Properties of Phosphate-based Cements with High Fly Ash Content

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Synopsis:

Compared to the hydration process of traditional Portland cements, phosphate-based cements rely on an acid/base reaction process to quickly achieve strong, lightweight and durable binders with lower embodied energy. Since the binding action relies on the chemical composition of the initial components, the rheological and mechanical properties of the resulting ceramic concretes can also be influenced by other mix components including fly ash, fillers and aggregates. This paper reports on an ongoing study examining properties of concretes produced with magnesium potassium phosphate cement binders that incorporate fly ash contents of up to 80% of the total binder mass. Highly flowable mixes were developed with setting times that could be controlled through use of commonly available admixtures. The highest compressive strength of the binders and mortars were achieved when the fly ash content was 50% of the total binder mass. The produced binders and sand mortars had densities of 1800 kg/m^3 [3034 lb/yd^3] and 2100 kg/m^3 [3540 lb/yd^3] and compressive strengths of 35 MPa [5.0 ksi] and 60 MPa [8.7 ksi] after 28 days of simple ambient curing. Decreases in both strength and density were observed as the fly ash content was increased further, but remained within practical ranges for common construction applications with high fly ash contents.

Keywords: magnesium potassium phosphate cement, fly ash, sand mortar, compressive strength, flexural strength, elastic modulus

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INTRODUCTION

Phosphate cements

Concrete is a widely used composite construction material composed of a cement binder and aggregates. The most common binder is Portland cement and most design codes for reinforced or prestressed concrete structures have been developed based on the mechanical properties of Portland cement concrete. It is well known, however, that very high environmental impacts occur during manufacture of Portland cement due to both the energy consumption for the kiln and the resulting greenhouse gas emissions. The production of 1 tonne of Portland cement consumes approximately 1.5 tonnes of raw materials and directly results in emissions of 1 tonne of carbon dioxide (CO_2) into the environment, with similar CO_2 emissions also attributed to the energy source (e.g., Li et al. 2004). Thus, there is a clear need to consider alternative cementitious materials with lower environmental impacts.

In recent years, phosphate cements have gained attention as alternatives to Portland cement, with most of the commercially available cements based on either a magnesium-phosphate or calcium-phosphate reaction system (Wagh 2004; Wagh et al. 1997). As a binder, superior properties result from the type of inter-molecular bonding formed within the hardened phosphate cements. Phosphate cement binders have either ionic or covalent bonds, whereas the hydration products formed in traditional Portland cement binders have comparatively weaker bonds relying on van der Waals forces (Wagh 2004). Phosphate cements can be formulated to set and cure rapidly with high early strengths. These cements will approach their maximum compressive strengths in a much shorter duration than Portland cements blended to achieve a comparable 28 day compressive strength. Phosphate cements typically exhibit superior durability (e.g., Wagh 2004). Further, due to their relatively neutral pH after curing, they also offer superior resistance to chemical attack and deicer scaling (e.g., Wagh 2004). Phosphate cements exhibit good dimensional stability during curing. While magnesium phosphate cements have higher initial costs compared to Portland cement, these can be offset by alternative construction practices and the superior properties which potentially allow for extended service life with lower life cycle costs.

In addition to the superior properties, magnesium-phosphate cements are generally recognized as having lower environmental impacts than Portland cements. Kiln temperatures required to process the raw materials for magnesium-phosphate cements are lower than for Portland cement, leading to significant reductions in the energy demands (Wagh 2004). This lowers the embodied energy and the corresponding greenhouse gas emissions. The refining processes do not directly result in CO_2 production from the raw materials, as does Portland cement production. Further, prior research has shown that magnesium-phosphate cements can allow the use of a high fly ash loading (Wagh 2004; Ding and Li 2005b). As fly ash used in these cements is an industrial by-product from coal-fired thermal power stations, use of high fly ash loadings can help to further reduce the equivalent environmental impacts for a given volume of concrete. Fly ash is of lower cost than the other components of magnesium-phosphate cements, so expanded use of fly ash can have significant economic implications.

This study focusses on magnesium potassium phosphate cements (MPPC) originally developed by Wagh and his colleagues (Wagh et al. 1998; Wagh 2004). These binders use readily available components and are easy to prepare with common concrete-industry equipment. Of particular importance in the selection of MPPC, earlier work by Wagh has shown that the use of a potassium component gives a cement with a more controlled reaction rate, good long-term chemical stability and lack of off-gassing, all issues that have caused concern with some other magnesium phosphate cements. The properties of the resulting MPPC binders, mortars or concretes can be

tailored through changes to the mix proportions or the inclusion of additives and fillers. For example, prior research has examined the properties of MPPC binders and sand mortars that included moderate volumes of fly ash (Ding and Li, 2005a, 2005b; Qiao 2009, 2010). Tassew and Lubell (2010, 2012) reported on lightweight concretes produced with MPPC binders and different aggregate types. However, there have only been limited studies to understand the influence on the properties of binders and sand mortars for mixes containing high volumes of fly ash.

Research significance

Magnesium potassium phosphate cement binders can be formulated to allow adequate working time but high early age strength gain with good dimensional stability. These binders also allow incorporation of large amounts of fly ash in the mix, leading to concretes with lower environmental impacts from the energy and resource consumption as well as reduced greenhouse gas emissions during their manufacture.

This paper reports on a laboratory study conducted to quantify the influence of the mix composition on the properties of magnesium potassium phosphate cement binders and sand mortars. Special emphasis was placed on the use of high fly ash volumes at up to 80% by mass of the binder. Mixes considered in the study were targeted to have compressive strengths and workability appropriate for use in either pre-cast or site mixed concrete construction applications.

MIX DEVELOPMENT

Overview of magnesium phosphate cements

Commercially available magnesium-phosphate cement based mortars produced by reacting magnesium oxide and ammonium hydrogen phosphate or ammonium dihydrogen phosphate are widely used as fast setting grouts or as rapid repair materials for roads, industrial floors and airport runways (e.g., Abdelrazig et al. 1988). However, widespread use of mortars based on ammonium-phosphate precursors is somewhat restricted as the chemical reaction process will emit ammonia gas during mixing and curing (Wagh 2004). This can lead to hardened mortars with undesired voids, corrosion of mixing containers, and unpleasant odours that can be hazardous in confined spaces (e.g., Ding 2005).

Wagh and his colleagues (Wagh et al. 1998; Wagh 2004) developed an alternative magnesium-phosphate cement that does not emit gas by reacting calcined magnesium oxide (MgO) with monopotassium phosphate (KH_2PO_4) in water. The reaction process is commonly termed an acid-base reaction and was given by Wagh as:

$$MgO + KH_2PO_4 + 5H_2O = MgKPO_4.6H_2O \quad (1)$$

Wagh et al. (1997) reported that pure MPPC binders based on Eq. (1) have typical compressive strengths of 20 to 25 MPa [2.9 to 3.6 ksi].

According to Wagh (2004) and Ding and Li (2005a), the compressive strength of MPPC is enhanced by inclusion of a moderate mass fraction of fly ash (FA) during mixing. It is noted that fly ash obtained from coal-fired thermal power stations contains high concentrations of silicates that can preferentially react with the mix components that would otherwise react according to Eq. (1). Fly ash also contains calcium-oxide (CaO) which can potentially react with the KH_2PO_4 in place of the MgO. Fly ash particles may also act as gap fillers and aid in lubrication during mixing, similar to their role as supplementary cementing admixture in Portland cement concretes. Prior study by Wagh (2004) suggested that the highest compressive strength of MPPC binders is obtained when the FA loading is between 50 and 60% of the total mass of the dry binder ingredients. However, systematic investigation of mixes with very high fly ash loadings has not been previously reported.

The properties of MPPC sand mortars have been reported by several researchers (e.g., Ding and Li 2005a, 2005b; Qiao et al. 2009, 2010). Qiao et al. (2009) reported that the setting time of MPPC binders and sand mortars was greatly reduced as the reactivity of the magnesium oxide increased. Ding and Li (2005a) and Qiao et al. (2010) found that increasing the sand to binder ratio decreased the compressive strength. Ding et al.

(2005b) reported that an increase in the water to binder ratio reduces both the compressive strength and the elastic modulus of sand mortar made using MPPC binders.

Tassew and Lubell (2012) reported on the development of structural lightweight concretes produced using MPPC binders and different lightweight aggregate types. Their study showed that the mechanical properties of the lightweight concretes were also influenced by the water to binder ratio, the aggregate to binder ratio and the aggregate type.

Expanded use of fly ash in MPPC can be beneficial for environmental, unit cost and material performance criteria. The research reported in this paper examines the physical and mechanical properties of MPPC binders with different fly ash loading. The properties of sand mortars made with MPPC binders were also examined.

Materials

All materials used in this study were commercially available. Municipal tap water from Edmonton, Alberta was used for all mixes.

Calcined magnesium oxide (MgO) was used in this study. Earlier work by the research group showed that the specific surface area of the MgO has a significant influence on the reaction rate of Eq. (1). Qiao et al. (2009) also reported that the reaction rate was dependent on the purity of the MgO supply, which indirectly influences the reactivity. To produce mixes with targeted setting times of 60-120 minutes, suitable for pre-cast or site-mixed concretes, MgO with a specific surface area of 0.3 m^2/g was used. Other manufacturer specifications for the selected MgO indicated its purity at 97% MgO by weight with a minimum 95% of particles passing the 200-mesh size.

Monopotassium phosphate (KH_2PO_4) is a water-soluble fertilizer commonly used in hydroponics-based agriculture. The agriculture grade KH_2PO_4 used in this study was obtained from a local farm supply warehouse. It is noted that the production process for KH_2PO_4 will result in an essentially pure compound, but the presence of trace impurities was not verified in the current study.

Class C fly ash was obtained from a local coal-fired thermal power station. The fly ash source was the same as earlier studies by the authors so that the chemical composition was relatively consistent (Tassew and Lubell 2012). It is noted that some mixes using Class F fly ash were also prepared in the earlier reported work in Tassew and Lubell (2012). Among other characteristics, Class F fly ash contains a lower concentration of CaO which could substitute for the MgO in the reaction given in Eq. (1). As the respective CaO and MgO reactions may occur at different rates based on concentration or particle size, this can influence the fresh and hardened properties of the binders. The available Class C fly ash gave better mix performance than the available Class F fly ash and thus Class C fly ash was used in all mixes reported in this paper.

For sand mortars reported in this study, angular quartz sand was obtained from a local supplier. The sand had a maximum particle size of 1.25 mm [0.05 in.] with the particle size distribution presented in Fig. 1. The sand had a specific gravity of 2.65 and was used in a dry condition as stored in the ambient laboratory environment.

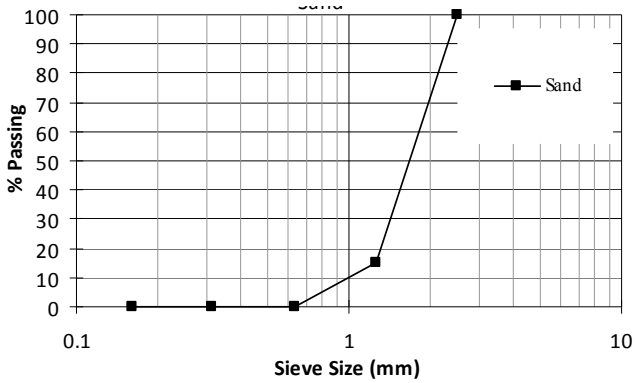


Figure 1—Particle size distribution of sand (1 mm = 0.039 in.)

To control the reaction rate and retard the setting time, two different admixtures were investigated. Borax in powder form was obtained from a local supermarket. A lignosulphonate retarder commonly used for Portland cement concrete was obtained in a liquid format from a concrete admixture supplier.

Mixing and curing procedures

Two groups of mixes were prepared in this study. The first group of mixes comprised MPPC binders. The second group of mixes comprised sand-cement mortars using MPPC binders with sand aggregates. The mixing and curing procedures were similar for both mix groups. The mix proportions are presented in Table 1.

Table 1 – Normalized mix proportions by mass

Mix Type	Mix ID	Materials mass ratio				
		$MgO+KH_2PO_4$	FA[a]	b[a]	b/S[a]	w/b[a]
MPPC (Group 1)	BC4/ BC5/BC6/ BC7/ BC8	1	0.67/1.0/1.5/2.35/4.0	-	-	0.16-0.26
	B5	1	1.0	-	-	0.20
	B7	1	2.35	-	-	0.20
SCM (Group 2)	MC5	1	1.0	1	1-3.0	0.20
	MC7	1	2.35	1	1-3.0	0.20
	M5	1	1.0	1	1.5	0.20
	M7	1	2.35	1	1.5	0.20

[a] FA : Fly ash; b: binder as $MgO+KH_2PO_4+FA$; S: sand aggregate; w: mixing water

All MPPC binders reported in this study used a mass ratios of $MgO:KH_2PO_4=1:3.4$ based on the molar ratios in Eq. (1). Fly ash loadings of 40 to 80 % by mass of the total dry binder ingredients (i.e. $MgO+KH_2PO_4+FA$) were considered. MPPC binders prepared with fly ash loadings of 40, 50, 60, 70 and 80% of the total dry binder mass were denoted as mixes BC4, BC5, BC6, BC7 and BC8, respectively. For these mixes, the water to binder mass ratio w/b was varied from 0.16 to 0.26. As discussed later, two MPPC binders with 50% and 70% fly ash loading and a fixed w/b ratio were selected for further study and denoted as mixes B5 and B7.

In the second phase of the study, the B5 and B7 binders were combined with the aggregates to produce sand ceramic mortars (SCM). Different binder to sand mass ratios of b/S =1, 1.5, 2, 2.5 and 3 were considered wherein binder refers to the combined mass of $MgO+KH_2PO_4+FA$. These mixes were denoted as MC5 and MC7, while later mixes with a fixed b/S ratio of 1.5 were denoted as M5 and M7. The water to binder (w/b) mass ratio of all SCM mixes was kept constant at 0.2 as shown in Table 1.

Each mix was prepared using similar procedures. A 20 *l* [21.1 qt] capacity portable drum mixer was used to dry mix together the MgO, KH_2PO_4 and FA. Mixing duration was approximately 5 min at a drum speed of 60 RPM. For the SCM mixes, the sand was also included in this dry mix. The water was combined with the retarder in the mixing bowl of a 5 *l* [5.3 qt] Hobart planetary mixer. The dry mix was then gradually added and the entire batch was mixed together for 5 to 10 min at a mixing speed of 28.5 RPM. The mixes were placed into plastic molds using a scoop and vibrated for 45 seconds using a vibrating table. Specimens were removed from the molds after 3 hrs and stored in the ambient laboratory environment (23 ± 2^oC [73 ± 4^oF] with a relative humidity of 50 ± 5%) until testing. All test data presented in this paper is the average of three specimens unless noted otherwise.

Testing procedures

The mix development study mainly focussed on the compressive strength and density of the binders and mortars. Additional mechanical properties were also measured for selected mixes. The test procedures used to evaluate the different properties of MPPC and SCM are discussed as follows.

Workability and setting time – No flow or slump tests were completed for the mixes. However, all mixes were observed to be homogenous in nature and could easily be poured from the mixing vessel without visible segregation. The mixes were qualitatively similar in consistency to mixes reported by Tassew and Lubell (2012) where more detailed workability measurements were obtained. While the overall trends suggest that the mixes had self-compacting like ability, all mixes were externally vibrated to assist in consolidation.

Setting time was measured using a Vicat needle apparatus according to ASTM C191. Since the difference between the initial and final setting times was very short, only the final setting times are reported in this paper.

Compression tests – The cube compressive strength f_{cu} was determined using 50×50×50 mm [2×2×2 in.] specimens according to ASTM C39. The tests were completed using a Forney testing machine with capacity of 3100 kN [700 kips] at a loading rate of 0.25 MPa/s [35 psi/s]. To establish the strength development with time, cube compression tests were conducted at ages of 2, 7, and 24 hrs and at 3, 7 and 28 days after casting.

The modulus of elasticity was evaluated from uniaxial compression tests on 100×200 mm [4×8 in.] cylinders in accordance with ASTM C469. Tests were conducted in a stiff MTS frame with capacity of 2600 kN [585 kips]. Displacement controlled loading at a machine stroke of 1.25 mm/min [0.05 in./min] was used. Axial deformations of the cylinders were measured using three LVDTs arranged at 120º separation about the longitudinal axis and operating over an initial gauge length of 100 mm [4 in.]. Cylinders were sulphur capped before testing as per ASTM C617.

Flexure tests – The flexure response was determined from 50×50×200 mm [2×2×8 in.] prisms under 4-point bending according to ASTM C78. The universal test machine had a 30 kN [6.75 kip] capacity. Tests were carried out at the age of 28 days at a loading rate of 0.1 mm/min [0.004 in./min].

CHARACTERIZATION OF BINDERS

Setting time

Tests were completed to investigate the viability of controlling the working time by using either Borax or a commercial lignosulphonate as a retarder. After some trial mixes to establish appropriate dosages, Borax at 4% by mass of the MgO and a commercially available lignosulphonate admixture at 6.6% by mass of the MgO were examined.

Fig. 2 compares the final setting times for binders B5 and B7 prepared with Borax or lignosulphonate. The final setting times for the B5 binder were approximately 1 hr and 2 hrs when Borax and lignosulphonate were used, respectively. However, negligible difference in the final setting time was observed for B7 binders prepared with the two admixtures, with a setting time of about 2.5 hrs in both cases. Due to the extended working time and simpler mix procedures for a liquid additive, the lignosulphonate admixture at a dosage of 6.6% by mass of MgO was used for all subsequent mixes reported in this paper.

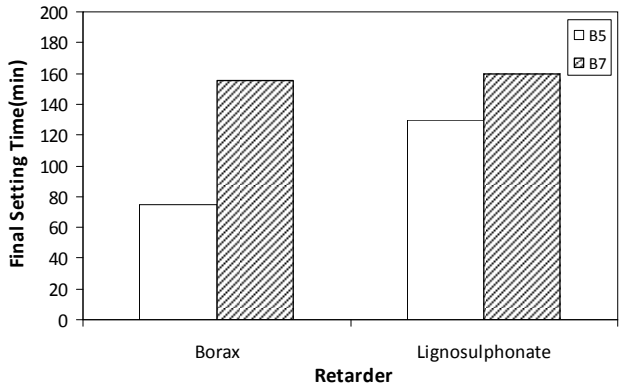


Figure 2—Influence of retarder type on the binder setting times

Influence of mixing time

Fig. 3 shows the influence of mixing time on the average cube compressive strength of type B5 and B7 binders with *w/b* = 0.20. The mixing time was measured from the addition of the dry ingredients to the liquid components. As the mixing time increased, the 7-day cube compressive strength increased for both the B5 and B7 binders. Uniformity of the mix was also visually observed to improve as mixing time increased due to improved dispersion of the constituent elements as mixing proceeded. A mixing time of approximately 7.5 minutes was selected for use in all subsequent mixes reported in this paper.

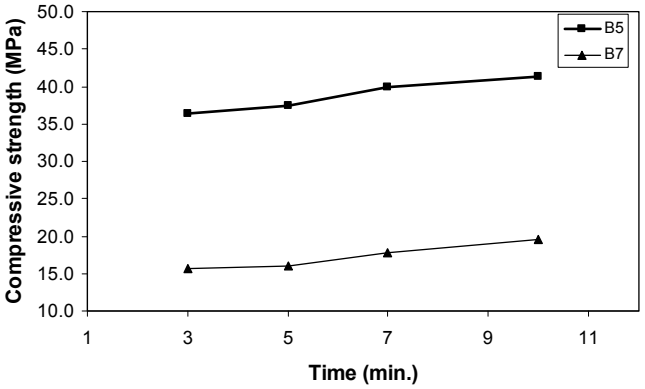


Figure 3—Influence of mixing time on average 7-day compressive strength (1 MPa = 0.145 ksi)

Influence of fly ash loading on density

The influence of the fly ash loading on average density of the hardened MPPC binder is shown in Fig. 4. All mixes in Fig 4 had *w/b*=0.22. It can be observed that the density decreases as the fly ash content is increased. This occurs because the fly ash has a lower unit weight than the $MgO+KH_2PO_4$ reactive components, thereby reducing the overall density of the binder. The average density ranged between 1553 kg/m^3 [2618 lb/yd^3] and 1820 kg/m^3 [3068 lb/yd^3] for fly ash variation between 80% and 40% of the total mass of binder.

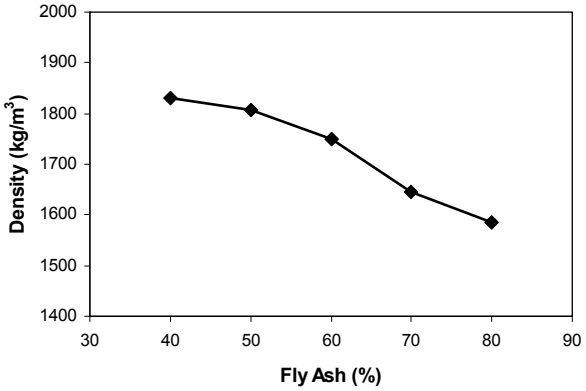


Figure 4 —Average density vs fly ash loading by mass of binder (1 kg/m^3=1.685 lb/yd^3)

Effect of water/binder ratio and fly ash loading on compressive cube strength

The influence of varying the *w/b* ratio on the average 7-day cube compressive strength for MPPC binders with different fly ash content is presented in Fig. 5. It is observed that the influence of *w/b* on the compressive strength is dependent on the fly ash loading.

For moderate fly ash loading (i.e. 40%-60%), the compressive strength increases as the *w/b* increases up to about 0.2, but then decreases. These trends were similar to the prior study by Ding and Li (2005a). It appears that there may be an optimum minimum water content of approximately *w/b*=0.2 for these mix compositions and too little water may hinder the ability to adequately blend the materials and remain available to support the reaction from Eq. (1). Beyond *w/b*=0.2, excess water that cannot be used in the reaction process contributes to material with a higher void ratio. It should be noted that even at *w/b*=0.2, the total mixing water is less than the water requirement for full reaction of the MgO and KH_2PO_4 in Eqn (1) for low fly ash loadings. The low permeability of the hardened products is thought to prevent water access to allow complete reaction in all cases.

For mixes with a high fly ash loading (i.e. 70% and 80%), the average compressive strength was observed to decrease as the *w/b* ratio increases. For these mixes only $w/b \geq 0.18$ could be considered due to difficulty with mix workability for smaller *w/b* ratios.

Fig. 5 also shows that the average compression strength f_{cu} was a maximum when the fly ash loading was between 40% and 60% for the MgO:KH_2PO_4 and *w/b* ratios studied. This result is similar to the findings of previous research (e.g., Wagh 2004; Ding and Li 2005a). The binder with 50% fly ash content and a *w/b* ratio of 0.2 provided the highest average compressive strength in this study.

From the results in this initial phase which confirmed the influence of the fly ash loadings on strength, two binders were selected for more detailed evaluation in the second phase: a mix resulting in high compressive strength (using 50% fly ash loading and denoted B5) and a mix resulting in a comparatively low strength (using 70% fly ash loading and denoted B7). Since fly ash has a unit cost substantially lower than the other binder components, the B7 mix will have a lower unit cost than the B5 binder. A *w/b* ratio of 0.2 was used in both B5 and B7 binders. See Table 1.

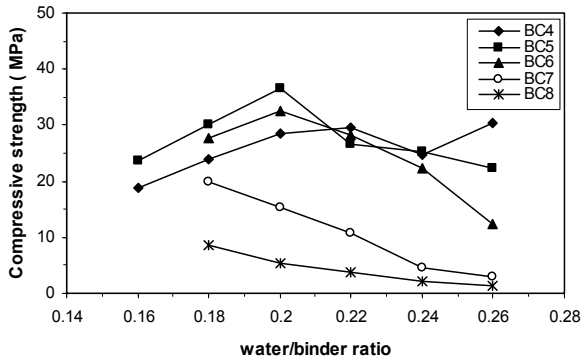


Figure 5—Influence of *w/b* loading on average compressive strength (1 MPa = 0.145 ksi)

Fig. 4 showed that the average density decreased as the fly ash loading increased, while Fig. 5 showed that the average compressive strength generally decreased as the fly ash loading increased. The relationship between the average 7-day cube compressive strength and the average density for mixes with *w/b*=0.2 is presented in Fig. 6. The plot shows that there is a correlation between the compressive strength and density of MPPC binders, regardless of the fly ash loading. This trend suggests that, within practical limits, the fly ash loading can be adjusted in the mix design to achieve the density corresponding to a desired strength.

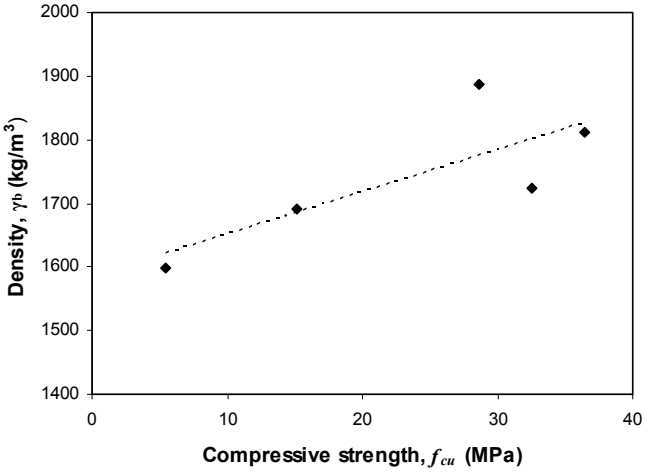
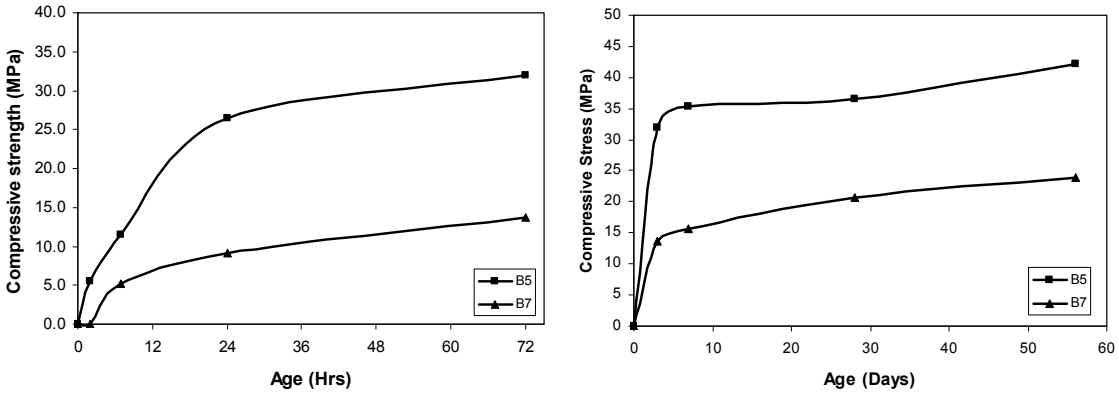


Figure 6 —Relationship between binder average compressive strength and average density (1 MPa = 0.145 ksi; 1 kg/m^3 = 1.6855 lbs/yd^3)

Compressive strength development

The strength development with time for binders B5 and B7 is shown in Figure 7. Strength development over the first 72 hours is shown in Fig. 7a, with results over 56 days shown in Fig. 7b. Note that average results for three samples of each mix time at a given time interval are shown, with the coefficient of variation between the specimens in each age group falling within the range normally achieved for Portland cement based samples. Both binders exhibited rapid strength gains over the initial 24 hours following casting, and a continual gain in strength over the 56-day study period. Early age strength gains are considered important in evaluating the viability of using these binders in construction systems that require rapid construction, early formwork removal or early introduction of imposed loads. The average 28-day compressive strengths of the B5 and B7 binders were measured as 36.6 and 20.6 MPa [5.31 and 2.99 ksi], respectively. Binder B5 exhibited 15% of its 28-day compressive strength within 2 hrs after casting, but no strength was available for B7 at 2 hrs as B7 had not yet reached the final setting time. At 7 hours after casting, binders B5 and B7 reached 31.4% and 25.2% of their 28-day compressive strengths, respectively. Further, B5 and B7 exhibited 72.1% and 44.2% of their 28-day

strengths within 24 hrs, respectively. The difference is explained by B5 having a higher concentration of the MgO and KH_2PO_4 reactive components compared to B7 due to relative fly ash loadings. The higher concentrations of these components lead to a faster reaction process. The compressive strengths of B5 at 3, 7 and 56 day were 87.2%, 96.7% and 115% of the 28 strength, respectively. For B7, the 3, 7 and 56 day compressive strengths were 66.5%, 76.2% and 116% of the 28 strength, respectively. These results indicate that while initial strength development of B5 is faster compared to B7, after 28 days the strength development appeared to be similar.



(a) (b)

Figure 7—Strength development with time (a) Early age results (b) 56 day study period (1 MPa = 0.145 ksi)

Modulus of elasticity

Fig. 8 shows typical compressive stress-strain curves for cylinders made from B5 and B7 binders and tested at 28-days according to ASTM C469. It is observed that the ascending branch of the stress-strain curve for B5 was nearly linear up to the peak stress value of 47.6 MPa [6.9 ksi]. A brittle response occurred in the post-peak region. However, mix B7 showed a more curved stress-strain response up to the peak stress of 25.6 MPa [3.7 ksi] with a more gradual loss of strength in the post-peak region. The peak stress and the strain at peak stress were both smaller for B7 than B5. See Table 2.

The modulus of elasticity of B5 and B7 were determined as secants to the stress-strain response according to ASTM C469. The modulus of elasticity of B5 and B7 were 13.6 GPa [1973 ksi] and 10.8 GPa [1566 ksi], respectively, indicating that the modulus of elasticity varies with the compressive strength.

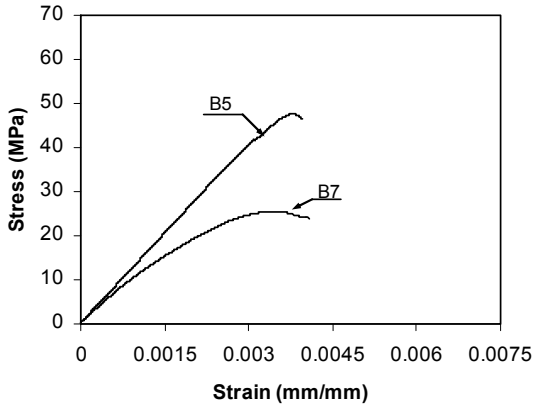


Figure 8—Compressive stress-strain response of binders B5 and B7 (1 MPa = 0.145 ksi)