

## **Reactivity of cement combinations containing Portland cement, fly ash, silica fume and metakaolin**

**FOLAGBADE Samuel Olufemi**

Department of Building, Faculty of Environmental Design and Management, Obafemi Awolowo University, Ile-Ife, 0220005, Nigeria.

### **ABSTRACT**

To examine the reactivity of cement combination, this paper investigated the  $\text{Ca(OH)}_2$  consumption of cement combination pastes containing Portland cement, fly ash, silica fume and metakaolin. Pozzolanic reaction is slow and it would take a long time to complete. Due to the disparity in their fineness, silica fume is more reactive than metakaolin and metakaolin is more reactive than fly ash. The  $\text{Ca(OH)}_2$  consumption per unit percentage of the cement additions reduced with increasing content with silica fume consuming more than metakaolin and metakaolin consuming more than fly ash. The  $\text{Ca(OH)}_2$  consumption of the cement additions, increased with increasing age and increasing fly ash content up to 35%. Hence, for optimum performance, fly ash as a binary cement should be limited to 35% content. Where higher reactivity up to 28 days is required, silica fume or metakaolin as binary cement components would perform better at 5% content than at 10% content. However, beyond 28 days, either 5% or 10% content could be used as there was no difference in the quantity of  $\text{Ca(OH)}_2$  consumed at both levels. The  $\text{Ca(OH)}_2$  consumption and reactivity of the ternary cement pastes is higher than that of the binary cement pastes. Also, the quantity of  $\text{Ca(OH)}_2$  consumed per unit content of the ternary cements increased with increasing content up to 10%. 15% would be more than the optimum content of metakaolin as both binary or ternary cement component.

**Keywords:** Blended cement;  $\text{Ca(OH)}_2$  consumption; cement combination; degree of hydration; pozzolanic reactivity.

### **1. Introduction**

To reduce cost and make concrete more environmentally compatible, cement additions such as silica fume, metakaolin and fly ash are used in concrete. However, the pozzolanic reactivity of the cement additions is dependent on the alkalinity of pore water which is influenced by the quantity of  $\text{Ca(OH)}_2$  released by the hydration reaction of Portland cement.

Due to its availability, low cost and quality control, fly ash constitutes the primary pozzolana for majority of blended cements[1]. However, the pozzolanic reactivity of fly ash is delayed when the alkalinity of the pore water is low[2]. While this would result in poor performance at early ages[3, 4,], its improved pozzolanic reactivity with curing age would produce better performance at later ages[5]. Finer pozzolanic materials, like silica fume and metakaolin, would generate more nucleation sites to accelerate hydration reactions[6]. Hence, the addition of silica fume would lead to improved early age performance. The active silica content of silica fume would accelerate cement hydration[7] and compensate for the early strength loss and slow rates of reactions associated with fly ash[8]. Also, metakaolin would accelerate hydration reaction to enhance both early and later age strength and performance of concrete and mortar[9, 10, 11]. Hence, when combined, these cements would play complimentary roles in concrete performance.

The pozzolanic reactivity and therefore performance of cement combinations would depend on the  $\text{Ca(OH)}_2$  consumption of these cement additions. While literature permits the use of silica fume of up to 10%[12, 13], metakaolin of up to 15%[14] and fly ash of up to 55%[12], data from the European Ready Mixed Concrete Organisation[15] show that the cement addition (majorly GGBS and fly ash) content of the total cement consumption in ready-mixed concrete was less than 20%. Hence, in order to examine their reactivity, this paper investigated the  $\text{Ca(OH)}_2$  consumption of some binary and ternary cement combinations within these permitted limits.

### **2. Experimental materials and cement combinations**

The cements used were Portland cement (PC, 42.5 type) conforming to BS EN 197- 1, siliceous or Class F fly ash (FA) conforming to BS EN 450, silica fume (SF) in a slurry form (50:50 solid/water ratio by weight) conforming to BS EN 13263 and a calcined natural pozzolana (metakaolin, MK) conforming to BS EN 197- 1. The properties of the cements are presented in Table 1.

Table 1: Physical and chemical properties of cements

PROPERTY	CEMENTS			
	PC	FA	MK	SF
Blaine fineness, m <sup>2</sup> /kg	395	388	2588	*
Loss on ignition, % <sup>a)</sup>	1.9	6.1 <sup>b)</sup>	0.9	2.7
Particle density, g/cm <sup>3</sup>	3.17	2.26	2.51	2.17
% retained by 45µm sieve <sup>b)</sup>	-	11.0	-	-
Particle size distribution, cumulative % passing by mass <sup>c)</sup>				
125 µm	100	100	100	100
100 µm	98.2	99.2	100	100
75 µm	93.2	96.5	99.8	100
45 µm	81.8	87.0	99.4	100
25 µm	57.1	66.2	96.0	98.8
10 µm	30.1	40.6	76.2	93.8
5 µm	13.5	24.1	50.7	87.5
2 µm	5.6	10.9	18.2	85.5
1 µm	2.9	4.8	4.7	78.7
0.7 µm	1.3	1.9	1.4	50.7
0.5 µm	0.2	0.3	0.1	10.5
Bulk oxide composition, % <sup>d)</sup>				
CaO	64.5	3.2	0.0	0.4
SiO <sub>2</sub>	20.0	52.0	57.6	96.6
Al <sub>2</sub> O <sub>3</sub>	4.6	26.0	38.9	0.7
Fe <sub>2</sub> O <sub>3</sub>	3.7	10.1	0.6	0.2
MgO	2.5	1.5	0.3	0.6
MnO	0.1	0.1	0.0	0.0
TiO <sub>2</sub>	0.3	1.5	0.0	0.0
K <sub>2</sub> O	0.7	2.8	2.4	0.8
Na <sub>2</sub> O	0.3	1.2	0.1	0.3
P <sub>2</sub> O <sub>5</sub>	0.1	0.5	0.1	0.1
Cl	0.1	0.0	0.0	0.1
SO <sub>3</sub>	3.1	1.1	0.0	0.2

\* Fineness for SF = 15,000-30,000 m<sup>2</sup>/kg[16]

a) In accordance with BS EN 196-2 (except for FA)

b) In accordance with EN 450- 1

c) Obtained with the Laser Particle Sizer

d) Obtained by x-ray fluorescence (XRF)

Potable water, conforming to BS EN 1008, was used for mixing the paste samples and curing the paste specimens. The cement combinations (Table 2) were investigated at a free water content of 165 litre/m<sup>3</sup>.

### 3. Experimental method

Cement paste was prepared to BS 196- 3 using a small mixer bowl conforming to BS 196- 1. The materials were carefully added to water in the mixer bowl and mixed carefully to avoid the loss of the materials and ensure thorough mixing and

uniform consistency. Tests were carried out on hardened specimens of cement pastes at the water/cement ratios of 0.50 to investigate the reactivity of the cement combinations. The paste specimens 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.

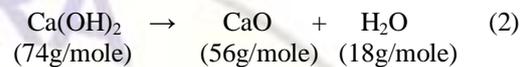
The quantity of Ca(OH)<sub>2</sub> consumed at a particular age was obtained as the difference between the quantity of Ca(OH)<sub>2</sub> present in the

Portland cement paste specimen and the quantity of  $\text{Ca(OH)}_2$  present in the other cement paste specimens at that age. The quantities of  $\text{Ca(OH)}_2$  present in the cement paste specimens were determined by thermogravimetric (TG) analysis which involves measuring the weight loss of a sample with respect to temperature change. From the plot of the sample weight against the temperature, physical and chemical changes that involve thermal decomposition (or weight loss) were identified and measured. To avoid weight gain which could result if the sample reacts with atmospheric gases, the experiment was conducted in an inert atmosphere using Nitrogen gas. The TG equipment also allows constant replacement of its internal atmosphere in order to flush out the gases evolved and prevent reactions between the volatilized substances in the material which could complicate the interpretation of the thermogravimetric plots. The TG equipment used is a STA- 1 installation unit fitted with a 1500°C capacity furnace connected to a computer which automatically log and analyse the data generated.

After crushing the 75mm hardened cement paste cube into pieces, fragments from its core were selected, quenched in acetone to stop the hydration process, oven-dried at 40°C to avoid carbonation, cooled to room temperature in a dessicator containing silica gel and ground into powder. A minimum powder sample of 10mg was placed in a platinum crucible, installed on the TG equipment and heated to a temperature of 1000°C

at a rate of 10°C/minute. The TG plot produced was used to determine the quantity of  $\text{Ca(OH)}_2$  left in the samples at the respective ages as stated below. The % water loss (wL) from the dehydroxylation region (defined by a temperature range of 400-500°C on the graph of the first derivative) was obtained and used in conjunction with equation 2 to determine the % $\text{Ca(OH)}_2$  content as stated in equation 1.

$$\% \text{Ca(OH)}_2 = \frac{wL}{18} \times 74 \quad (1)$$



#### 4 Analysis and discussion of results

The  $\text{Ca(OH)}_2$  contents and consumption of the cement pastes, at the curing ages of 28, 90 and 180 days and water/cement ratio of 0.50, are presented in Table 2. As expected, the quantity of  $\text{Ca(OH)}_2$  in the Portland cement paste increases with increasing curing age. On the other hand, due to the dilution effect (reduction due to Portland cement replacement) and the consumption of  $\text{Ca(OH)}_2$  by the pozzolanic reactions of the cement additions, the quantity of  $\text{Ca(OH)}_2$  in the binary and ternary cement pastes reduced with increasing curing age and increasing content of the cement additions.

Table 2: Hydration properties and  $\text{Ca(OH)}_2$  consumption of cement combination pastes

Ca(OH) <sub>2</sub> CONTENT AND CONSUMPTION OF CEMENT PASTE, % Cement Mass									
MIX COMBINATION	w/c = 0.50								
	28 DAYS			90 DAYS			180 DAYS		
	CH <sup>1</sup>	CH <sup>2</sup>	CH <sup>3</sup>	CH <sup>1</sup>	CH <sup>2</sup>	CH <sup>3</sup>	CH <sup>1</sup>	CH <sup>2</sup>	CH <sup>3</sup>
100% PC	22.4	-	-	23.3	-	-	23.7	-	-
80%PC+20%FA	18.2	0.0	0.00	17.2	1.4	0.07	16.5	2.5	0.13
80%PC+15%FA+5%MK	17.5	0.4	0.08	16.5	2.1	0.21	15.8	3.2	0.27
80%PC+15%FA+5%SF	16.7	1.2	0.24	15.8	2.8	0.35	15.2	3.8	0.39
65%PC+35%FA	14.5	0.0	0.00	13.2	1.9	0.05	12.1	3.3	0.09
65%PC+30%FA+5%MK	14.2	0.4	0.06	12.9	2.2	0.11	11.8	3.6	0.15
65%PC+25%FA+10%MK	13.5	1.1	0.10	12.2	2.9	0.15	11.0	4.4	0.20

65%PC+30%FA+5%SF	13.8	0.8	0.14	12.5	2.6	0.19	11.2	4.2	0.27
65%PC+25%FA+10%SF	12.8	1.8	0.17	11.5	3.1	0.22	10.4	5.0	0.26
45%PC+55%FA	10.1	0.0	0.00	9.3	1.2	0.02	8.7	2.0	0.04
45%PC+45%FA+10%MK	9.6	0.5	0.05	8.7	1.8	0.08	8.0	2.7	0.11
45%PC+40%FA+15%MK	9.4	0.7	0.05	8.4	2.1	0.08	7.6	3.1	0.11
45%PC+45%FA+10%SF	9.2	0.9	0.09	8.0	2.5	0.15	7.2	3.5	0.19
95%PC+5%MK	20.1	1.2	0.24	19.2	2.9	0.58	18.5	4.0	0.80
90%PC+10%MK	19.4	0.8	0.08	18.1	2.9	0.29	17.3	4.0	0.40
85%PC+15%MK	18.9	0.1	0.01	17.5	2.3	0.15	16.8	3.3	0.22
95%PC+5%SF	19.2	2.1	0.42	17.8	4.3	0.86	17.0	5.5	1.10
90%PC+10%SF	18.5	1.7	0.17	17.0	4.0	0.40	16.2	5.1	0.51

1)  $\text{Ca}(\text{OH})_2$  content measured

2) %  $\text{Ca}(\text{OH})_2$  consumed by additions = (Expected %  $\text{Ca}(\text{OH})_2$  released by PC minus %  $\text{Ca}(\text{OH})_2$  content measured). Expected %  $\text{Ca}(\text{OH})_2$  released by PC is assumed = 100%PC content x %PC content of mix. Hence for 80%PC+20%FA,

the expected %  $\text{Ca}(\text{OH})_2$  released by PC at 90 days would be  $23.3 \times 0.8 = 18.6$  and the %  $\text{Ca}(\text{OH})_2$  consumed by 80%PC+20%FA at 90 days would be  $18.6 - 17.2 = 1.4$  as shown on the Table.

3) % $\text{Ca}(\text{OH})_2$  consumed per unit percentage of the binary and ternary cement content.

Hence for 80%PC+20%FA at 90 days, % $\text{Ca}(\text{OH})_2$  consumed per unit binary cement =  $1.4/20 = 0.07$  as shown on the Table. And for 80%PC+15%FA+5%MK at 90 days, % $\text{Ca}(\text{OH})_2$  consumed per unit ternary cement =  $[2.1 - (15 / 20 \times 1.4)] / 5 = 0.21$ .

#### 4.1 $\text{Ca}(\text{OH})_2$ consumption of binary cements

Though the quantities of  $\text{Ca}(\text{OH})_2$  consumed by the binary cement pastes increased with increasing curing age due to pozzolanic reactivity but they were generally low at 28 days probably due to the delay in the commencement of the pozzolanic reaction of the cement additions. The addition of 20%, 35% and 55% fly ash shows no consumption of  $\text{Ca}(\text{OH})_2$  at 28 days. However, the  $\text{Ca}(\text{OH})_2$  consumption levels increased progressively with increasing curing age and were 2.5%, 3.3% and 2.0% respectively at 180 days. The  $\text{Ca}(\text{OH})_2$  consumption increased with increasing content of fly ash from 20-35% and reduced with increasing content of fly ash from 35-55%. The latter might be due to the reduced content of Portland cement (dilution effect), resulting in  $\text{Ca}(\text{OH})_2$  content lower than needed for pozzolanic reaction at that higher contents of fly ash. Hence, for better reactivity, fly ash content of a fly ash binary cement combination should not exceed 35%. Also, the quantity of  $\text{Ca}(\text{OH})_2$  consumed per unit percentage of fly ash beyond 28 days increased with curing age and decreased with increasing content of fly ash. This might be due to the reduction in the content of Portland cement (dilution effect) with increasing content of fly ash. Silica fume at equal age and replacement level consumed more  $\text{Ca}(\text{OH})_2$  than metakaolin. At 28 days, the quantities of  $\text{Ca}(\text{OH})_2$  consumed by silica

fume and metakaolin, as binary cement components, increased with increasing curing age and decreased with increasing content of the cement additions. Since silica fume binary cement combinations consumed higher quantities of  $\text{Ca}(\text{OH})_2$  than metakaolin binary combinations at equal replacement level, hence where higher reactivity for early age performance up to 28 days is required silica fume would be preferred to metakaolin and lower content of silica fume or metakaolin (5% SF or MK) would be preferred to 10% content of silica fume or metakaolin.

Beyond 28 days, while there is little or no difference in the quantity of  $\text{Ca}(\text{OH})_2$  consumed at 5% and 10% silica fume content or at 5% and 10% metakaolin content, the quantities of  $\text{Ca}(\text{OH})_2$  consumed at 15%MK content were lower than at 10%MK content. While silica fume would consume more  $\text{Ca}(\text{OH})_2$  than metakaolin at equal replacement level, there is no difference between their performances at 5% or 10% contents. Hence, the choice of content between 5% and 10% would depend on other factors like cost and environmental compatibility. Since the quantities of  $\text{Ca}(\text{OH})_2$  consumed at 15%MK content were lower than at 10%MK, it shows that 15%MK content might be more than the optimum content of metakaolin as a binary cement component.

The quantity of  $\text{Ca(OH)}_2$  consumed per unit percentage of silica fume and metakaolin increased with increasing curing age and reduced with increasing content of silica fume and metakaolin. The quantity of  $\text{Ca(OH)}_2$  consumed per unit percentage of silica fume and metakaolin were higher than that of fly ash. This is probably due to the higher fineness of silica fume and metakaolin, compared with fly ash, resulting in more nucleation sites for the pozzolanic reaction with  $\text{Ca(OH)}_2$ . In the same token, the quantity of  $\text{Ca(OH)}_2$  consumed per unit percentage of silica fume is higher than that of metakaolin at equal replacement level.

The comparison, at 180 days, of the  $\text{Ca(OH)}_2$  content of Portland cement and the  $\text{Ca(OH)}_2$  consumed by the binary cement pastes shows that the quantities of  $\text{Ca(OH)}_2$  consumed by the binary cement pastes were much lower than the quantity of  $\text{Ca(OH)}_2$  released by the hydration reaction of Portland cement. It could therefore be inferred that the pozzolanic reaction would be somehow slow and would take a long time to complete.

#### **4.2 $\text{Ca(OH)}_2$ consumption of ternary cements**

Compared with the fly ash binary cement pastes, the addition of silica fume and metakaolin reduced the  $\text{Ca(OH)}_2$  contents of the pastes with increasing curing age and increasing content of the ternary cement. Hence, the addition of silica fume and metakaolin as ternary cement components would result in increased consumption of  $\text{Ca(OH)}_2$  and therefore increased pozzolanic reactivity of the ternary cement pastes. Also, the quantity of  $\text{Ca(OH)}_2$  consumed per unit content of the ternary cements increased with increasing curing age and increasing content of the ternary cement component up to 10%. At the total replacement level of 55%, the quantity of  $\text{Ca(OH)}_2$  consumed per unit content at 10% and 15% MK content were the same at all the ages. This is probably because the optimum level of MK at 15% MK must have been exceeded. Also, the  $\text{Ca(OH)}_2$  consumed per unit content of the ternary cement components reduced with increasing total replacement level of the cement additions and this would be due to the reduction in the content of Portland cement with increasing content of fly ash (dilution effect). Also, silica fume ternary cement pastes at equal replacement levels, consumed more  $\text{Ca(OH)}_2$  than metakaolin ternary cement pastes. Hence higher pozzolanic reactivity would be expected in silica fume pastes than in metakaolin pastes and therefore concretes. As observed earlier at 180 days, the quantities of  $\text{Ca(OH)}_2$  consumed by the ternary cement pastes were much lower than the quantity of  $\text{Ca(OH)}_2$  released by the hydration reaction of Portland cement. This also shows that the pozzolanic

reaction is somehow slow and would take a long time to complete.

#### **5. Conclusion**

As opposed to Portland cement whose  $\text{Ca(OH)}_2$  content increased with increasing age, the  $\text{Ca(OH)}_2$  contents of the binary and ternary pastes reduced with increasing curing age and increasing content of the cement additions due to pozzolanic reactivity and/or dilution effect due to reduction of Portland cement by the cement additions. The  $\text{Ca(OH)}_2$  consumption and the quantity of  $\text{Ca(OH)}_2$  consumed per unit percentage of the cement additions, as binary and ternary cement component, also increased with increasing age.

The  $\text{Ca(OH)}_2$  consumption of the cement additions, as a binary cement component, increased with increasing fly ash content up to 35%. Hence, for optimum performance, fly ash as a binary cement should be limited to 35% content. As binary cement component, silica fume consumed more  $\text{Ca(OH)}_2$  than metakaolin at equal age and replacement level. Hence, silica fume is more reactive than metakaolin. Where higher reactivity up to 28 days is required, silica fume would perform better than metakaolin. Also silica fume or metakaolin would perform better at 5% content than at 10% content. Beyond 28 days, there was no difference in the quantity of  $\text{Ca(OH)}_2$  consumed at 5% and 10% contents of silica fume or metakaolin. Hence, the choice between 5% and 10% content for silica fume or metakaolin beyond 28 days would depend on other factors like cost and environmental compatibility. The quantity of  $\text{Ca(OH)}_2$  consumed per unit percentage of the cement additions reduced with increasing content of the additions with silica fume consuming more than metakaolin and metakaolin consuming more than fly ash. As higher fineness would result in more nucleation sites for the pozzolanic reaction with  $\text{Ca(OH)}_2$ , this disparity would be due to the relative difference in their fineness.

Due to the higher fineness of silica fume and metakaolin than fly ash, the  $\text{Ca(OH)}_2$  consumption and reactivity of the ternary cement pastes is higher than that of the binary cement pastes. Also, the quantity of  $\text{Ca(OH)}_2$  consumed per unit content of the ternary cements increased with increasing content of the ternary cement component up to 10%. 15% content of metakaolin would be more than the optimum content of metakaolin as a binary or ternary cement component. Also, the pozzolanic reaction is somehow slow and would take a long time to complete.

**References**

- [1] Antiohos S. K., Papadakis V. G., Chaniotakis E., Tsimas S., Improving the performance of ternary blended cements by mixing different types of fly ashes, *Cement and Concrete Research*, 37 (6), 2007, 877-885.
- [2] Fraay A. L. A., Bijen J. M. and De Haan Y. M., The reaction of fly ash in concrete: a critical examination, *Cement and Concrete Research*, 19 (2), 1989, 235-246.
- [3] Hassan, K. E., Cabrera, J. G., Maliehe, R. S., The effect of mineral admixtures on the properties of high-performance concrete, *Cement and Concrete Composites*, 22 (4), 2000, 267-271.
- [4] McCarthy M. J. and Dhir R. K., Development of high volume fly ash cements for use in concrete construction. *Fuel*, 84, 2005, 1423-1432.
- [5] Lam L., Wong Y. L., Poon C. S., Effect of fly ash and silica fume on compressive and fracture behaviours of concrete, *Cement and Concrete Research*, 28 (2), 1998, 271-283.
- [6] Mehta, P. K. and Aitcin P. C., Principles underlying production of high-performance concrete, *Cement, Concrete and Aggregates*, 12, 1990, 70-78.
- [7] Langan B. W., Weng K. and Ward M. A., Effect of silica fume and fly ash on heat of hydration of Portland cement, *Cement and Concrete Research*, 32 (7), 2002, 1045-1051.
- [8] Lynsdale C. J. and Khan M. I., Chloride and oxygen permeability of concrete incorporating fly ash and silica fume in ternary systems, in: V.M. Malhotra (Ed.), *Proceedings of the 5<sup>th</sup> CANMET/ACI International Conference on Durability of Concrete*, Barcelona, Spain, 2000, 739-753.
- [9] Wild S., Khatib J. M., Jones A., Relative strength pozzolanic activity and cement hydration in superplasticised metakaolin concrete, *Cement and Concrete Research*, 26 (10), 1996, 1537-1544.
- [10] Bai J., Sabir B. B., Wild S. and Kinuthia J. M., Strength development in concrete incorporating PFA and metakaolin, *Magazine of Concrete Research*, 52 (3), 2000, 153-162.
- [11] Bai J. and Wild S., Investigation of the temperature change and heat evolution of mortar incorporating PFA and metakaolin, *Cement and Concrete Composite*, 24 (2), 2002, 201-209.
- [12] BS EN 197- 1: 2000, Cement- Part 1: Composition, specifications and conformity criteria for common cements (British Standards Institution, London, 2000).
- [13] Dunster A., Silica fume in concrete: Technical Information Paper 5/09 (BRE, 2009).
- [14] Advanced Cement Technologies available at <http://www.advancedcementtechnologies.com> (accessed 31 January 2013).
- [15] European Ready Mixed Concrete Organisation available at <http://www.ermco.eu/documents> (accessed 31 January 2013).
- [16] Holland, T. C., Silica Fume User's Manual: Technical report (Silica Fume Association, Lovettsville, VA 22180, USA, 2005).