy using a JEOL JSM-6610LV scanning electron microscope (JEOL Ltd., Tokyo, Japan). Compression tests were performed on a Forney test equipment with 2227 kN force capacity. EDX analyses were also conducted in the course of scanning electron microscopy. The mineralogy of cement paste was assessed via X-ray diffraction (XRD) using a Bruker D8 daVinci diffractometer equipped with Cu X-ray radiation operating at 40 kV and 40 mA. Peak intensities were obtained by counting with the Lynxeye detector every 0.05° 2θ /min at a reflection angle range of $2\theta = 10^\circ$ – 80° .

4 Experimental results and discussion

4.1 Particle size analysis and blaine fineness

The particle size distributions for the as-received coal fly ash, blend of raw materials milled separately, and the hydraulic cement subjected to mechanochemical processing are presented in Fig. 3. The milling action caused some reduction of the ash particle size. The median (D_{50}) values of particle size for the as-received coal fly ash, blend of raw materials milled separately and the hydraulic cements subjected to mechanochemical processing were 12.3, 7.9 and 8.1 μm , respectively. Milling of the raw materials separately or together produced comparable results as far as the particle size distribution is concerned. The differences in their reactivity and hydration qualities can thus be attributed to the mechanochemical phenomena induced during combined milling of raw materials rather than the commutation effects of milling.

Table 3 compares the measured values of Blaine fineness for the as-received coal fly ash, blend of raw materials milled separately, and the hydraulic cement subjected to mechanochemical processing. Milling the raw materials separately or together (in the case of mechanochemical processing) causes a rise in fineness. Milling the raw materials separately or together, on the other hand, has a relatively small effect on the fineness of the resultant powder.

4.2 pH

Figure 4 compares the pH values in a dilute solution versus time for the blend of raw materials that were milled separately, and the mechanochemically processed hydraulic cements milled in air. The blend of raw materials milled separately exhibits higher alkalinity at all times. The mechanochemically activated hydraulic cement exhibits lower alkalinity than the blend of raw materials that were milled separately, which supports the hypothesis that the alkali and alkaline earth metal cations were diffused into ash particles during mechanochemical processing. The rate of pH rise is also lower for the mechanochemically processed hydraulic cement, which could be due to the slower release of alkali and alkaline earth metal cations incorporated into cement particles when compared with those available as separate particles.

4.3 Heat of hydration

The heat of hydration of hydraulic cement reflects upon the intensity of exothermic reactions at each point in time. Figure 5 presents the rates of heat release versus time for mechanochemically processed hydraulic cements. An exothermic peak (a) appears immediately when water is mixed with cement, which can be attributed to the instant absorption of solution on the surface of cement particles, dissolution of the highly soluble components (e.g. NaOH), and hydration of CaO. The exothermic peak (b) is significantly higher than that of (a) implying that the alkaline solution is more intensively adsorbed, and OH^- anions begin attacking the Si–O and Al–O bonds [22]. The rapid declining of peak (a) could be due to the slowing down of wetting process and the initially slow reactions. After peak (a) declined for about 130 min, the second exothermic peak (b) appeared, suggesting drastic breakdown of the geopolymer cement particles



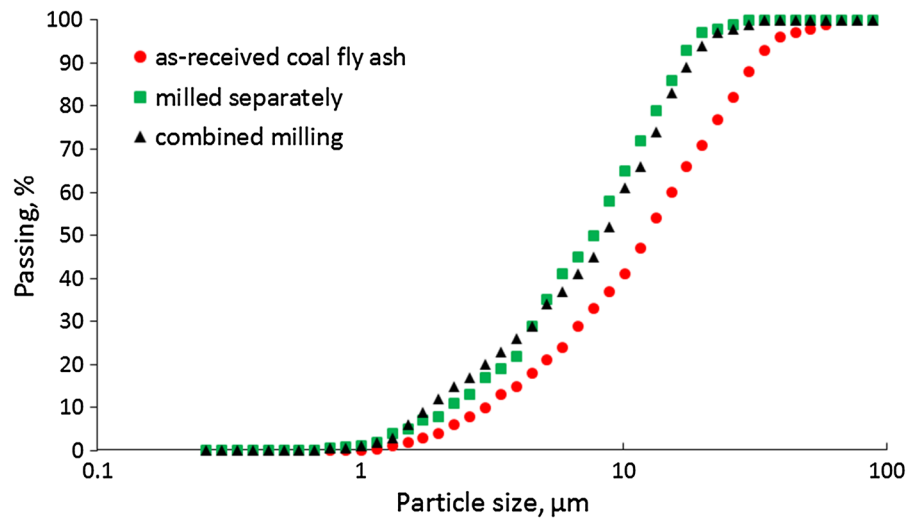
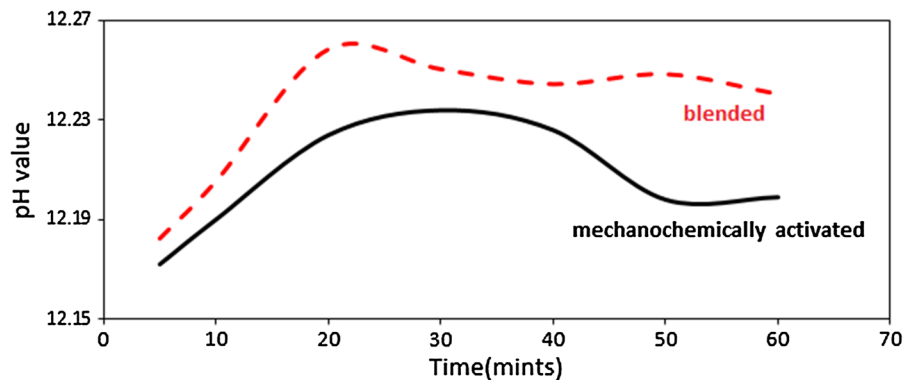


Fig. 3 Particle size distributions of the as-received fly ash, blended ingredients milled separately, and the mechanochemically activated hydraulic cement

Table 3 Specific surface area results (Blaine fineness), cm^2/g

As-received coal fly ash	Milled separately	Combined milling
2130	3182	2977

Fig. 4 pH values versus time for the blend of raw materials milled separately versus hydraulic cements subjected to mechanochemical processing

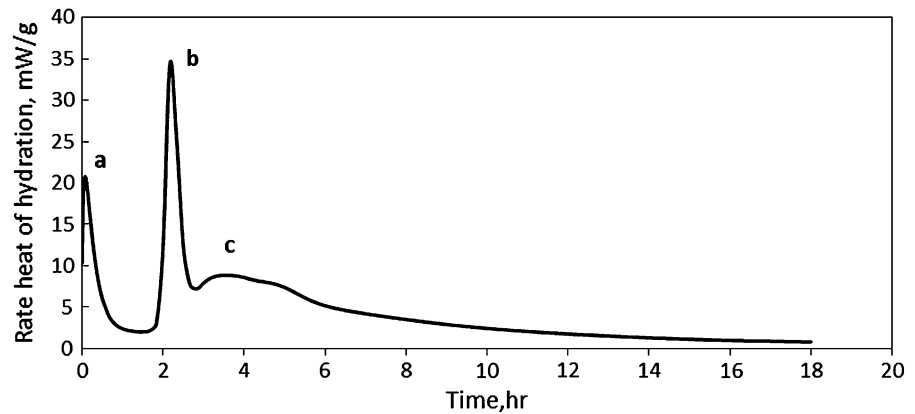


in combination with the formation of a few of alumina/silica-hydroxyl species and oligomers such as $\text{OSi}(\text{OH})_3^-$, $\text{Al}(\text{OH})_4^-$, $(\text{OH})_3\text{-Si-O-Al-(OH)}_3$ etc. [23]. The polymerization process is exothermic, and becomes the main factor governing heat evolution (see peak (c), mainly beginning at 170 min). After about 900 min, the process goes into a thermally steady stage, during which the freshly formed gels are probably transformed into larger networks by local reorganization.

4.4 Workability and set time

The flow table and set time test results are presented in Table 4. The mix incorporating one-part geopolymers (hydraulic) cement used in this investigation provides static and dynamic flow (workability) attributes which are comparable to those offered by normal (Portland cement) concrete. Static and dynamic flows reflect upon the yield strength and viscosity of fresh mixtures. The relatively high rate of setting is a characteristic

Fig. 5 Rate of heat release versus time for the fly ash-based hydraulic cement



feature of geopolymer concrete versus normal Portland cement concrete. The initial and final set times of one part-based hydraulic geopolymer cement suits many concrete construction applications.

4.5 Compressive strength

Figure 6 compares the compressive strength test results for concrete materials prepared with the three systems introduced earlier. Residual strengths were measured after immersion of concrete specimens in tap water for 48 h at room temperature. Concrete specimens made with the cement comprising raw materials milled separately provided the lowest compressive strengths at all ages compared with those made with hydraulic cements processed mechanochemically. When cement comprised raw materials milled separately (without mechanochemical effects), the resulting concrete materials were not stable upon immersion in water. Mechanochemically processed hydraulic cements, on the other hand, produced moisture-resistant concrete materials. The concrete prepared using cement with raw materials milled separately exhibited decreasing levels of compressive strength with time.

Figure 7 shows the surface appearances of concrete specimens made with different hydraulic cement types after 7 days of room-temperature curing in sealed condition. Specimens made with a cement comprising

the raw materials milled separately exhibited surface cracking and swelling, which explain the drop in compressive strength with time. These trends may have been caused by expansive phenomena associated with delayed hydration reactions (e.g., those of residual MgO and free lime remaining after initial hardening of the paste) that form crystals in a solid medium, or by formation of highly hydrophilic compounds which imbibe water and swell. It should be noted that the solubility of calcium compounds decreases with increasing pH, which could lead to delayed formation of calcium hydroxide crystals [24]; this is a possible explanation for the swelling and cracking tendencies observed when the raw materials were milled separately. The XRD data presented later point at the presence of MgO crystals (periclase) in hydrated cement paste, the delayed hydration of which could be the cause of unsoundness.

4.6 Microstructure and chemical structure

Figure 8 compares SEM images of fly ash particles prior to and after mechanochemical. Surface changes can be observed on particles after mechanochemical processing, which could be interpreted as buildup of mechanochemically produced compounds on fly ash particles. Buildup of matter on the spherical fly ash particle is a distinct feature observed in Fig. 8b, which has been attributed to mechanochemical effects. While some fly ash particles are known to incorporate smaller fly ash particles within their core, one cannot rule out that some products of mechanochemical reaction or even raw materials have been incorporated into the core of ash particle during milling. Figure 9 present the EDX spectra obtained at the surfaces of

Table 4 Workability and set time test results

Flow (cm)		Setting time (min)	
Static	Dynamic	Initial	Final
54	82	38	210



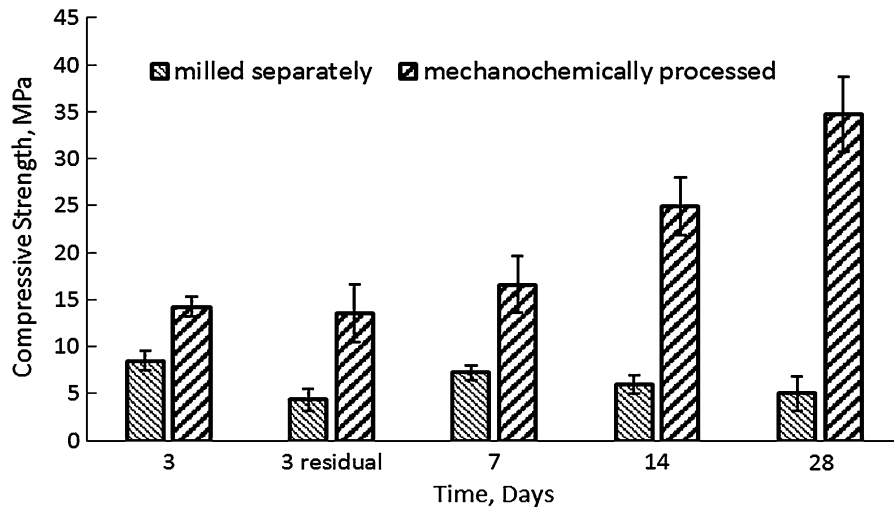


Fig. 6 Compressive strength test results (mean values and 95% confidence intervals) **a** Milled separately **b** combined milling

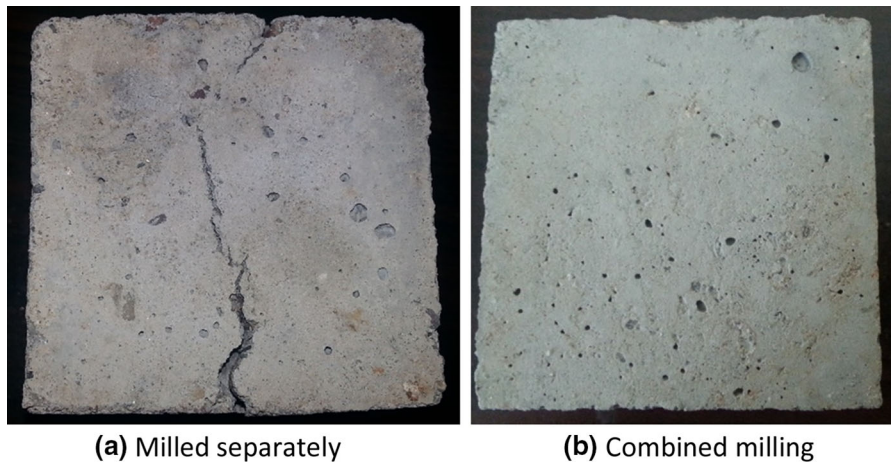


Fig. 7 Surface appearances after 7 days of room-temperature curing for concrete specimens made with cements comprising raw materials milled separately **(a)** and processed mechanochemically via combined milling of raw materials **(b)**

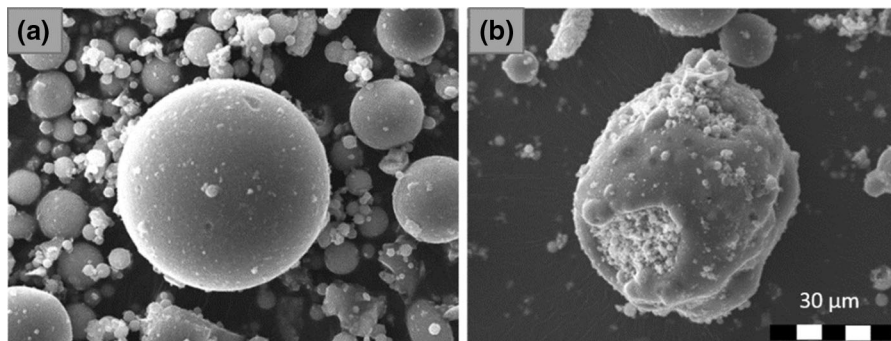


Fig. 8 SEM images of particles of **a** fly ash; **b** fly ash-based hydraulic cement processed mechanochemically

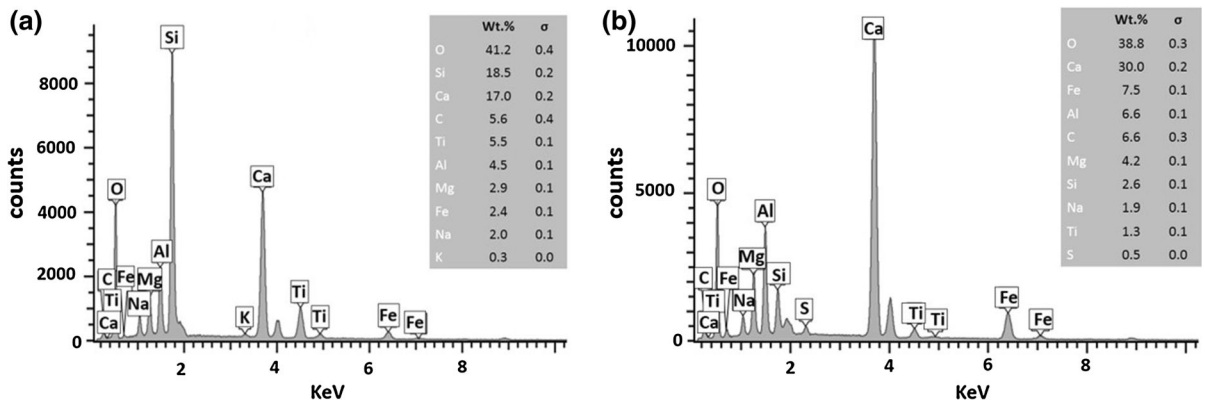


Fig. 9 EDX spectra of **a** coal fly ash and **b** mechanochemically processed geopolymer cement

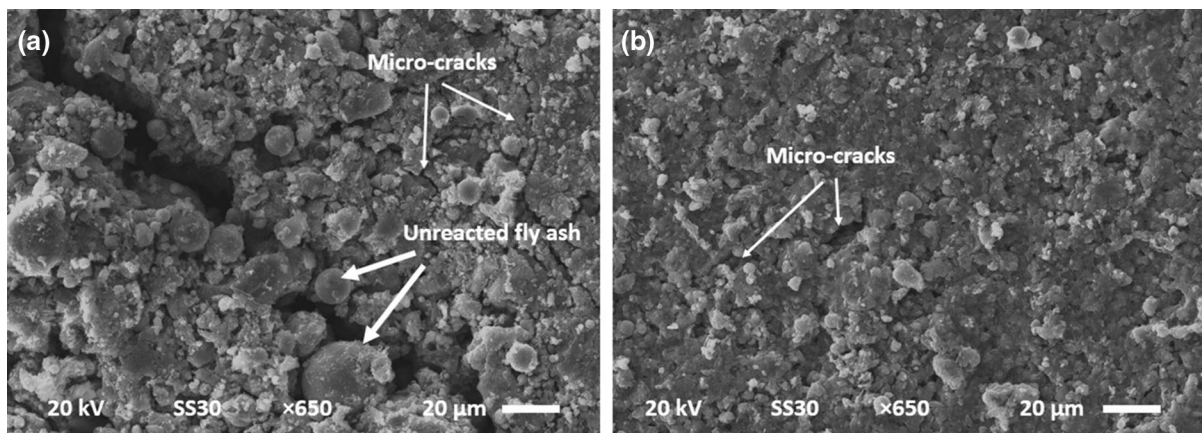


Fig. 10 SEM images of hydrated cement paste for **a** cement made with raw materials milled separately; **b** hydraulic cement processed mechanochemically via combined milling of raw materials

raw fly ash particles and the mechanochemically processed fly ash-based geopolymer cement. It should be emphasized that EDX spectra reflect the surface elemental composition, and do not provide information on the surface compound composition or the elemental composition within the body of the material. Mechanochemical processing of fly ash via milling with other raw materials into a one-part hydraulic cement has raised the Ca concentration (this is not unexpected, noting that calcium is added as a raw material, CaO, and milled with fly ash). The detected Na concentration, however, remained unchanged. This finding provides support for the hypothesis that the matter built-up on fly ash particles is not the sodium hydroxide (another raw material milled with fly ash). This finding could also be used to explain the reduced pH of the one-part geopolymer cement

subjected to mechanochemical processing (via milling of blended raw materials); the absence of Na on the surface could reduce its availability to the solution.

Figure 10 shows SEM images of hydrated pastes for the three type of cements considered here. Cracks and microcracks can be clearly seen in the paste of cement made with raw materials milled separately; unreacted fly ash particle can also be detected in this image. With hydraulic cements subjected to mechanochemical processing, hydrated pastes do not exhibit a granular morphology or any sign of cracking (except for minor microcracking which could have been caused by preparation of specimens in vacuum); instead, the hydrated gel seem to have formed. While one could argue that cracks could be formed due to drying shrinkage under vacuum when the specimens are being prepared for scanning electron microscopy,

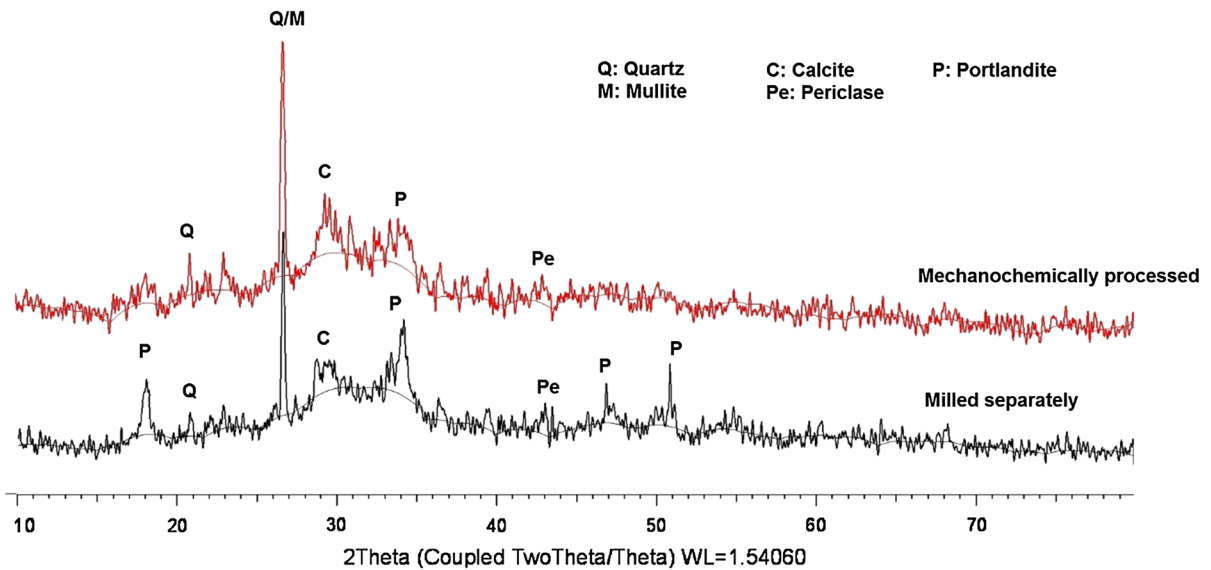


Fig. 11 X-ray diffraction results for geopolymer paste made with cements comprising raw materials milled separately and processed mechanochemically via combined milling of raw materials

the fact that all specimens have been subjected to vacuum and some exhibit notable cracking supports the above findings.

Figure 11 compares the XRD spectra for geopolymer pastes at 7 days of age made with cements comprising raw materials milled separately or processed mechanochemically via combined milling of raw materials. The paste made with the raw materials milled separately shows Portlandite $\text{Ca}(\text{OH})_2$ peaks at angles at $2\theta = 18^\circ, 34^\circ, 46^\circ$ and 51° . The presence of calcium hydroxide peaks could explain the swelling and surface cracking tendency observed in the paste made of raw materials milled separately. Mechanochemical processing of raw materials (by milling their blend) produces pastes which do not exhibit the Portlandite peak. The formation of calcite in both samples (it is higher in the case of mechanochemical processing where milling was performed on the blend of raw materials) points at the presence of free calcium in both samples. Considering the measured values of pH for the two systems, one can speculate that Portlandite formation in the case with raw materials milled separately can be attributed to the rate of release of alkalis to the solution. More investigations into the chemical structure of this one-part geopolymer cement hydrates are warranted. Solid-state NMR could be a powerful tool for resolving this structure.

5 Conclusions

- A new class of hydraulic cement was developed with the objective of realizing significant environmental and performance benefits when compared with conventional Portland cement. The new cement relies primarily upon alkali aluminosilicate hydrates to render binding effects, in lieu of the calcium silicate hydrate produced upon hydration of Portland cement.
- Mechanochemical effects rendered by simple milling of blends of raw materials were used to transform coal fly ash into hydraulic cement. This required supplementing the chemistry of coal fly ash as an aluminosilicate precursor with relatively small concentrations of compounds incorporating alkali/alkaline earth metal cations. The mechanochemical effects are hypothesized to produce a disordered aluminosilicate framework embodying alkaline earth and/or alkali metal cations.
- Addition of alkaline compounds enhanced the process of destabilizing the aluminosilicate structures with input of mechanical energy. This explains why milling of the blend of raw materials produced hydraulic cements with improved

performance when compared with separately milled raw materials that were blended after milling.

- Microstructural, chemical and crystallographic investigations of hydraulic cements provided support for the role of mechanochemical phenomena in production of hydraulic cements with controlled rates of hydration reactions. Calorimetry studies highlighted the steps involved in hydration reactions of alkali aluminosilicate-based hydraulic cements.
- The simple approach to processing and the extensive use of recycled materials provide the new hydraulic cement with important sustainability and economic advantages. These attributes of the viable properties of the new hydraulic cement point at its commercial potential. Further investigations into the chemical structure of the hydraulic cement, and more comprehensive assessment of the engineering properties of the cement and its hydrates are warranted. Concrete materials made with the new hydraulic cement should also be thoroughly characterized in an effort to verify its ability to meet performance requirements in different fields of application.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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