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LETTER

Relative strengths of phosphoric acid-reacted and alkali-reacted metakaolin materials

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The use of binders such as phosphoric acid to consolidate aluminosilicates to form refractory products has been reported since the 1940s [1]. Another class of materials formed by reacting concentrated alkaline silicate solutions with metakaolin (MK) has been termed geopolymers by Davidovits [2]. MK is made by heating (~750 °C) of kaolin to render it X-ray amorphous and thus more reactive. In a geopolymer, the aluminosilicate is composed of cross-linked AlO_4^- and SiO_4 tetrahedra, charge balanced with Na^+ or K^+ ions. It was shown by Cao et al. [3] that PO_4^{3-} can be incorporated in the geopolymer structure. Derrien et al. [4] added calcium phosphates to geopolymers, but they did not show whether the phosphate was part of the geopolymer structure. MacKenzie et al. [5] showed that the P occupied tetrahedral sites in the geopolymer with a different chemical shift from that of the aluminium phosphate reactants. Cao et al. [3] made nine compositions with Si/P molar ratios of 0.13–0.63 by adding H_3PO_4 to metakaolin and the maximum strength obtained was 55 MPa for the composition with Si/P = 0.21 molar ratio. Mackenzie et al. [5] made one composition of molar ratio of Si/P = 25 by adding a small amount of aluminium phosphate to an MK-based geopolymer, having molar ratios of Si/Al = 1.6 and Si/Na = 2.6.

In the work reported here, the microstructure and the cold crushing strength (CCS) of the materials produced by alkaline-bonding and phosphoric acid-bonding of MK have been studied as a preliminary effort to develop these materials as replacements in some current uses and for future applications.

Batches of 100 g of different compositions were made as listed in Table 1. The approximate chemical compositions of the nominal batch compositions based on the chemical analyses of the precursors from the suppliers resulted in molar ratios of Si/Al = 2 and Na/Al = 1 for MK-based geopolymers (MKGP). Similarly, the phosphoric acid-bonded MK (MKP) had molar ratios for Si/Al = 1 and Al/P = 1.

MKGP (see Table 1) was prepared by adding MK to the sodium silicate solution. MKP was made by first mixing the deionised water (DIW) with 85 mass% H_3PO_4, then adding MK to the acid. Minimum amount of water was added to achieve the required workability, because any excess of water would increase the porosity and thus decrease strength. All the batches were mixed in a dental mixer (Renfert, Dental mixer, UK) for ~5 min under vacuum at 300 rpm. To the MKGP and MKP batch compositions (see Table 1), 40 mass% sand was added before mixing (i.e. MKSGP and MKSP). Ordinary washed beach sand of size fractions, 81 mass% 250–500 μm, 17 mass% 125–250 μm and 2 mass% <125 μm, was used. Generally, sand is added in making mortar for building applications; hence, it was added for comparison with ordinary Portland cement mortar.

The slurries produced in each instance were cast to form 25 mm dia × 40 mm long cylindrical specimens in sealed polycarbonate containers for subsequent physical and mechanical testing. The cast items were kept at room temperature for 2 h before curing at 60 °C for 24 h in an oven. After removing the seals, the samples were left at ambient temperature for 4 days before demoulding for MKGP. The MKP and MKSP samples were demoulded after 14 days when they were dry (they were still wet after

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Table 1 Batch compositions of materials prepared

Sample Id.	Compositions/mass%	Si/Al	Na/Al	Al/P
MKGP	MK: 33.6; D: 63.1; DIW: 3.3	2	1	–
MKSGP[a]	MK: 24.0; D: 45.1; DIW: 32.3; sand: 28.6	2	1	–
MKP	MK: 38.1; H_3PO_4: 47.5; DIW: 14.4	1	–	1
MKSP[a]	MK: 27.9; H_3PO_4: 34.8; DIW: 12.2; sand: 25.1	1	–	1

Note: MK (The XRD analysis showed an amorphous phase with trace amounts of anatase and quartz. The clay contained ~1 mass% quartz, TiO_2 and Fe_2O_3 according to the supplier) = Kaolin clay (Snobrite 80, Unimin, Australia Pty. Ltd.) heated at 750 °C for 15 h; D = Sodium silicate solution, consisting of (mass%) Na_2O: 14.7, SiO_2: 29.4 and water: 55.9; Grade D, PQ Corporation, Australia; DIW = deionised water; H_3PO_4: 85 mass% phosphoric acid, Ajax Chemicals, UK; sand: Washed beach sand, Australian Foundry Services Pty. Ltd., Australia

[a] Excluding sand when calculating the molar ratio

7–10 days, as they contained bleed water) and firm. Water requirement was different for the two types and it was not possible to keep the water content constant.

The bulk densities of all the materials were determined by measuring the mass and the volume with a Hg pycnometer. Open porosities were determined by immersing each specimen in octane (non-polar liquid) for 24 h and measuring the mass absorbed. This method of determining open porosity is a comparative method and not an absolute determination as the open porosity may be higher because of incomplete permeation of the liquid into the pores. Saturation with water was not considered as suitable due to the high leachability potential of ionic species such as Na^+ [6]. Diametral shrinkage was calculated on a wet to dry basis. The wet diameter was assumed to be the diameter of the container and the dry diameter was the measurement made after 7 or 14 days at ambient.

All the materials were analysed by X-ray diffraction (XRD) and examined by electron microscopy (both scanning—SEM and transmission—TEM). Preparatory details and instrument descriptions are listed elsewhere [7]. Chemical analysis was carried out by energy dispersive X-ray spectroscopy (EDS) on the specimens for both SEM and TEM. The maximum variation of EDS analysis based on at least three separate analyses was 2%. However, there may be errors because of migration of Na under the electron beam and the presence of moisture (not analysed by EDS) even after drying and evacuating in the SEM. Under the TEM selected area, electron diffraction (SAED) patterns were observed to determine whether areas of the samples were crystalline or amorphous.

Cold crushing strength (CCS) specimens 25 mm in diameter and 40 mm in height were cast for each batch. Each specimen was ground flat (flat surfaces) and parallel using silicon carbide paper prior to testing. The CCS tests were conducted at ambient temperature in a servo-electric universal mechanical testing machine (Instron 8562) with a 100-kN load cell. The specimens were tested at a crosshead speed of 5 µm/s, with a minimum of five specimens for each composition being studied.

The XRD traces of the MKP and MKGP showed essentially single broad diffuse peaks. The former material yielded a peak centred at ~0.34 nm and that in the latter was centred at ~0.32 nm, as found by others [8, 9]. Low intensity reflections due to impurity phases such as crystalline anatase and quartz in the MK were also observed [8, 9]. The backscattered SEM image of the MKP is shown in Fig. 1a and it is similar to that of MKGP (Fig. 1b). The MKGP showed some unchanged MK relics, quartz and anatase (as determined by EDS analysis) in a relatively uniform geopolymer matrix (Na, Al, Si), as found by others [10–13]. The matrix phase of MKGP is amorphous as shown above by XRD and by TEM [7, 11, 14]. The quartz and anatase originated from the clay precursor and they do not dissolve in the acid or alkali mixtures within the implemented reaction times. The cracks observed were generated during SEM sample preparation using vacuum impregnation of the mounting resin. No cracks in the original samples were seen using optical microscopy, as shown in previous work [15].

Multinuclear ^{31}P, ^{27}Al and ^{29}Si solid state MAS NMR measurements were performed at ambient temperatures on a Bruker MSL-400 operating at frequencies of 161.92, 104.23 and 79.49 MHz, respectively. All ^{31}P and ^{27}Al data were obtained using a Bruker 4-mm double-air-bearing probe from which MAS frequencies of 10 and 15 kHz, respectively, were implemented for data acquisition. The ^{27}Al measurements used single pulse (Bloch decay) methods with selective $\pi/8$ excitation pulses of 0.6 µs and recycle delays of 5 s, with ^{27}Al chemical shifts being referenced to 1 M $Al(NO_3)_3$. Each ^{31}P analysis utilised both single pulse and cross-polarisation methods; the latter used ^1H $\pi/2$ pulse times of 3.5 µs, Hartmann-Hahn contact periods of 5 ms and recycle delays of 15 s, while the single pulse experiments were derived from this set-up with ^{31}P $\pi/4$ pulse times of ~1.7 µs and recycle delays of 30 s. All ^{31}P chemical shifts were referenced to 85% H_3PO_4. ^{29}Si MAS NMR data were acquired using a Bruker 7-mm double-air-bearing probe, which enabled MAS frequencies of ~5–6 kHz. For a quantitative estimate of Si speciation,

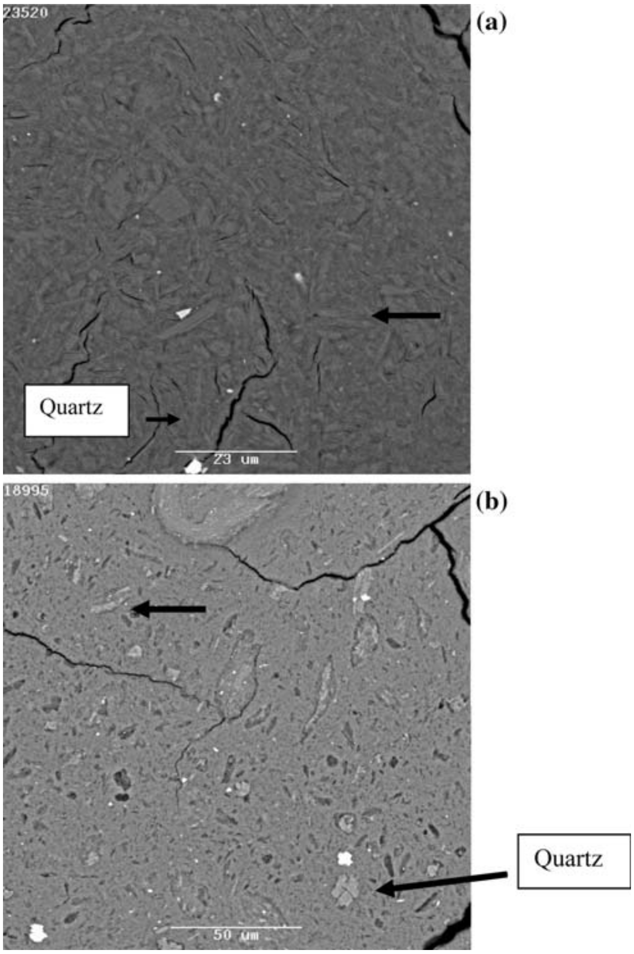


Fig. 1 Backscattered SEM images of (**a**) MKP, showing MK relics (arrow), quartz and anatase (white regions) and (**b**) MKGP showing similar relics, quartz and anatase

these measurements used single pulse (Bloch decay) methods with selective $\pi/4$ excitation pulses of 3.0 µs and recycle delays of 30 s, with ^{29}Si chemical shifts externally referenced to TMS via a secondary kaolin standard.

The matrix phase of MKP, amorphous as already indicated by XRD, was also observed to be amorphous in the TEM (Fig. 2). The EDS analyses under the TEM showed the presence of Si, Al, P and O, but it was not possible to determine a meaningful mean value because the composition varied by a factor >3.

The Si/Al molar ratios calculated from SEM EDS analyses for MKGP and MKP were 2.2 and 1.1, respectively, for the matrix phases. These values are close to the calculated analyses of the batch compositions (see above). However, the molar ratios of Na/Al (0.6) for MKGP and for Al/P (1.6) for MKP were different than that of the starting stoichiometries. The former was less, perhaps due to Na migration under the beam and the latter was significantly greater. During EDS analysis of the MKP matrix phase, the presence of only partially reacted MK may have contributed to a higher Al value. If a reaction of H_3PO_4 with $Al_2O_3 \cdot 2SiO_2$ (MK) was to produce polymeric units of $[PO_4]^{3-}$ and $[SiO_4]$, then with Al^{3+}, they would form a bond similar to geopolymers with charge compensation. For this to occur, there should be an equal amount of Al and P, which was present in the starting composition (Table 1). The X-ray maps of Si, Al and P were carried out and there was a uniform distribution of P.

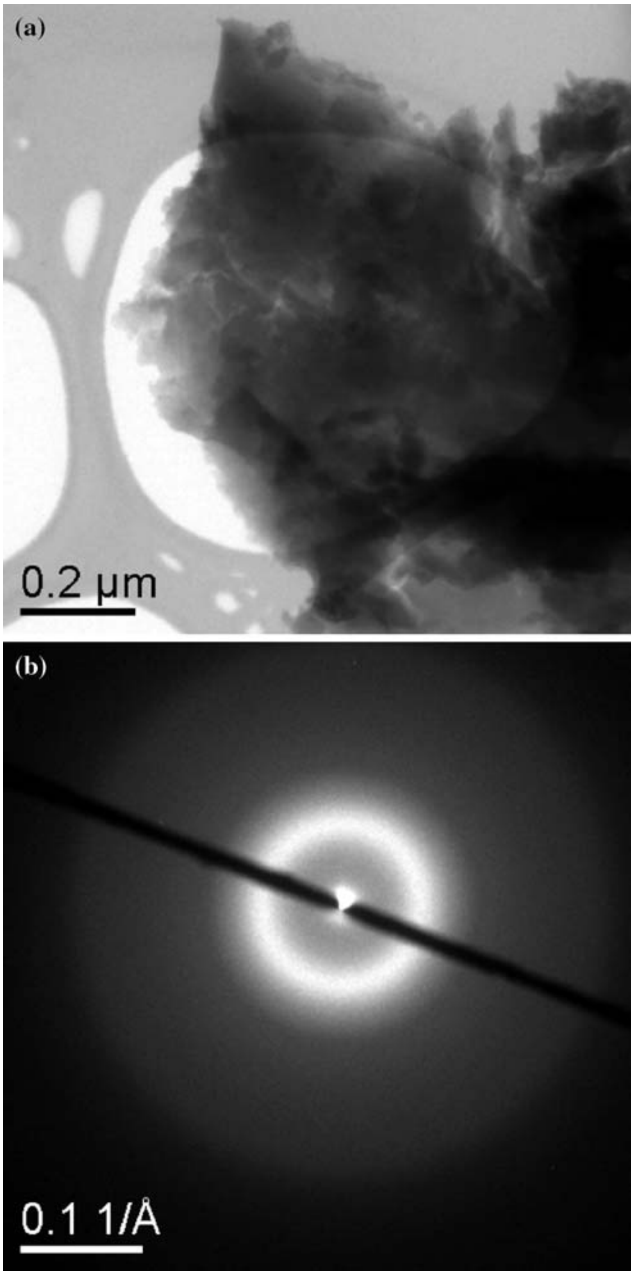
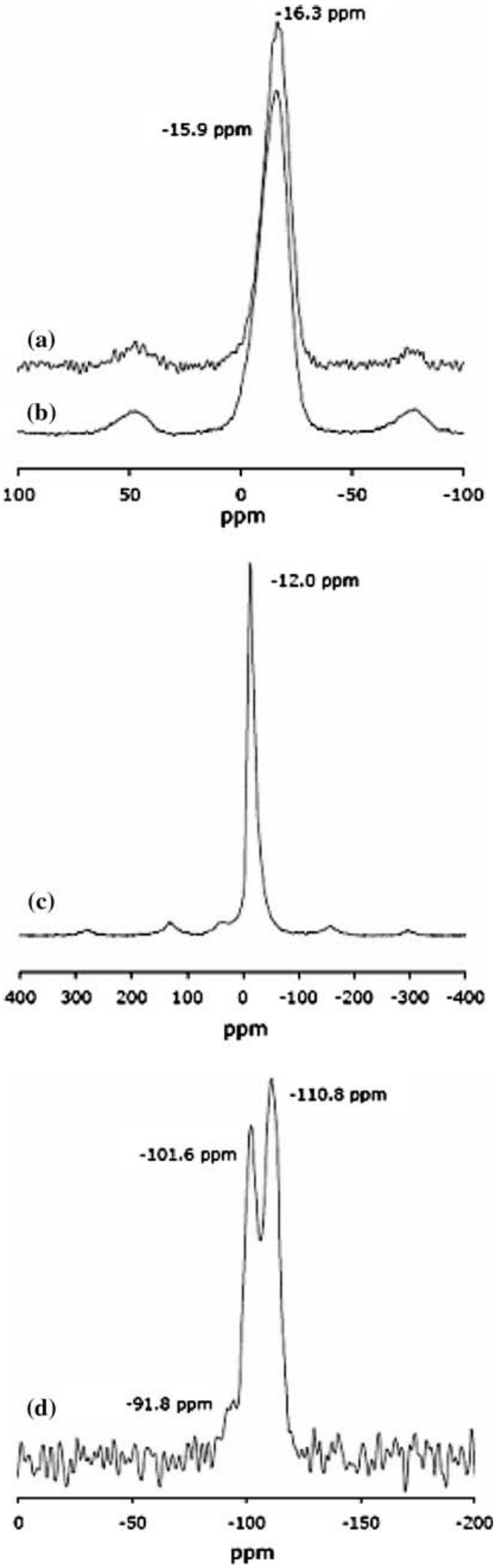


Fig. 2 TEM image of MKP, (**a**) showed the presence of Si, Al, P and O in the amorphous phase; (**b**) the SAED of the area shown in (**a**)

The MAS NMR analysis of the MKP geopolymer was undertaken to investigate this proposition and is shown in Fig. 3. The ^{31}P single pulse (MAS, Fig. 3a) and



◀ **Fig. 3** (**a**) ^{31}P single pulse MAS spectrum of sample MKP; (**b**) ^{31}P CPMAS spectrum of sample MKP; (**c**) ^{27}Al MAS NMR spectrum of sample MKP showing that the dominant Al speciation is represented by a resonance at an apparent shift of ~ -12 ppm, with this upfield position indicating some influence from the P in the stoichiometric inventory; (**d**) ^{29}Si CPMAS spectrum of sample MKP showing clearly resolved Q^3, $Q^4(m\text{Al},n\text{P})$ and Q^4 Si environments from reordered kaolin, phosphoric acid-initiated polymerization species and amorphous silica components, respectively, comprising the MKP network

cross-polarisation (CPMAS, Fig. 3b) results provide very similar spectra, with a single PO_4^{3-} resonance being observed at $\delta \sim 16$ ppm; however, this asymmetric lineshape can be further deconvoluted into two resonances observed at $\delta \sim -4$ and $\delta \sim -16$ ppm. A cross-polarisation experiment selectively enhances the dominant $\delta \sim -16$ ppm component in comparison to the quantitative MAS data, thus emphasizing that this component of P speciation experiences some ^{1}H-^{31}P dipolar contact through closer proximity to H_2O and/or OH^-. The smaller component represented by the $\delta \sim -4$ ppm resonance probably represents that hindered fraction of P speciation close to the disordered aluminosilicate sheets of the original metakaolinite layer structure, or it could possibly represent regions of incompletely mixed PO_4^{3-} structures agglomerated in the MKP network. Corresponding ^{27}Al MAS NMR data (see Fig. 3c) suggest that the Al speciation of this system is dominated by six coordinate Al as evidenced by the single resonance at an apparent shift of $\delta \sim -12$ ppm. This resonance exhibits a significant upfield shift in comparison to previously reported ^{27}Al resonances assigned to six coordinate Al positions in various condensed and intermediate aluminas, aluminium hydroxide precipitates and aluminosilicates, which are conventionally observed in the $\delta \sim 0\text{–}13$ ppm range [16–21]. This suggests that phosphoric acid-initiated polymerization produces a mixed octahedral Al environment $[\text{Al}(\text{O–P})_x(\text{O–Si})_{6-x}]$ with both P and Si influencing the oxo-bridged second coordination sphere. From the large linewidth ($\Delta\nu_{1/2} \sim 1{,}600$ Hz) and the extended tailing of the high field side of this quadrupolar dominated resonance, it can be inferred that a marked distribution of chemical shifts and electric field gradients contribute to the disorder characterizing this Al environment [22–24]. Much of this will be generated by the many possibilities available to the $[\text{Al}(\text{O–P})_x(\text{O–Si})_{6-x}]$ structural moiety. From the ^{29}Si MAS NMR data acquired under quantitative conditions (see Fig. 3d), three resonances at δ −91.8 ppm, δ −101.6 ppm and δ −110.8 ppm are observed describing Q^3, $Q^4(m\text{Al},n\text{P})$ and Q^4 silicon environments, respectively. The lowest intensity ^{29}Si resonance at δ −91.8 ppm represents some segments of a re-ordered kaolin structure, which is highly characteristic of a Q^3 environment, while the more intense δ −101.6 ppm resonance describes mixed environment $Q^4(m\text{Al},n\text{P})$ species

Table 2 Physical and mechanical properties of the materials

	MKGP	MKSGP	MKP	MKSP
BD (g/cm^3)	1.46	1.60	1.82	1.89
OP (%)	20	20	0.0	0.0
CCS (MPa)	72 (5)	70 (6)	146 (17)	96 (10)
Shrinkage[a] (%)	+0.7	+0.6	4.0	3.9

One standard deviation listed within brackets

[a] Diametral shrinkage wet to dry on a wet basis, + indicates expansion

resulting from the phosphoric acid-initiated polymerization. Of greatest intensity is the Q^4 δ −110.8 ppm resonance describing siliceous, Al-free portions of the original metakaolinite structure, and dealuminated structural segments as a result of polymerisation process.

The bulk density, open porosity and CCS values of some of the materials are compared in Table 2. It is seen that MKP has twice the strength of MKGP and has a lower open porosity. Generally, having a lower porosity would yield a higher strength, and so it would be expected the MKP to have a higher strength. However, it is possible that the bonding is also stronger in the MKP than in MKGP, but further work needs to be carried out to determine if this is indeed the case. The strength values obtained in this work (~146 MPa) are almost three times those obtained by Cao et al. [3], who reported a maximum CCS value of only 55 MPa (as discussed above). The maximum strength obtained for a MK-based geopolymer by Duxson et al. [25] was 80 MPa at a Si/Al molar ratio of 1.9 and by Rowles and O'Connor [8] it was 64 MPa at 2.3. The latter also obtained a minimum strength value at a Si/Al molar ratio of 3.

The presence of sand has reduced the CCS value of MKSP compared to the material free of sand (MKP) for no change in porosity, although the bulk density increased because of the higher density of sand. Similarly, the bulk density increased for MKGP with sand addition, but the CCS value was almost the same. Sand was added in the previous work to increase the fracture toughness [15].

It is clearly seen that using these materials, products can be cast to the required shape and have reasonable wet to dry shrinkage (slight expansion for MGP and MKSGP,—see Table 2) compared to most ceramic greenware (~4–7% [26]). The ease of fabrication is a distinct advantage over other methods such as powder pressing. Clearly, phosphoric acid-bonding results in much higher strength materials with aluminosilicate precursors than alkali-bonding. The bonding in the MKP sample is quite complex from the NMR measurements and more such data are necessary on a range of materials with different P/Si ratios.

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