

SETTING TIMES OF PORTLAND CEMENT-METAKAOLIN-FLY ASH BLENDS

David Snelson¹, Stan Wild², Martin O'Farrell³

 ^{1,2}Faculty of Advanced Technology, University of Glamorgan, Llantwit Road, Trefforest, Pontypridd, Mid Glamorgan, Wales, United Kingdom, CF37 1DL
 ³Taylor Woodrow, Technology Centre, Stanbridge Road, Leighton Buzzard, Bedfordshire, England, United Kingdom, LU7 4QH
 E-mails: ¹dgsnelso@glam.ac.uk (corresponding author); ²swild@glam.ac.uk; ³martin.ofarrell@taylorwoodrow.com

Received 17 Aug. 2009; accepted 05 Jul. 2010

Abstract. In the present study two pozzolanic materials are used, Metakaolin (MK) and Fly Ash (PFA), as binary and ternary partial replacement binders with Portland cement (PC) to investigate their effect on standard consistence and setting times of paste. To maintain standard consistency for MK–PC pastes increasing w/b ratios are required with increasing MK levels, whereas PFA has little influence on consistency. For binary MK–PC pastes there are substantial increases in initial and final setting times at 5% MK followed by decreases at 10 and 15% MK before further increases at 20% MK. For binary PFA–PC pastes however setting times increase at approximately the same rate up to 30% PFA and then increase more sharply between 30% PFA and 40% PFA. In general the effects of both PFA and MK on consistency and setting times in binary pastes are reflected in the behaviour of the ternary pastes although the two pozzolans do not behave completely independently of each other. The different ways in which the two pozzolans influence setting times is explained in terms of differences in their pozzolanic activities and in the manner in which they influence the availability of water for hydration.

Keywords: cement paste, fly ash, metakaolin, pozzolans, standard consistence, setting time.

1. Introduction

Knowledge of the setting characteristics of concrete is important in the field of concrete construction (Brooks et al. 2000). It assists in the scheduling of the various stages involved in concrete construction operations such as transporting, placing, compacting and finishing of concrete. When placing concrete in formwork there are other factors to take into consideration apart from setting time that can cause the concrete to stiffen for example impact of concrete discharge, permeability/watertightness of formwork and plan shape of cast section (Clear and Harrison 1985). The loss or displacement of water from the mix can cause the structure of the fresh concrete to change from a quasi liquid to relatively stiff mix with water contained within the voids (Clear and Harrison 1985). When water is mixed with cement various reactions occur leading to the formation of hydration products which cause an increase in stiffness of the cementitious matrix as a function of time. The stiffening behaviour of the matrix is determined by the initial and final times of setting. The initial time of setting of the matrix refers to the beginning of hardening for a given mixture. At this stage concrete can neither be properly re-tamped nor can it be handled and placed. The final setting refers to the stage when the mixture attains sufficient hardness to support stress (Naik et al. 2001).

Chen and Older (1992) investigated 16 cement pastes made from cements of different laboratory-made

clinker compositions and containing different amounts and forms of calcium sulfate. A water-cement ratio of 0.3 was used except in two pastes with 0.4 and 0.5. The beginning and end of setting was investigated, the latter being determined by the Vicat method as specified in ASTM C–191. The authors found that "normal" setting of Portland cement is associated with C₃S and/or C₃A (+C₄AF) hydration and formation of C–S–H gel and ettringite. Ettringite formation appears to have an important function in cements with high C₃A content. Although, during setting, the paste acquires some strength, for practical purposes it is important to distinguish setting from hardening, which refers to the gain of strength of a set cement paste (Neville 1995).

Brooks *et al.* (2000) reported initial and final setting times of concrete (from tests performed on mortar obtained by sieving freshly mixed concrete) with binary PC-FA blends as binder and with 10, 20 and 30% replacement of PC by a FA. In this case a sulphonated vinyl co-polymer superplasticiser was used in the mixes and the Class F FA did not exceed 30% PC replacement. The authors observed increased retardation at increased FA replacement levels for initial and final setting times. As replacement level was increased to 30% FA, the initial and final setting times increased by a factor of 1.6 and 1.5 respectively. At the same replacement level, the results of Eren *et al.* (1995) showed that the initial and final setting times increased by factors of 1.28 and 1.21. One reason suggested by the authors for this difference in the results

was the use of superplasticiser in their investigation. (In the current work no SP was employed and an even higher replacement level of 40% FA was used). The work by Brooks et al. (2000) supports earlier work by Carette and Malhotra (1984) who found that in general, apart from one FA, all the FA samples employed caused an increase in the initial and final setting time of concrete. The retardation of the setting time depended upon the source of FA used. FA from various sources was used with the calcium oxide (CaO) content varying in the range of 1 to 13%. In addition Mailvaganam et al. (1983) observed, when investigating setting times of ternary blended concrete made with a slag and FA, that concrete mixtures made at 20 °C with 30% FA had extended initial setting times in the range of 1 to 1.75 hours. Concrete mixtures were prepared using various chemical admixtures at two different temperatures. Neville (1995) suggests that the retarding effect of the initial set, typically of about one hour, is probably caused by the release of SO₄ present at the surface of the FA particles. Lee et al. (1999) investigated properties of classified fly ashes by using an electrostatic precipitator and the modification of fly ashes by carbon removal. Nine fly ashes were classified by using an electrostatic precipitator and modified by calcination at 500 °C or treated in a plasma reactor. The authors reported that early hydration of cement was retarded by the addition of superfine fly ashes.

In contrast MK has a very different effect on setting times compared to FA. Although there is an increase in both initial and final setting times at low MK levels, a drop at 15% replacement was reported by Brooks et al. (2000). This was in contrast to the other mineral admixtures investigated (silica fume (SF), FA and ground granulated blastfurnace slag (GGBS)), which all showed increasing setting times with increasing replacement level and with higher effective superplasticiser (SP) dosage. The authors pointed out that the effect at around 15% MK was peculiar to the MK pozzolan and did not occur with SF which is also a highly active pozzolan. The initial and final setting times of concrete (tests performed on mortar obtained by sieving freshly mixed concrete) with binary PC-MK blends as binder and with three (5%, 10% and 15%) replacement levels of PC by MK was investigated. The authors used a superplasticiser in the mixes based on sulphonated vinyl co-polymer. In the current work no SP was used with MK and an even higher replacement level of 20% MK was used.

Vu *et al.* (2001) investigated standard consistence and initial and final setting of pastes with up to 30% replacement of PC by calcined kaolin (K). The K was produced by heating kaolin at 800 °C for two hours. At low replacement levels of PC by MK (10% and 20%) the initial and final setting times were similar to that of the PC control indicating little retardation. Beyond this range the initial and final setting times increased by about 10 and 15 minutes respectively (Vu *et al.* 2001). The authors proposed that this was due to the lower cement and relatively higher water contents involved. Over the replacement range of 10% to 30% replacement of PC by K the w/b ratio to achieve standard consistence varied from 0.3 to 0.41 with the PC control at 0.25. Overall, to achieve standard consistence with increasing replacement levels of K, an increase in w/b ratio is required.

From previous reports it is apparent that when FA replaces PC in binary binders there is retardation in the initial and final set of mortar and concrete, with greater retardation occurring at higher replacement levels. This also applies when MK is used as a binary binder with PC at low MK levels but reverses at 15% replacement (Brooks et al. 2000). This is an interesting observation as replacing PC with increasing levels of pozzolans increases the separation distances between PC particles which, assuming negligible initial pozzolanic reaction, generally has the effect of increasing setting times as more hydration product is required to develop a rigid 3dimentional interconnected network. This paper reports on two pozzolanic materials, MK and PFA, as binary and ternary partial replacement binders with PC to investigate their effect on standard consistence and setting times.

2. Experimental procedure

A Vicat apparatus was used to measure standard consistence, and initial and final setting time after the reactants were mixed together and placed in a mould.

2.1. Materials and mixing

Data on the oxide compositions, and properties of the cementitious materials used in this research including the phase composition of Portland cement calculated using Bogue's equations, are shown in Table 1. A single batch

Table 1. Compositions and physical properties of PC and PFA, MK

Ovside ^d	Compositions (%)			
Oxside	PC ^a	MK ^b	PFA ^c	
SO ₂	20.80	52.10	49.80	
Al ₂ O ₃	4.80	41.00	26.40	
Fe ₂ O ₃	3.60	4.32	9.30	
CaO	63.40	0.07	1.40	
MgO	1.10	0.19	1.40	
SO_3	3.10	Ι	0.80	
Na ₂ O	0.13	0.26	1.50	
K ₂ O	0.84	0.63	3.50	
TiO ₂	0.30	0.81	1.00	
Cl	_		0.01	
Freelime	1.40		-	
Bogue's composition (%)	PC	MK	PFA	
Tricalcium aluminate (C ₃ A)	6.63	Ι	-	
Tricalcium silicate (C ₃ S)	53.7	I	-	
Dicalcium silicate (C_2S)	19.21	-	-	
Tricalcium alumina ferrate (C ₄ AF)	10.95	_	-	
Properties	PC ^a	MK ^b	PFA ^c	
Loss on ignition	1.90	0.60	4.90	
Specific surface area (m ² /g)	0.44 ^e	12.00 ^e	0.53 ^e	
Initial setting time (mins)	130 ^f		-	
Final setting time (mins)	165 ^f	_	_	
Standard consistency (%)	$27^{\rm f}$	-	_	
True material density (g/cm ³)	3.07 ^g	2.34 ^g	2.47 ^g	

Data supplied by: ^a Rugby Cement Ltd; ^b Imerys; ^c UKQAA Experimentally determined: ^d XRF; ^e Malvern Particle Size Analyser (Mastersizer 2000); ^f Vicat apparatus; ^g Density bottle method

of South Ferriby Portland cement, in accordance with BS EN 197–1 (British Standards Institute 2000) supplied by Rugby Cement was used. Imerys supplied the MetaStar 501 MK and its composition is given in Table 1. United Kingdom Quality Ash Association (UKQAA) formerly Ash Resources Ltd supplied the class F, low lime PFA, in accordance with BS EN 450 (European Standard 1995) and its composition is given in Table 1. The reactive silica content was determined by double evaporation method (Associate Cement Cos. Ltd, India) as per BS EN 196–2 (British Standards Institute 1995a) is 34.3%, thus approximately 69% of the silica content in the PFA is reactive.

The PC, PFA and MK were blended by hand until a uniform colour was achieved and a total solids content of 500g per pozzolan was investigated. The details of the mix proportions are presented in Table 2.

 Table 2. Mix proportions for standard consistence and setting time

	(wt.%)		ant			(g)			
	PC	PFA	MK	Total replaceme (%)		PC	PFA	МК	Standard consis tence w/b ratio
1	100	0	0	0	Control	500	0	0	0.268
2	95	0	5	5	MK only	475	0	25	0.88
3	90	0	10	10		450	0	50	0.306
4	85	0	15	15		425	0	75	0.333
5	80	0	20	20		400	0	100	0.364
6	90	10	0	10	PFA only	450	50	0	0.267
7	80	20	0	20		400	100	0	0.268
8	70	30	0	30		350	150	0	0.269
9	60	40	0	40		300	200	0	0.271
10	90	5	5	10	10	450	25	25	0.87
11	80	15	5	20	20	400	75	25	0.284
12	80	10	10	20		400	50	50	0.308
13	80	5	15	20		400	25	75	0.334
14	70	25	5	30	30	350	125	25	0.282
15	70	20	10	30		350	100	50	0.305
16	70	15	15	30		350	75	75	0.348
17	70	10	20	30		350	50	100	0.397
18	60	35	5	40	40	300	175	25	0.293
19	60	30	10	40		300	150	50	0.318
20	60	25	15	40		300	125	75	0.356
21	60	20	20	40		300	100	100	0.388

2.2. Standard consistence and initial and final setting times

Standard consistence, and initial and final setting time tests on the PC, PFA–PC, MK–PC and MK–PFA–PC pastes were carried out using a Vicat apparatus in accordance with BS EN 196–3 (British Standards Institute 1995b). Both the standard consistence tests and the setting time tests were carried out at (20 ± 1) °C. The deion-

ized mix water was allowed to equilibrate to ambient temperature for 24 hours prior to mixing. Mixing was carried out in a Kenwood Chef Major KM250 mixer in accordance with BS EN 196–3 (British Standards Institute 1995b), for a total mixing time of $3^{1}/_{4}$ minutes. The paste was placed in a cylindrical 75 mm diameter by 40 mm long mould. The surface of the paste was smoothed, in preparation for the test to be completed at four minutes. Details of the mixing duration are presented in Table 3.

Time zero	Overall time	Duration	Operation	
	seconds	seconds		
	-	5 to 10	Add blend to water	
	0	0	End of adding blend	
			to water	
	90	90	Initial slow mix	
	105	15	Scrapping and	
4			clearing of bowl	
minutes	195	90	Second slow mixing	
	240	45	Transfer to mould-	
			Vicat apparatus	
41/2	270	30	Penetration	

Table 3. Mixing duration for standard consistence and settingtime in accordance with BS EN 196–3 (British Stan-dards Institute 1995b), Kinuthia (2000)

The standard consistence was that recorded for the test in which the plunger of the Vicat apparatus penetrated the paste to a depth of thirty-four mm (i.e. (6 ± 1) mm from plunger to mould base plate) in 30 seconds. The value recorded was an average of two equivalent tests. Once the paste's standard consistence had been established the setting time was determined.

The initial setting time was determined from a series of penetration measurements at ten minute intervals, on a paste of standard consistence BS EN 196–3 (British Standards Institute 1995b). The initial setting time value recorded was an average of two equivalent tests. After determination of the initial set the mould was inverted and a penetration test performed every 30 minutes with the appropriate needle. The final set value recorded was an average of two equivalent tests.

3. Results

3.1. Standard consistence

The results from standard consistence, and initial and final setting time tests are presented and discussed in the following paragraphs.

3.1.1. Standard consistence of binary MK–PC and PFA–PC pastes

The results showing the w/b ratios at standard consistence for the different binary pastes are presented in Fig. 1. In MK binary pastes the w/b ratio needed to give standard consistence increases with increasing MK replacement levels, whereas with PFA binary paste the w/b ratio needed to give standard consistence is similar to that for PC at all replacement levels.



Fig. 1. w/b ratios at standard consistence for binary MK–PC and PFA–PC pastes

3.1.2. Standard consistence of ternary MK-PFA-PC pastes

The results showing the w/b ratios at standard consistence for the different ternary MK–PFA–PC pastes are presented in Fig. 2. In ternary MK–PFA–PC paste as in binary MK–PC paste the w/b ratio for standard consistence increases with increasing MK replacement level (Fig. 1 and Fig. 2a). More water is required for the wetting of the MK surface than for that of the PFA or PC because of its much larger surface areas, this is supported by earlier work of Bai and Gailius (2009). However although at 0% MK content the w/b ratio at standard consistence remains relatively unchanged with increasing PFA content, at increasingly fixed MK levels (Fig. 2b dotted curves) the w/b ratio at standard consistence tends to increase with increasing PFA content, suggesting that the two pozzo-lans are not operating independently.

Vu *et al.* (2001) also reported similar results to those obtained by the author for standard consistence of pastes with binary metakaolin – PC blends as binders with up to 40% replacement of PC by calcined kaolin (K) (which was produced by incinerating Kaolin powder at 800 °C for two hours). The replacement range of 10 to 40% replacement of PC by MK the w/b ratio at standard consistence varied from 0.3 to 0.45.

3.2. Initial and Final setting time

3.2.1. Initial and Final setting times for binary PFA–PC and MK–PC paste

Fig. 3 shows the change in initial and final setting time at standard consistence of binary PFA–PC paste compositions. As might be expected both the initial and final setting times increase with increasing PFA content although the increase between 30 and 40% PFA is significantly greater than for the other intervals.

Fig. 4 shows the change in initial and final setting time at standard consistence of binary MK–PC paste compositions. For the binary MK–PC blends the initial setting time shows a substantial increase at 5% MK and then decreases slightly at 10 and 15% MK before increasing further at 20% MK. A similar trend but more well defined is also observed for the final setting time. This suggests that the MK is contributing to and influencing hydration and setting in a non-systematic manner.



Fig. 2. w/b ratios at standard consistence for binary and ternary MK–PFA–PC pastes



Fig. 3. Initial and final setting times for binary PFA-PC pastes



Fig. 4. Initial and final setting times for binary MK-PC pastes

3.2.2. Initial and final setting time of ternary MK-PFA-PC paste

Figs 5 and 6 show respectively the changes in initial and final setting times with increasing PFA content at standard consistence, for ternary MK-PFA-PC pastes. For ternary binders with a fixed MK content the general trend of increasing setting time (initial and final) with increasing PFA content is still maintained. However the way in which each setting time - PFA content curve shifts as the MK content increases is again non-systematic and mirrors approximately the way in which the setting time of the binary MK-PC blends vary with increasing MK content (Figs 4 and 6). That is, a significant increase in setting time when 5% MK is incorporated, very little further change in setting time (or a reduction in setting time for the lower PFA levels) when 10% or 15% MK are incorporated, and then a further increase in setting time when 20% MK is incorporated. However at high total replacement levels (i.e. 40%) the setting time minimum does shift to lower MK contents (and consequently higher PFA content).

Brooks et al. (2000) reported initial and final setting times of mortar with binary MK-PC blends as binder and with up to 15% replacement of PC by MK. However the authors used superplasticiser in the mixes and did not exceed 15% PC replacement. Interestingly however their



Fig. 5. Initial setting times for binary and ternary MK-PFA-PC pastes

eral admixtures investigated (SF, FA and GGBS) which all showed increasing setting times with increasing replacement level and with higher effective superplasticiser (SP) dosage. The authors suggested that the anomalous behaviour at 15% MK content might be due to the increased water demand which produces a denser binder phase that speeds up setting, this effect being offset by lower PC content and the higher effective SP dosage. However in the current work where no SP was used there is a further marked increase in setting time at 20% MK replacement level even though there is still a fall in setting time at the 15% MK level. Brooks et al. (2000) also pointed out that the effect at around 15% MK was peculiar to the MK pozzolan and did not occur with SF which is also a highly active pozzolan. This again suggests that the MK is having a very significant and non-systematic influence on the hydration process even when combined with PFA.

4. Discussion

The binary MK-PC and PFA-PC and ternary (MK-PFA)-PC paste blend results for standard consistence and initial and final setting times indicate the way in which the individual components of the blends influence the



Fig. 6. Final setting times for binary and ternary MK-PFA-PC pastes

uptake of water both by physical absorption and by hydration and also the way in which each impacts on the hydration process. PC was used, without the addition of MK and PFA, as a control to assess the difference if any, that the effect of the replacement materials made to the standard consistence and setting times of the various compositions. It should however be noted that standard consistence is measured more or less immediately after water is added whereas setting times are measured over a period of between two and five hours after adding water so the two properties have no direct equivalence.

The influence of the two pozzolans PFA and MK on consistency is clearly illustrated in Fig. 1. Replacing PC with up to 40% PFA has a negligible effect on standard consistence, indicating that the PFA has a similar effect on immediate water demand as does PC. However partially replacing PC with up to 20% MK has a substantial effect on consistency, in that increasing w/b ratios are required to maintain standard consistence as the MK level increases. This indicates that MK has a much greater effect on immediate water demand than does the PC. The increased water demand by the MK is also clearly apparent in the ternary MK-PFA-PC Apastes Fig. 2a, where for a given PC total replacement level the w/b ratio to maintain standard consistence again increases with increasing MK content. Also the steepness of the increase appears to be greater at higher total replacement levels. In addition, although at 0% MK content the w/b ratio at standard consistence remains approximately constant with increase in PFA content (Fig. 2b), at increasing "fixed" MK levels the gradients of the w/b ratio - PFA content curves increase. This suggests that the two pozzolans do not operate completely independently of each other with respect to standard consistence.

The large water requirement of the MK is explained by its very large specific surface $(12 \text{ m}^2/\text{g})$ in comparison with that of PFA (0.53 m^2/g), which is similar to the PC $(0.47 \text{ m}^2/\text{g})$. The consistencies of the pastes are measured immediately after the addition of water and are related to the amount of free water available to reduce viscosity and act as a lubricant. However between the addition of water and setting (which occurs between 2 and 5 hours after adding water), the chemical reactions which are initiated (principally the hydration of PC and the pozzolanic reaction of MK) have a profound influence on both the solid to liquid ratio and of the water adsorption/absorption properties of the solids present. For example the chemical loss of water prior to setting, but whilst the paste is still fluid, will tend to cause solid particles to move closer together particularly when surface tension effects begin to operate, and the paste will naturally stiffen. Stiffening is followed by setting and setting occurs when a rigid interconnected network of reaction products develops which bind the solid particles together.

When PC is partially replaced by a pozzolan that experiences little change in its propensity to adsorb/ absorb water or to react during the period from adding water to initial set (i.e. it behaves as a broadly inert solid), the setting time of such a paste would be expected to increase with increase in pozzolan content. This is because as the pozzolan content increases the hydrating cement particles are forced further apart, thus increasing the time period for production of sufficient reaction products to form a rigid interconnected network. It appears from the current results Fig. 4 that PFA–PC pastes behave in this manner in that both initial and final setting times increase continuously with PFA content up to 40% PFA. In fact the highest PFA content (40%) results in a steeper increase in both initial and final set than do the previous increases, which might be expected in that for very high replacement levels cement particle separation distances will become so great that setting will not occur at all.

Clearly MK–PC pastes do not behave in this simple manner (Fig. 4) in that setting times (both initial and final) initially increase (5% MK), and then decrease (10% and 15% MK), and then increase again (20% MK). These results confirm previous reports by Brooks *et al.* (2000) and Vu *et al.* (2001). However, unlike PFA, MK does not act initially as an inert material. It has a high water requirement, therefore increasing water additions are needed as the MK content increases, in order to maintain standard consistency and determine setting times. Also it is a highly active pozzolan and interacts with Ca²⁺ very rapidly modifying its water adsorption/absorption properties, and subsequently producing cementitious reaction products.

The pozzolanic reaction of MK is known to be highly complex. The direction of the MK reaction is strongly influenced by the composition of the blend. At low MK to PC ratios the abundant supply of Ca²⁺ leads to formation of C₄AH₁₃ and C-S-H gel (see Wild et al. 1998) whereas at high MK to PC ratios the MK reaction products are C₂ASH₈ and C-S-H gel. The water demand of the former reaction (Wild et al. 1998) is higher than for the latter reaction, thus contributing to the water demand of the MK, particularly at low MK to PC ratios. Interestingly Wild et al. (1998) reported a minimum in chemical shrinkage for PC-MK pastes at 15% MK and attributed this minimum to reduced formation of C₄AH₁₃ and increased formation of C2ASH8. Also the reaction of MK with Ca^{2+} is limited by the supply of Ca^{2+} which is controlled by the relative amount of PC present and the rate of PC hydration. Clearly as the MK to PC ratio increases, although the w/b ratio is increased (to maintain standard consistency) the rate of formation of CH from the hydrating PC will be insufficient to sustain the MK-CH reaction delaying the formation of cementitious reaction products. It is likely that all these factors will have some bearing on setting times of the MK-PC pastes.

One possible explanation for the none systematic behaviour of the setting times of MK–PC pastes is that at low MK levels (and hence low w/b ratios) the MK–PC reaction (and hence the formation of cementitious products from the pozzolanic reaction) is limited by the supply of water, which is rapidly consumed by the hydrating PC. Thus (as with PFA–PC pastes) setting times are retarded. However as the proportion of MK is increased the w/b ratio is also increased and the proportion of PC is reduced. Hence the supply of water available for the pozzolanic reaction is greater and there is more rapid formation of cementitious reaction products between the hydrating cement particles leading to a reduction in setting time. However as the MK level is further increased and the relative proportion of PC becomes even lower, although the w/b ratio is further increased the supply of Ca^{2+} needed to sustain the MK pozzolanic reaction will become insufficient, thus reducing the rate of formation of cementitious products and again increasing the setting time. However to confirm this hypothesis further detailed work is required to determine the heat evolution rates of MK–PC and MK–PFA–PC pastes at standard consistency during the periods over which the pastes are setting.

5. Conclusions

The main conclusions that can be drawn from this experimental study may be summarised as follows:

The results clearly demonstrate that the two pozzolans MK and PFA have different effects on both standard consistence and setting times of binary pastes, and the latter indicates that they influence hydration in different ways:

(i) Partial replacement of PC by PFA has little influence on consistency. This suggests that the water adsorption / absorption properties of PFA are similar to PC. However setting times increase continuously with increase in PFA content up to 40% PFA. This is explained in terms of the fact that increasing amounts of PFA generate increasing separation distances between hydrating cement particles, hence increasing the time period at which an interlocking network of hydration products form. Over this period the PFA is considered to act as an essentially inert material.

(ii) To maintain standard consistency for MK–PC pastes increasing w/b ratios are required with increasing MK levels. This is attributed to the very high specific surface of the MK and the resulting high levels of water adsorption/absorption. Setting times of binary MK–PC pastes do not show consistent changes with increase in MK content. Small amounts of MK lead to setting time increases, followed by decreases in setting times as MK levels increase further, and then at even greater MK levels setting times of MK–PC pastes with change in paste composition is attributed to the very complex interdependent nature of the PC hydration and MK–CH–H hydration reactions, and the availability of both water and Ca²⁺ at the different compositions to sustain these reactions.

(iii) In general the effects of both PFA and MK on consistency and setting times in binary pastes are reflected in the behaviour of the ternary pastes although the two pozzolans do not behave completely independently of each other.

Acknowledgements

The authors wish to thank EPSRC for funding the project and the Faculty of Advanced Technology for providing infrastructure and facilities. The authors also wish to thank Ash Resources for supplying the PFA, Imerys for supplying the metakaolin and in particular Dr. J. Bai for his supervision of D. G. Snelson's PhD project.

References

- Bai, J.; Gailius, A. 2009. Consistency of fly ash and metakaolin concrete, *Journal of Civil Engineering and Management* 15(2): 131–135. doi:10.3846/1392-3730.2009.15.131-135
- *British Standards Institute.* 2000. Cement Part 1: Composition, Specification and Conforming Criteria for Common Cements. BS EN 197–1.
- *British Standards Institute*. 1995a. Methods of Testing Cement, Chemical analysis of cement. BS EN 196–2.
- *British Standards Institute*. 1995b. Methods of Testing Cement, Part 3. Determination of setting times and soundness. BS EN 196–3.
- Brooks, J. J.; Johari, M. A.; Mazloom, M. 2000. Effect of admixtures on the setting time of high-strength concrete, *Cement and Concrete Composites* 22(4): 293–301. doi:10.1016/S0958-9465(00)00025-1
- Carette, G. G.; Malhotra, V. M. 1984. Characterisation of Canadian fly ashes and their performance in concrete, in *CANMET Technical Report MRP/MSL 8U–137*, Ottawa.
- Chen, Y.; Odler, I. 1992. On the origin of Portland cement setting, *Cement and Concrete Research* 22(6): 1130– 1140. doi:10.1016/0008-8846(92)90042-T
- Clear, C. A.; Harrison, T. A. 1985. Concrete pressure on formwork, in CIRIA report R 108, London.
- Eren, O.; Brooks, J. J.; Celik, T. 1995. Setting times of fly ash and slag-cement concretes as affected by curing temperature, *Cement, Concrete and Aggregates* 17(1): 11–17. doi:10.1520/CCA10331J
- European Standard. 1995. *Fly Ash for Concrete Definitions*, Requirement and Quality Control, Brussels, BS EN 450.
- Kinuthia, J. M. 2000. *Building Materials Research Unit*. University of Glamorgan, Unpublished work.
- Lee, S. H.; Sakai, E.; Watanabe, K.; Yanagisawa, T.; Daimon, M. 1999. Properties of classified fly ashes by using an electrostatic precipitator and the modification of fly ashes by the removal of carbon, *Journal of the Society of Materials Science* 48(8): 837–842.
- Mailvaganam, N. P.; Bhagrath, R. S.; Shaw, K. L. 1983. Effects of admixture on Portland cement concretes incorporating blast furnace slag and fly ash, in *The 1st International Conference on the use of Fly Ash, Silica Fume, Slag, and other Mineral By-products in Concrete (CANMET/ACI):* Proceedings, vol. 1. July 31–August 5, 1983, Montebello, Quebec. Canada: American Concrete Institute, ACI SP79, 519–537.
- Naik, T. R.; Singh, S. S.; Ramme, B. W. 2001. Time of setting influenced by inclusion of fly ash and chemical admixtures, in *The 7th International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete* (CANMET/ACI): Proceedings, vol. 1. Ed. by V. M. Malhotra. July 22–27, 2001, Madras, India, 393–413.
- Neville, A. M. 1995. *Properties of Concrete*. Harlow Pearson Educational Limited. 655 p.
- Vu, D. D.; Stroeven, P.; Bui, V. B. 2001. Strength and durability of calcined kaolin-blended Portland cement mortar and concrete, *Cement and Concrete Composite* 23(6): 471– 478. doi:10.1016/S0958-9465(00)00091-3
- Wild, S.; Khatib, J. M.; Roose, L. J. 1998. Chemical shrinkage and autogenous shrinkage of Portland cement-metakaolin pastes, *Advances in Cement Research* 10(3): 109–119.

PORTLANDCEMENČIO, METAKAOLINO IR LAKIŲJŲ PELENŲ MIŠINIŲ RIŠIMOSI TERMINAI

D. Snelson, S. Wild, M. O'Farrell

Santrauka

Šiame tyrime naudojamos dvi pucolaninės medžiagos – metakaolinas (MK) ir lakieji pelenai (PFA), kaip dviejų ir trijų komponentų dalinio pakeitimo rišikliai su portlandcemenčiu (PC), siekiant ištirti jų poveikį standartinėms konsistencijoms ir reguliuoti mišinio kietėjimo laiką. Siekiant išlaikyti standartinę MK–PC mišinio konsistenciją, didinant vandens ir rišamųjų medžiagų santykius, reikia didinti MK lygį, nes PFA turi mažai įtakos konsistencijai. Dviejų komponentų MK–PC mišiniams svarbu padidinti pradinius ir galutinius kietėjimo laikus 5 % MK, po sumažėjimo 10 ir 15 % MK, prieš tolesnį padidinimą 20 % MK. Dviejų komponentų PFA–PC mišinių kietėjimo laikui padidinti maždaug tokiomis pačiomis normomis iki 30 % PFA ir tuomet didinti atsargiau tarp 30 % PFA ir 40 % PFA. Apskritai PFA ir MK poveikis konsistencijai ir kietėjimo laikui abiejuose mišiniuose matomas iš trijų mišinio komponentų elgsenos, nors du pucolanai nėra visiškai nepriklausomi vienas nuo kito. Kiti būdai, kuriais du pucolanai daro įtaką kietėjimo laikui, yra pristatyti kalbant apie jų pucolaninės veiklos skirtumus ir jų elgseną, kurios metu jie daro įtaką vandens galimybei hidratuotis.

Reikšminiai žodžiai: cemento mišiniai, lakieji pelenai, metakaolinas, pucolanai, standartinė konsistencija, kietėjimo laikas.

David SNELSON. Doctor, Research Fellow, Materials Testing Officer in the Faculty of Advanced Technology at the University of Glamorgan. A member of the Chartered Institution of Wastes Management and a fellow of the Royal Society for Public Health. His areas of interest are in the fields of waste management, air quality and public health.

Stan WILD. Doctor, Emeritus Professor in the Faculty of Advanced Technology at the University of Glamorgan, and Honorary Fellow of the University of Glamorgan. He has published widely in the field of cementitious materials.

Martin O'FARRELL. Doctor, Principal Materials Consultant in the Building Pathology division at VINCI Construction (UK) Ltd Technology Centre. A Fellow of the Geological Society of London, his area of interest is the use of industrial by-products as cement replacement materials.