Absorption Characteristics of Cement Combination Concrete Containing Portland Cement, fly ash, and Metakaolin

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Abstract: The resistance to water penetration of cement combination concretes containing Portland cement (PC), fly ash (FA), and metakaolin (MK) have been investigated at different water/cement (w/c) ratios, 28-day strengths, and depths of water penetration using their material costs and embodied carbon-dioxide (eCO₂) contents. Results revealed that, at equal w/c ratio, eCO₂ content reduced with increasing content of FA and MK. MK contributed to the 28day strengths more than FA. Compared with PC, FA reduced cost and increased the depth of water penetration, MK increased cost and reduced the depth of water penetration, and their ternary combinations become beneficial. At equal strengths and levels of resistance to water penetration, most of the cement combination concretes are more environmentally compatible and costlier than PC concrete. Only MK binary cement concretes with 10%MK content or more and ternary cement concretes at a total replacement level of 55% with 10%MK content or more have higher resistance to water penetration than PC concrete.

Keywords: Blended cement; fly ash; metakaolin; permeation resistance; waterabsorption.

Introduction

The use of blended cement or cement combination will improve the performance and environmental compatibility of concrete at reduced cost [1-4] and it is supported, among others, by cement and concrete standards like BS EN 197- 1 [5], BS EN 206- 1 [6], and BS 8500 [7,8]. Cement combinations, by virtue of their delayed strength development at early ages[1,3], would also be more suitable for mass concreting and concrete work in hot climate than Portland cement.

Fly ash, due to its availability, low cost, and quality control, constitutes the primary pozzolana for blended cements [9] and the use of gas-fired and cocombustion fly ash would ensure the availability of quality fly ash for future use in concrete [10]. Fly ash is characterised by low water demand and reduced water/cement ratio for equal consistence and improved workability [11,12]. This is due to the spherical shape [13,14] and electronic dispersion of its particles[15]. Fly ash concrete has relatively poor characteristics at early ages [16] but its pozzolanic reactivity would improve its resistance in aggressive media at later ages [17]. Metakaolin is a highly reactive non-crystalline fine pozzolana and its fineness would result in closer packing of materials, reduced bleeding and pore size [14], and more nucleation sites to accelerate hydration reactions [18], increase pore refinement [19,20], and enhance both early and later age performance of concrete [21]. However, its high specific surface and chemical reactivity would cause workability problems [22] or increase superplasticiser dosage in concrete [21]. Hence, it is used as replacements between 5-15% by mass to increase the strength and reduce the permeability of concrete [23].

Fly ash requires a higher alkalinity of pore water for its reactivity [24], but due to the higher fineness and pozzolanic reaction of metakaolin, its pozzolanic reactivity in the presence of metakaolin is reduced [25]. Hence, while fly ash is cheaper and would improve the workability of concrete than Portland cement and metakaolin, it would delay hydration reaction at early ages. Therefore, to complement the performance of the supplementary cements, ternary combinations of Portland cement, fly ash, and metakaolin are worthwhile. This is because, while metakaolin would support early age performance, fly ash would continue to refine the properties of the hardened concrete as it matures to produce better performance at later ages [26]. The use of ternary cement combinations will also reduce admixture dosage [27]. Also, since concrete is specified on the basis of strength in practice and the use of cement combinations could result in better performance at equal strength than at equal water/cement ratio [28,29], it becomes expedient to investigate the

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absorption characteristics of the concretes at equal strengths in order to provide more information on their durability and therefore suitability as alternatives to Portland cement concrete.

Permeation in concrete is related to its porosity [14,30] and while fly ash would increase the porosity of concrete due to delayed pozzolanic reactivity [31], metakaolin would reduce it due to its higher fineness and improved pozzolanic reaction [32]. Hence, in order to minimize permeation and reduce the ingress of chloride or sulphate into concrete [33,34], the use of ternary combination of Portland cement, fly ash, and metakaolin would be an advantage. But despite their beneficial effect over Portland cement concrete, cement combination concretes have been underutilized in construction. While BS EN 197-1 [5] permits the use of metakaolin of up to 15% and fly ash of up to 55% cement content by mass, data from the European Ready Mixed Concrete Organisation [35] show a total cement addition replacement level of less than 20% by mass in ready-mixed concrete.

Hence, this paper investigated the effect of cement combinations containing fly ash as a binary cement component (up to 55% cement content) and metakaolin as both binary and ternary cement components (up to 15% cement content) on the depth of water penetration of concrete at equal water/ cement ratios. Also, while concrete is specified in practice on the basis of strength, most researches in literature have been conducted at different water/ cement ratios. Hence, using the material costs and embodied carbon dioxide contents of the concretes, the cost implication and environmental compatibility of the cement combinations were also examined at equal strengths and equal levels of resistance to water penetration.

Experimental Materials and Method

The cements used were Portland cement (PC, 42.5 type), siliceous or Class F fly ash (FA), and metakaolin (MK). The properties of the cements are presented in Table 1. The aggregates consisted of

 Table 1. Properties of Cements

_	Cements					
Property	PC	FA	MK			
Blaine fineness, m ² /kg	395	388	2588			
Loss on ignition, % ^{a)}	1.9	6.1 ^{b)}	0.9			
Particle density, g/cm ³	3.17	2.26	2.51			
% retained by 45µm sieve ^{b)}	-	11.0	<u> </u>			
Particle size distribution, cumulative % passing b	oy mass ^{c)}					
$125\mu{ m m}$	100	100	100			
100 µm	98.2	99.2	100			
75 μm	93.2	96.5	99.8			
$45\mu{ m m}$	81.8	87.0	99.4			
$25\mu{ m m}$	57.1	66.2	96.0			
10 µm	30.1	40.6	76.2			
$5~\mu m$	13.5	24.1	50.7			
$2\mu{ m m}$	5.6	10.9	18.2			
1 μm	2.9	4.8	4.7			
0.7 μm	1.3	1.9	1.4			
0.5 μm	0.2	0.3	0.1			
Bulk oxide composition, % d)						
CaO	64.5	3.2	0.0			
${ m SiO}_2$	20.0	52.0	57.6			
Al_2O_3	4.6	26.0	38.9			
$\mathrm{Fe_2O_3}$	3.7	10.1	0.6			
MgO	2.5	1.5	0.3			
MnO	0.1	0.1	0.0			
${ m TiO_2}$	0.3	1.5	0.0			
K_2O	0.7	2.8	2.4			
Na ₂ O	0.3	1.2	0.1			
P_2O_5	0.1	0.5	0.1			
Cl	0.1	0.0	0.0			
SO_3	3.1	1.1	0.0			

a) In accordance with BS EN 196-2 [36]

b) In accordance with BS EN 450-1 [37]

c) Obtained with the Laser Particle Sizer

d) Obtained by x-ray fluorescence (XRF)

0/4mm fine aggregates and 4/10 mm and 10/20 mm coarse aggregates. The coarse aggregates were uncrushed and they come in varied shapes. The 4/10 mm aggregates have rough texture and the 10/20 mm aggregates were smooth. The properties of the aggregates are presented in Table 2. Potable water, conforming to BS EN 1008 [38], was used for mixing, curing, and testing the concrete specimens. In order to provide reasonably workable concretes and a uniform basis for comparing concrete performance at equal water content and water/cement ratio, a superplasticiser based on carboxylic ether polymer conforming to BS EN 934-2 [39] was applied during mixing to achieve a consistence level of S2 defined in BS EN 206-1 [6], by a nominal slump of 50-100mm. The concrete mix proportions were obtained using the BRE Design Guide [40] and a free water content of 165 kg/m³ to avoid an excessively sticky mix.

Concrete was prepared to BS EN 12390- 2 [41] and the specimens (72 cubes for compressive strength test and 216 cubes for water penetration test) were cast, cured under a layer of damp hessian covered with polythene for about 24 hours, demoulded, and cured in water tanks maintained at about 20°C until the tests' dates. Tests were carried out on hardened concrete specimens to determine their cube compressive strengths and the depths of water penetration at the water/cement ratios of 0.35, 0.50, and 0.65. The cube compressive strengths at 28 days of the concrete specimens were obtained in accordance with BS EN 12390- 3 [42] using 100 mm cubes.

Table 2: Properties of Fine and	d Coarse Aggregates
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	Fine	Coarse aggregates			
Property	aggregates 0/4 mm	4/10 mm	10/20 mm		
Shape, visual	-	Varied	Varied		
Surface texture, visual	-	Rough	Smooth		
Particle density *	2.6	2.6	2.6		
Water absorption, % *	1.0	1.7	1.2		
% passing 600 µm sieve	55.0	-	-		

* In accordance with BS EN 1097-6 [43]

The depth of water penetration was determined in accordance with BS EN 12390- 8 [44] using 150 mm cubes at the ages of 28, 90, and 180 days. Immediately after demoulding, the side surface to be exposed to water pressure was roughened with wire brush and the specimen was stored till the test age in a water curing tank. At the required test age, the roughened surface of the saturated specimen was exposed to a water pressure of 500 kN/m² for 72 ± 3 hours as shown in Figure 1. At the end of the exposure period, the specimen was uninstalled, wiped to remove excess water, and split in half (perpendicular to the face subjected to water pressure) and left with the test face down for about

1-2 minutes so that the water penetration front could be clearly seen. The maximum depth of water penetration was marked and recorded.

The material costs and the embodied carbon dioxide contents (a measure of carbon dioxide released into the atmosphere during manufacture) were used to respectively assess the economic and environmental implications of using the cement combinations in concrete. The costs and embodied carbon dioxide (eCO₂) contents were obtained, at the respective water/cement ratio, with the aid of the mix proportions as the summation of the costs and eCO₂ values (Table 3) over the constituent materials. Hence, where two concretes have the same strength or water absorption value, the one with lower cost or eCO₂ content would be preferred.



Figure 1. Wire-brushed Surface of 150 mm Cube is Subjected to a Water Pressure of 500 kN/m^2

Table 3.	Cost and eCO ₂	Content of	Concrete	Materials
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Concrete material	Cost and eCO ₂ content of materia					
	Cost ^{a)} ,	eCO_2				
	£/tonne	content ^{b)} ,kg/tonne				
Portland cement (PC)	60.00	930				
Fly ash (FA)	20.00	4				
Metakaolin (MK)	100.00	300				
Aggregates	10.00	4				
Water	10.00	0.3				
Superplasticiser	1300.00	0.72				

a) Supplier

b) Mineral Products Association (MPA) figures

Analysis and Discussion of Results

Effect of Cement Combination on the Depth of Water Penetration at Equal Water/Cement Ratio

Table 4 presents the 28-day cube compressive strengths, material costs, and embodied carbon

dioxide (eCO₂) contents of Portland cement and the cement combination concretes at the water/cement ratios of 0.35, 0.50, and 0.65. The Table shows that compressive strength reduced with increasing water/ cement ratio and increasing content of fly ash as a binary cement component. While the addition of metakaolin resulted in binary cement concretes with comparable strengths with Portland cement concrete, the addition of metakaolin as a ternary cement component resulted in concretes with higher strengths than the respective fly ash binary cement concretes. However, due to the strength reducing effect of fly ash at this age, the strengths of the ternary cement concretes were lower than that of the Portland cement concretes and they reduce with increasing content of fly ash.

The material cost of concrete decreased with increasing water/cement ratio (due to decreasing cement content) and increasing content of fly ash and increased with increasing content of metakaolin as a binary or ternary cement component. Also, due to the cost reducing effect of fly ash, the costs of the ternary cement concretes were lower than that of the Portland cement concretes and they reduce with increasing content of fly ash. The eCO_2 values of concretes decreased with increasing water/cement ratio (or decreasing cement content) and increasing content of the supplementary cements with fly ash contributing substantially to the reduction than metakaolin. Hence, the ternary cement concretes have higher eCO_2 values than the respective fly ash binary cement concretes.

Table 5 presents the depth of water penetration of the concretes at the water/cement ratios of 0.35, 0.50, and 0.65 at the curing ages of 28, 90, and 180 days. The Table shows that the depth of water penetration increased with increasing water/cement ratio and decreased with increasing curing age. At equal water/cement ratios and curing ages, the depths of water penetration of fly ash binary cement concretes were higher than that of Portland cement concrete and they increased with increasing content of fly ash. This is probably because fly ash would require a higher level of alkalinity which increased progressively with the release of $Ca(OH)_2$ by the hydration reaction of Portland cement to increase

 Table 4. Cube Compressive Strength at 28 days, Material Cost and Embodied Carbon Dioxide (eCO2) Content of Concrete at Different Water/Cement Ratios

	Compressive strength at 28 days, cost and eCO ₂ content of concrete									
Mix combination	Strei	ngth, N/m	m^2		Cost, £/n	1 ³	e	eCO ₂ , kg/1	n^3	
	0.35	0.50	0.65	0.35	0.50	0.65	0.35	0.50	0.65	
100PC	80.0	54.0	38.5	50.48	41.82	37.43	449	315	245	
80PC+20FA	72.0	46.5	30.0	45.86	38.67	34.90	356	250	194	
80PC+15FA+5MK	82.0	53.0	33.0	48.23	40.40	36.36	364	259	199	
65PC+35FA	60.0	35.0	20.0	42.67	36.39	33.46	291	203	162	
65PC+30FA+5MK	64.0	42.0	24.0	45.09	37.93	34.90	299	208	166	
65PC+25FA+10MK	68.0	43.0	25.0	46.87	39.70	35.83	305	214	169	
45PC+55FA	42.0	24.0	12.0	38.10	33.55	30.81	199	143	111	
45PC+45FA+10MK	47.0	32.5	18.5	42.45	36.21	33.55	217	152	123	
45PC+40FA+15MK	50.0	33.0	20.0	44.63	38.06	34.78	224	158	127	
95PC+5MK	80.0	56.0	38.5	51.51	42.50	38.01	433	305	236	
80PC+10MK	78.0	54.5	38.0	52.52	43.47	38.51	416	292	229	
85PC+15MK	76.0	54.0	38.0	53.42	44.25	39.24	400	283	220	

Table 5. Depth of Water Penetration of Concrete at Different Water/Cement Ratios and Curing Ages

Mix combination	Depth of water penetration, mm									
		28 days			90 days			180 days		
	0.35	0.50	0.65	0.35	0.50	0.65	0.35	0.50	0.65	
100PC	13	22	30	9	17	26	6	13	19	
80PC+20FA	16	32	44	12	23	35	8	15	22	
80PC+15FA+5MK	15	27	35	10	21	27	7	12	19	
65PC+35FA	26	42	58	18	32	45	13	22	30	
65PC+30FA+5MK	24	34	42	17	25	30	12	18	23	
65PC+25FA+10MK	23	32	40	16	23	29	11	17	22	
45PC+55FA	30	45	65	24	34	48	15	25	36	
45PC+45FA+10MK	25	34	50	17	27	40	12	20	30	
45PC+40FA+15MK	18	28	40	14	20	28	11	15	21	
95PC+5MK	15	23	32	10	17	26	7	12	19	
80PC+10MK	14	21	29	10	16	25	7	11	18	
85PC+15MK	12	19	28	9	15	24	6	12	18	

Mix combination	Material cost, embodied CO2 content and depth of water penetration at equal strengths							
		35 N	l/mm ²					
	w/c	eCO ₂ , kg/m ³	Cost, \pounds/m^3	WP, mm	w/c	eCO ₂ , kg/m	³ Cost, £/m ³	WP, mm
100PC	0.71	236	36.02	33.0	0.63	251	37.77	29.0
80PC+20FA	0.59	211	36.00	40.0	0.55	226	37.04	37.0
80PC+15FA+5MK	0.63	204	36.68	34.5	0.59	218	37.52	32.5
65PC+35FA	0.50	204	36.39	42.0	0.46	223	37.74	38.0
65PC+30FA+5MK	0.55	189	36.46	36.5	0.51	204	37.60	34.5
65PC+25FA+10MK	0.56	191	37.76	35.5	0.52	205	38.99	33.5
45PC+55FA	0.40	178	36.38	34.5	0.36	195	37.74	31.0
45PC+45FA+10MK	0.47	162	37.17	32.0	0.41	187	39.53	28.0
45PC+40FA+15MK	0.48	165	38.75	26.5	0.43	185	40.72	23.0
95PC+5MK	0.69	227	37.58	35.0	0.63	242	38.35	31.0
80PC+10MK	0.69	223	37.88	31.5	0.62	238	39.17	27.5
85PC+15MK	0.69	213	38.61	31.0	0.62	229	39.91	26.5

Table 6. Material Cost, Embodied CO_2 Content and Depth of Water Penetration of Concrete at Equal Strengths of 35 and 40 N/mm^2

the resistance of its concretes to water penetration. Hence, the delay in having enough $Ca(OH)_2$ for the pozzolanic reaction of fly ash must have led to the increase in the depth of water penetration with increasing content of fly ash.

Table 5 also shows that while the addition of metakaolin at 5% content resulted in slightly higher depths of water penetration than Portland cement, the depth of water penetration reduced with increasing content such that at 10%MK content and above, the depths of water penetration were lower than that of Portland cement. The addition of metakaolin as ternary cement component also reduced the depth of water penetration with increasing content up to 15%. This must be due to the higher fineness of metakaolin (Table 2) resulting in better packing of the cements (within the paste matrixand at the interface zones between the cement paste and the aggregates)and more nucleation sites for Ca(OH)₂to improve the pozzolanic reactions of the supplementary cements. Despite the resistance of metakaolin as a ternary cement component, the depths of water penetration of the ternary cement concretes were still higher than that of the Portland cement concretes. However, the disparity in the depths of the ternary cement concretes, at the respective total replacement level, reduced with increasing content of metakaolin.

Effect of Cement Combination on the Depth of Water Penetration at Equal Strength

Since concrete is specified (in practice) on the basis of the 28-day strength, the depths of water penetration of the concretes at equal 28-day strength were determined and examined with the aid of the material costs and embodied CO_2 contents of the concretes. The 28-day cube compressive strengths, material costs, and embodied CO_2 contents of the concretes (Table 4) and the depths of water penetration of the concretes (Table 5) at the water/cement ratios of 0.35, 0.50, and 0.65 were interpolated to obtain the depths of water penetration, material costs, and embodied CO₂ contents of the concretes at the 28-day strengths of 35 and 40 N/mm²(Table 6). These strengths also satisfy the strength requirements in BS EN 206-1 [6] and BS 8500 [7,8].

Table 6 shows that the depth of water penetration reduced with increasing strength and that, at equal strength, all the cement combination concretes have lower embodied CO₂ contents and therefore would be more environmentally compatible than Portland cement concrete. Since higher material contents would be required, the cement combination concretes have higher costs than Portland cement concrete. Also, though at higher costs, some of the cement combination concretes are more resistant to water penetration than Portland cement concrete at equal strength and these are metakaolin binary cement concretes at 10% and 15% MK contents and metakaolin ternary cement concretes(at total replacement level of 55%) at 10% and 15% MK contents.

Table 6 also shows that the fly ash binary cement concretes have higher depths of water penetration (and higher costs) than Portland cement concrete and that the positive effect of fly ash would only be felt at a replacement level of 55% FA. The addition of metakaolin increased concrete resistance to water penetration with increasing content and cost. The metakaolin binary cement concretes (with the exception of the 5% MK binary cement concrete) have better resistance to water penetration, than Portland cement concrete, with increasing content up to 15% MK. Compared with the respective fly ash binary cement concretes, the addition of metakaolin as a ternary cement component also increased the resistance of concrete to water penetration with increasing content and cost. Also, the positive influence of metakaolin, as a ternary cement component, on the cost and resistance to water penetration of the cement combination concretes is highest at a total replacement level of 55%. Hence, a high content of the supplementary cements would be required to improve the resistance of cement combination concrete to water penetration and this might not be unconnected with the packing ability of the cements. That is, the fineness of metakaolin and spherical shape of fly ash.

Implication of Cement Combination at Equal Resistance to Water Penetration

Table 7 presents the material costs, embodiedCO₂ contents, 28-day strengths, and water/cement ratios of concretes at the depths of water penetration of 25 and 30 mm. The Table shows that equal resistance to water penetration would be achieved at different water/cement ratio and strength and therefore with different economic and environmental implications.

While more than half of the cement combination concretes have lower embodied CO₂ contents than Portland cement concrete, only one cement combination concrete at the total replacement level of 55% (45PC+40FA+15MK) is cheaper than Portland cement concrete at equal resistance to water penetration. The Table also shows that only a few of the cement combination concretes at not less than 10%MK binary content and ternary cement concretes at a total replacement level of not less than 55% (with not less than 10%MK) have equal resistance at lower strengths than Portland cement concrete. Hence, high volume of the supplementary cements (rather than high strength) would be needed, probably to ensure closer packing and denser microstructure, to resist water absorption.

Conclusion

This study has investigated the effect of fly ash and metakaolin on the permeation resistance of concrete at equal water/cement ratios, equal 28-day strengths, and equal levels of resistance to water penetration. The costs and embodied CO_2 contents of the concretes were also used to assess their economic implication and environment compatibility respectively. The following are the conclusions made from the study.

- 1. The eCO_2 content of concrete reduced with increasing water/cement ratio (due to decreasing content of cement), and increasing content of the supplementary cements with fly ash contributing more to the reduction than metakaolin.
- 2. While the compressive strength and material cost of concrete decreased with increasing water/ cement ratio and fly ash content, they increased with increasing content of metakaolin. Hence, due to the higher contents of fly ash than metakaolin, the ternary cement concretes have lower strengths and costs than Portland cement concrete at equal water/cement ratios.
- 3. The depth of water penetration of concrete increased with increasing water/cement ratio and decreased with increasing curing age up to 180 days. While fly ash increased the depth of water penetration with increasing content, metakaolin reduced it. Hence, compared with Portland cement concrete, the disparity in the depths of the ternary cement concretes, at the respective total replacement level, reduced with increasing content of metakaolin.
- 4. At equal strength, the cement combination concretes are more environmentally compatible than Portland cement concrete. However, cement combination concretes that are more resistant to water penetration than Portland cement were only obtained at not less than 10% content of

Table 7. Material Cost, Embodied CO2 Content and Strength at 28 days of Concrete at Equal Resistance to WaterPenetration

	Material	cost, embodied	l CO ₂ conte	ent and streng	th at 28	days (f _{28d}) of co	oncrete at e	qual depth of		
Min or ushin of in	water penetration									
Mix combination		25	mm			30	mm			
	w/c	eCO ₂ , kg/m ³	Cost, £/m ³	f_{28d} , N/mm ²	w/c	eCO ₂ , kg/m ³	Cost, \pounds/m^3	f_{28d} , N/mm ²		
100PC	0.55	285	40.35	47.5	0.65	246	37.21	38.5		
80PC+20FA	0.42	301	42.08	59.0	0.47	267	39.84	51.0		
80PC+15FA+5MK	0.47	277	41.66	58.0	0.54	239	38.95	47.0		
65PC+35FA	0.34	299	43.21	62.5	0.38	270	41.15	54.5		
65PC+30FA+5MK	0.36	292	44.49	62.5	0.44	239	40.30	50.5		
65PC+25FA+10MK	0.38	283	45.17	62.5	0.46	234	41.29	49.0		
45PC+55FA	0.28	233	40.85	52.5	0.35	199	38.10	42.0		
45PC+45FA+10MK	0.35	217	42.45	47.0	0.44	174	38.28	38.5		
45PC+40FA+15MK	0.46	172	39.49	37.5	0.53	149	37.14	30.5		
95PC+5MK	0.53	287	41.24	52.0	0.61	249	38.77	43.0		
80PC+10MK	0.57	256	40.65	46.0	0.66	228	38.33	37.5		
85PC+15MK	0.60	235	40.45	43.0	0.67	216	38.89	36.5		

metakaolin (as a binary cement component) and as ternary cement concretes at not less than 55% total content of the supplementary cements (with not less than 10% content of metakaolin as a ternary cement component).

5. Equal resistance to water penetration was achieved at different water/cement ratios, strengths, costs, and eCO_2 contents. While many of the cement combination concretes were more environmentally compatible than Portland cement concrete at equal resistance to water penetration, higher contents of the supplementary cements (at not less than 55% with not less than 10% content of metakaolin) would be needed to ensure equal resistance to water penetration of the cement combination concretes would depend on high volume content and the packing ability of the supplementary cements.

Hence, if appropriately selected, it is possible to have cement combination concretes with better resistance against water penetration at lower costs and embodied CO_2 contents than Portland cement concrete.

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