Hydration kinetics, pore characteristics and chloride ion diffusivity of blended cements

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Abstract

This study assesses the kinetics of hydration of Pulverised Fuel Ash and Metakaolin cement pastes and compares how the rate of reaction affects the pore-characteristics and resistance to ionic ingress. The degrees of hydration for the different mixtures were evaluated, both as a function of the calcium hydroxide and the chemically combined water contents. The reaction rates have been evaluated using the Jander mathematical model, which describes the hydration kinetics of the two materials. The results show that the reaction rate for specimens incorporating Metakaolin is several folds higher than those incorporating Pulverised fuel ash. The faster rate of reaction of the pozzolanic blends results in a faster rate of filling the pore spaces with hydration products, smaller pore volumes and reduced chloride ion diffusivity. The results from this investigation will provide engineers with a much needed understanding of the kinetics of hydration and setting characteristics of these types of cement systems and help in gaining an appreciation of the early structural development, how this affects the ease of placement, and subsequent evolution of properties.

Keywords: Blended cements, Chloride ion diffusion, Evaporable water, Hydration kinetics, MTK, PFA, Porosity.

1. Introduction

Pore structure is perhaps the most important characteristic of a cement system, which affects its strength, permeability and long-term durability. Knowledge of pore structure development is crucially important for the present day design Engineer who has to make a choice between the ever increasing number of commercially available cement types. Hydration rate is the key to pore-structure development. Some cement systems may experience a delay in their rate of hydration whereas others may experience greatly enhanced rate of reaction. Therefore a wrong choice of the material, or curing regime required to achieve the desired property may have grave constructional and economic consequence [1, 2].

For cement-pozzolan systems, the hydration mechanism is known to involve both a dissolution and diffusion process [3], the former being the dominant process [4, 5, 6]. During hydration, the reactive ions dissolve, forming hydrates which quickly constitute a barrier against the reactants such that further reaction proceed mostly by diffusion of ions through the already formed hydrates.

It is well known that the products of reaction of blended cement mixtures are very similar to those observed during the hydration of a pure Portland cement system. Differences exist mainly in the hydration rates and ratios of the hydrated species formed, such as: Calcium Silicate Hydrates(C-S-H); ettringite; tetra-calcium aluminate hydrate; monosulphoalluminate and calcium hydroxide [$Ca(OH)_2$], as well as the morphologies of these hydrates. The presence or absence of these compounds has been found to depend on the available C_3A and SO_3 as well as on the period of curing. Massazza [7], investigated the difference in composition of the hydrates by comparing the polysilicate/lime ratios obtained from hydrated paste specimens. He found a higher ratio in the blended cement pastes than for Portland pastes.

The various methods employed in evaluating pozzolanic reactivity has been reviewed by Massazza [7], Kotuku [8], and Taylor [9]. Broadly speaking, these may be categorised as indirect or direct methods. Greenberg [10] has described the utilisation of a conductivity technique proposed by Lea [11], to monitor indirectly, the depletion of calcium hydroxide by measuring the electrical conductivity of the test solution as reaction proceeds. This method assumes that electrical conductivity is proportional to the concentration of $Ca(OH)_2$ and that the silica and alumina hydrates formed possess negligible conductance. Many researchers have also used strength development as an indirect index of pozzolanic activity.

Direct methods usually employ a wet chemical or instrumental technique or combination of both, in measuring the actual amount of reacted $Ca(OH)_2$. Classical

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chemical methods make use of suitable solvents (e.g, HCL, NaOH or Aceto-acetic ester-isobutanol, etc), to extract and measure the unreacted $Ca(OH)_2$ before estimating the reacted fractions by difference [12]. The popular instrumental techniques include; quantitative TGA, DTA, XRD and calorimetric analysis. Previous work carried out on pozzolanic-lime mixes by Cabrera and Eddleston [13] and by Powers [14] for determining the non-evaporable water content of hardened Portland cement pastes, have shown that the kinetic parameters associated with reaction mechanism may be determined accurately by comparing the data obtained from isothermal thermogravimetry analysis (TGA) with data obtained from theoretical solid-state chemistry or by instrumental methods. The results obtained from any of the above techniques provide valuable information regarding the reactive potential of the material even though the absolute values obtainable may vary depending on the method used.

This study evaluates the degree of hydration of two different pozzolanic cement mixtures using TGA technique. Jander equation [15] was then used to determine the reaction rate constant of the mixtures whilst the total porosity and capillary pore-volume was determined using helium auto-pycnometry and mercury intrusion porosimetry.

2. Experimental

2.1. Materials used

The cement used was Portland cement [PC] supplied by Castle UK Ltd (current UK arm of Heidelberg.

The Pulverised Fuel Ash [PFA] used was supplied as an unclassified material produced from Drax Power Station in the North of England.

The Meta-kaolin used was obtained by thermal activation of natural clay of tropical origin in a furnace at 800oC for two hours. This temperature and residence time resulted in the collapse of the crystalline structure of the original ['raw'] clay mineral content, converting it to meta- kaolin. This final product is a semi-amorphous and highly reactive mixture of silica and alumina.

Table 1 and Fig. 1, show the main oxide composition and other physical and mineralogical properties of all the materials used.

2.2. Specimen preparation, curing and exposure conditions

Only paste specimens were used for all three types of tests carried out. The blended cement pastes contained 85% by weight of Portland cement mixed with 15% by weight of pozzolan. A water-cementitieous ratio of 0.4 was used in preparing all specimens. These were cast in 50mm diameter plastic cups, which were then placed on a vibrating table, to reduce air entrainment to a minimum. The specimens were covered with wet hessian in the laboratory for 24 hours before being demoulded. Curing was then continued in a fog room (constantly maintained at 20^oC and 99% relative humidity). At the end of the specified curing period of 1, 3, 7, 28, 90, 180, 365 and 730 days, specimens needed for TG Analysis, total porosity, helium Auto-pycnometry and mercury intrusion porosimetry (MIP) studies were removed from the curing room, dried in the oven for 24 hours at 110^oC.

For the chloride ion diffusion studies, similar specimens and curing regime as described Above were used. After curing for 60days in the fog room, four 3-4mm thick disks were cut from the interior part of each cylindrical specimen and were then polished to a smooth finish by means of emery paper before being set-up for the chloride diffusion experiment.

Table 1 Composition and characteristics of the cementitious materials used

| Chemical Oxide Composition [%]	PC	PFA	MTK1	MTK2
SiO_2	20.40	50.80	39.06	42.40
Al_2O_3	5.02	27.90	31.65	35.14
Fe_2O_3	2.92	11.70	12.89	3.61
MnO	0.06	-	0.07	0.02
TiO_2	0.21	1.00	0.83	1.67
CaO	64.25	1.20	0.09	0.11
MgO	2.83	1.50	0.52	0.41
Na_2O	0.39	0.80	0.27	0.17
K_2O	0.84	3.70	0.44	0.36
P_2O_5	0.08	-	0.18	0.09
SO_3	2.63	0.59	-	-
Loss on Ignition (LOI)	0.70	2.10	15.95	16.67
Other Properties				
Specific gravity (cc/g)	3.15	2.24	2.80	2.61
Specific surface m^2/g (BET)			44.30	37.80
Plasticity index			18.00	35.00
Amorphous Ferri-Alumino-Silicate (%)			12.38	9.04
Alkali soluble Silica + Alumina		36.17		
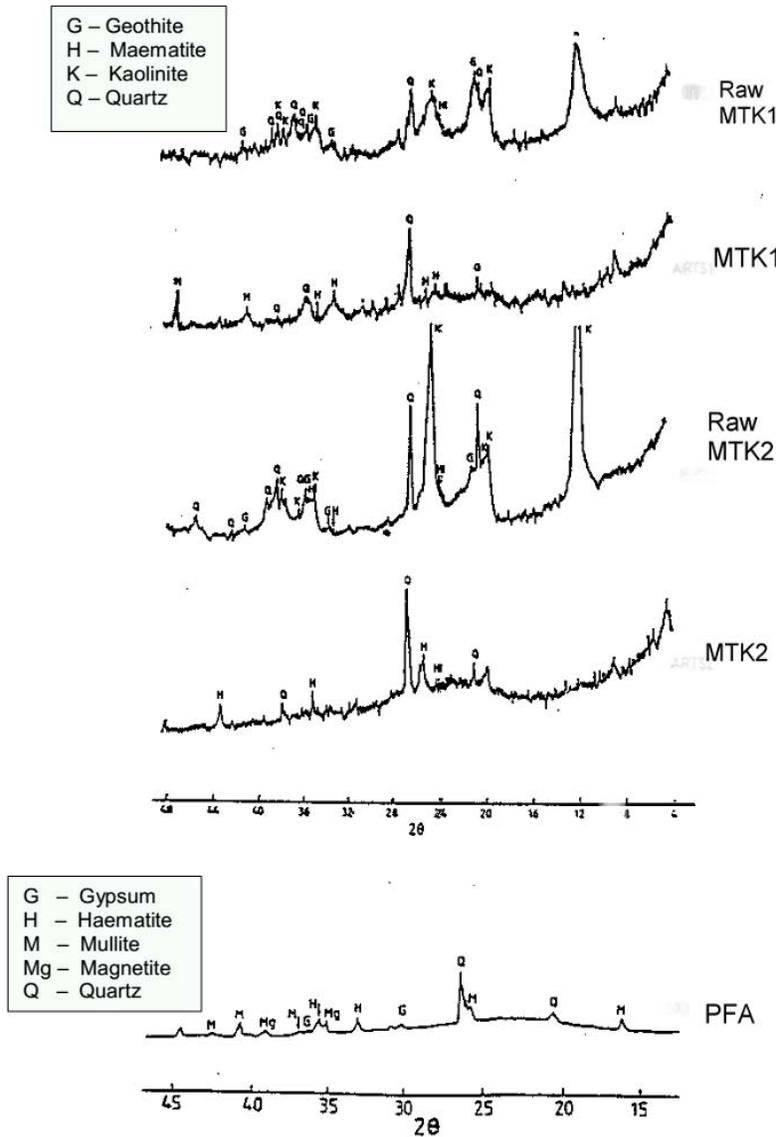
Fig. 1 XRD patterns showing the minerology of the pozzolanic materials used

3. Test Procedures

3.1. TG analysis

The apparatus used for the TG analysis was a stanton redcroft TG balance [model 750], equipped with a programmer unit and connected to a microcomputer and plotter. A representative samples was taken from each of the oven-dried specimens and the $Ca(OH)_2$ generated by the hydration of the Portland cement constituent of the mixture were determined using Standard TGA technique. It is worth noting that in studies of this kind, it is almost impossible to avoid carbonation of the hydrated paste, both during preparation of the samples and during the test. Carbonation of the sample would normally result in the formation of calcium carbonate (calcite) and consequent

reduction of the calcium hydroxide peak. Care was taken during preparation of the test samples to keep carbonation to a minimum by soaking the test sample in acetone and drying in a nitrogen environment.

3.2. Determination of the non-evaporable water

The amount of water left after drying a cement paste to constant weight at 110oC is defined as the non-evaporable water contents. It consists mainly of chemically bound water, which forms part of the hydration compounds and a small amount of physically adsorbed water, not actually held by chemical bonds. Depending on the curing regime and water-cementitious proportion used, the non-evaporable water may account for 15% to 25% of the weight of a mature Portland cement paste. Many reports exist in which this parameter has been used as an indicator of the degree of hydration [9, 14, 15]. For the purpose of

S.O. Nwaubani

this investigation, the evaporable water was removed by drying the samples to constant weight at

110°C thus enabling the non-evaporable part to be estimated from the differential weight loss

due to the hydrates between 110oC and about 450°C.

Account was taken of the fact that about 10% of this category of water is known to remain and is gradually lost at higher temperatures.

Thus, the non-evaporable (combined) water was estimated using the following

correction;

$$Wn = Mn + 0.1Mn \qquad (1)$$

where;

Wn = non-evaporable water content

Mn = total weight loss up to 450°C

Fig. (2), shows the non-evaporable water content [Wn] values expressed as a percentage of the ignited weight of the test sample (i.e, weight of test sample after heating to 1000 oC).

$$Wn = Ww/Ws \; x \; 100 \qquad (2)$$

Wn = non-evaporable water in the test sample (referenced to the ignited weight). Ww = weight loss up to 450°C (%).
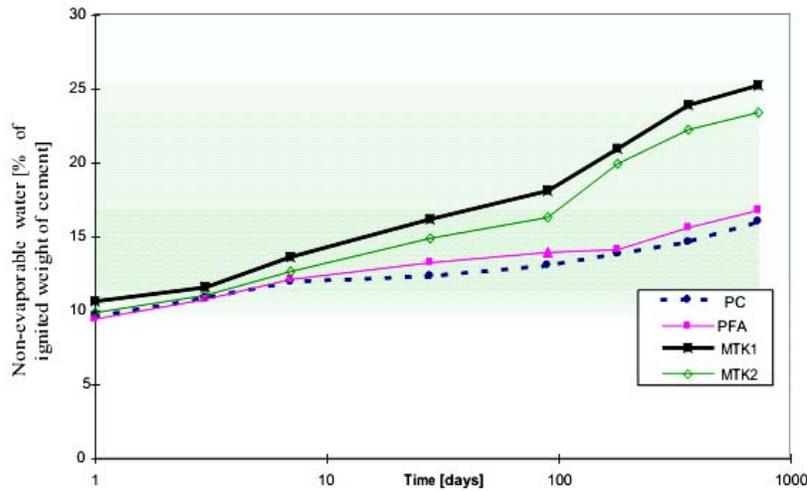
Ws = ignited weight of the sample (%).

Fig. 2 Chemically combined water content

3.3. Determination of the calcium hydroxide [Ca(OH)$_2$] content

The Portlandite [unreacted crystalline calcium hydroxide] present in the sample at each test age was determined by calculating the total weight loss between 450°C and 650°C. The values obtained were further corrected by adding the weight loss in the 650 to 700°C temperature range, known to be associated with the decomposition of calcium carbonate. Fig. (3) and Table (2a and 2b) show the amount of Ca(OH)$_2$ determined at different ages for the three mixtures investigated.
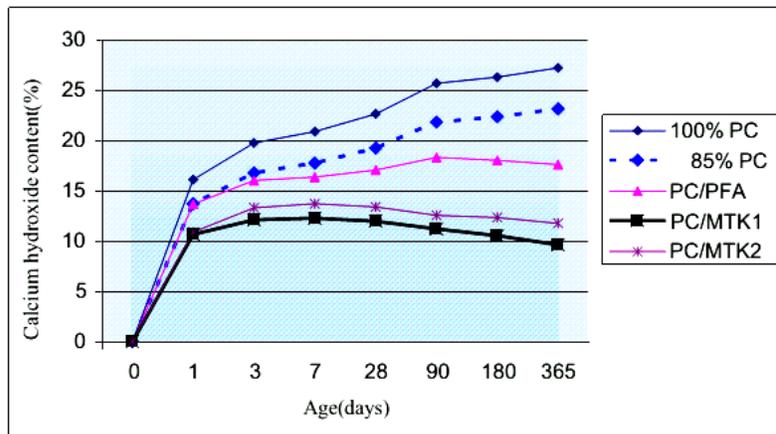

Fig. 3 Ca(OH)$_2$ content of the PC paste compared to those of the pozzolanic blends

Table 2a Ca(OH)$_2$ content and degree of hydration of PC paste at different ages

Age [days]	Ca(OH)$_2$ Content [% of ignited cement]		Degree of Hydration [%]
	100% PC	85% PC	
1	16.09	13.68	56.16
3	19.71	16.75	68.80
7	20.83	17.71	72.71
28	22.60	19.21	78.88
90	25.64	21.79	89.95
180	26.25	22.31	91.62
365	27.17	23.10	94.83
730	28.65	24.35	100.00

Table 2b Percentage of reacted and unreacted Ca(OH)$_2$ contents and the degree of hydration [reacted/unreacted lime] of the blended cement pastes

Age [days]	Ca(OH)$_2$ Content [% of ignited cement weight]								
	PC/PFA			PC/MTK1			PC/MTK2		
	Un Reacted	Reacted	Degree of hydration	Un reacted	Reacted	Degree of hydration	Un reacted	Reacted	Degree of hydration
1	13.65	0.03	0.41	10.63	3.05	28.69	10.87	2.81	25.85
3	16.00	0.75	4.69	12.08	4.67	38.66	13.29	3.46	26.03
7	16.34	1.37	8.38	12.24	5.47	44.69	13.69	4.02	29.37
28	17.02	2.19	12.87	11.96	7.25	60.62	13.38	5.83	43.59
90	18.29	3.50	19.14	11.18	10.61	94.90	12.54	9.25	73.76
189	17.99	4.32	24.01	10.51	11.80	112.27	12.33	9.88	80.13
365	17.56	5.54	31.55	9.60	13.50	140.63	11.74	11.36	96.76

3.4. Determination of the reaction rate constant

Having determined the quantity of Ca(OH)$_2$ which has reacted with age, the reaction rates for the mixtures were then estimated by applying the Jander equation [15,16]. The method is widely used in the study of hydration kinetics [17, 18, 19] and is based on Fick`s parabolic law of diffusion which assumes that if reaction interface is plane, the rate of chemical reaction would be inversely proportional to the thickness. It is essentially a linear equation having the following general form:

$$F(x) = Kt \tag{3}$$

where;
x = fraction of the particle which has reacted

K = reaction rate constant (slope of the line of best fit through the data points).
t = time of reaction

This being a linear equation ensures that a plot of F(x) against time would yield a straight line whose slope is equal to K (the reaction rate constant). Table (3a) shows the Jander F(x) values calculated from the results in Table 2b for the PFA and MTK pastes. Two distinct lines of best fit may be fitted through these points, at early and later ages as shown on Fig. (4). For each mix, the slopes of the fitted lines represent the reaction rate constants (K) at early (before 90 days) and at later ages. The equations of the linear regression lines relating the Jander Hydration Model with the reaction time (t) and the reaction rate constant are shown in Table (3b). All the Jander equations shown have a typical R2 value of between 0.98 and 0.99.

Table3a Jander F(x) values for the pozzolanic blends

Age (days)	F(x) value x 10^{-4}		
	PFA	MTK1	MTK2
1	0.001	1.055	0.089
3	0.063	2.501	1.362
7	0.215	2.992	1.845
28	0.548	6.134	3.930
90	1.394	13.625	10.135
180	2.135	16.802	11.861
365	4.181	23.933	16.893

Table 3b Jander F(x) equations which portrays the degree of hydration, as a function of time, for the various mixtures

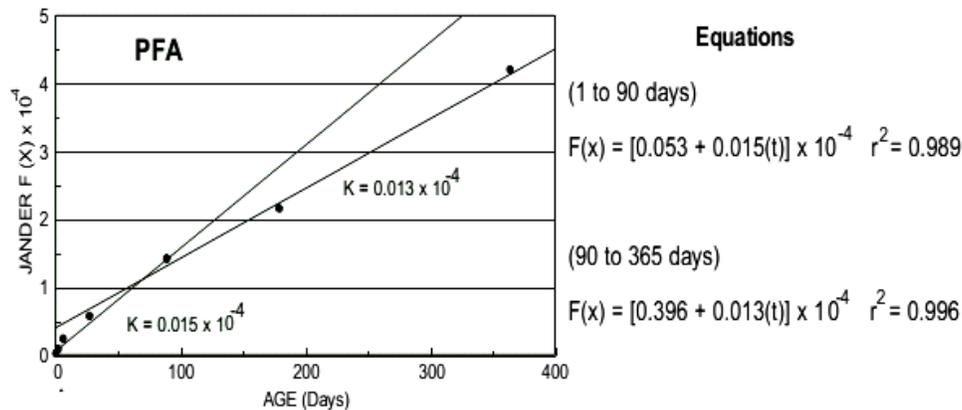| Mix	Period	Jander Equation
MTK1	1 to 28 days	$F(x) = [1.535 + 0.168(t)] \times 10^{-4}$
	1 to 90 days	$F(x) = [1.822 + 0.133(t)] \times 10^{-4}$
	90 to 365 days	$F(x) = [10.152 + 0.038(t)] \times 10^{-4}$
MTK2	1 to 90 days	$F(x) = [0.755 + 0.105(t)] \times 10^{-4}$
	90 to 365 days	$F(x) = [7.679 + 0.025(t)] \times 10^{-4}$
PFA	1 to 28 days	$F(x) = [0.017 + 0.019(t)] \times 10^{-4}$
	1 to 90 days	$F(x) = [0.053 + 0.015(t)] \times 10^{-4}$
	90 to 365 days	$F(x) = [0.396 + 0.013(t)] \times 10^{-4}$

Fig. 4 Typical plot of reaction rate versus time curve (for the PC/PFA mix)

3.5. Chloride diffusion test

The experimental procedure and technique used is similar to that previously used by Page et al [20] and descried in an earlier paper published by this author [21]. This essentially involves sandwiching the test specimen between two glass cells – one cell containing 1 mole of NaCl in saturated $Ca(OH)_2$ and the other containing saturated $Ca(OH)_2$. The diffusion cell is then placed in a bath maintained at a constant temperature of 30^oC throughout the period of the experiment. Due to the difference in ion concentration, chloride ions would move through the paste into the chloride-free compartment with time. The chloride concentration in the receiving compartment was determined from aliquots taken at intervals from this cell and analysed using a double-beam ultra-violet spectrometer and following standard spectrophotometric procedures. The Effective diffusion coefficient can then be obtained from the slope of the linear portion of the concentration/time curve according to Fick's' Law for quasi-steady state viz:

$$D = \frac{LV}{AC1} \; x \; \frac{dC2}{dt} \tag{4}$$

where:
D = Effective diffusion coefficient (cm^2/sec)
t = time (seconds)
L = specimen thickness (mm)
A = cross sectional area of specimen (cm^2)
V = volume of fluid in the receiving compartment (cm^3)
C1, C2 = concentrations of the chloride ions in the two compartments of the diffusion cell (mole/l).
dC2/dt = slope of the concentration versus time curve.

The Effective diffusion coefficients (average of 4 samples) obtained are shown on the first column of Table (4).

Table 4 The diffusion coefficients compared to the total porosity and capillary pore volumes of the specimens after 60 days curing at 20^oC

Mix	Diffusion Coefficients x 10^{-9} (cm^2/s)	Total Porosity (%)	Mercury Intrusion Volume (cc/g)	Capillary Pore Volume (%)
PC	44.16	26.07	0.1623	89.34
PFA	25.72	27.06	0.1812	82.30
MTK1	8.24	23.42	0.1427	70.01
MTK2	12.03	27.08	0.1798	71.86

3.6. Porosity and pore-size distribution

The total porosity and the pore-size distribution of the paste specimens were determined using the mercury intrusion technique. The apparatus used was a Micromeritics Model 9200 mercury intrusion porosimeter capable of generating mercury intrusion pressures of up to 414 MPa. The well-known technique is based on the relationship, which exists between pressure and intrusion pore diameter, obtained when the mercury-cement contact angle and the surface tension of mercury are known. For the test carried out in this study the contact angle was 1300 and the mercury surface tension was 484 dynes/cm. Helium Autopycnometry technique was used in determining the total porosity of the specimens.

The second column on Table (4) shows the results of the total porosities determined by both methods and the volume of capillary pores present in the paste specimens.

4. Results and Discussion

Clearly, the porosity and the chloride ionic diffusivity of the specimens studied were influenced by the kinetics of reaction, which was manifested by the calcium hydroxide or evaporable water content. Thus the results are discussed under these headings.

a) Calcium Hydroxide Content

Unlike the pozzolanic blends, the $Ca(OH)_2$ peak in the Portland cement pastes grew with age as the cement hydrates. It generated 16.09% of its own weight of $Ca(OH)_2$ after 1 day and 27.17% after 1 year curing.

In interpreting the results on the $Ca(OH)_2$ content, it should be noted that the pozzolanic blends contains only 85% percent of the weight of pure PC. If it is assumed that the pozzolanic content does not significantly modify the rate of reaction, then the quantity of $Ca(OH)_2$ generated by the PC/pozzolan mixtures will be:

$$Ca(OH)_2 \text{ generated} = Ca(OH)_2 \text{ generated by pure PC} \times 0.85 \tag{5}$$

This means that about 13.68% of $Ca(OH)_2$ may be expected to be generated in 1 day or about 23.10% after 1 year [Table (2a)].

Table (2b) shows that lower quantities of lime were detected at each age in the mixtures containing the pozzolans. The difference between the quantity of lime detected in the pure PC mix and those of the pozzolanic blends represent the amount consumed during the pozzolanic reaction process. The Metakaolin paste showed higher $Ca(OH)_2$ consumption than the fly ash paste implying a greater hydration rate.

b) Non-Evaporable Water Content

The results obtained for the non-evaporable water contents are shown in Fig.(3). and in table 5. The results show;

i) A steady increase in the amount of non-evaporable water, which is due to the formation of more hydration products with age;

ii) The PC/MTK mixtures contained much higher amounts of the chemically combined water than the PC and PC/PFA mix;

iii) The Wn values for the pure PC pastes at very early ages (i.e., before 3 days), are higher than those of the pozzolanic blends. However, as pozzolanic reaction proceeds, their values gradually superseded that of the PC such that at 2 years, the trend as seen on Table (5) becomes:

$$MTK1 > MTK2 > PFA > PC \tag{6}$$

Table 5 Chemically combined water in PC pastes compared with those of PC/PFA and PC/MTK mixes.

Age [days]	Non-evaporable water [% of the ignited weight of cement]			
	PC	PFA	MTK1	MTK2
1	9.56	9.40	10.60	9.83
3	10.80	10.70	11.53	11.00
7	11.91	12.08	13.58	12.60
28	12.28	13.20	16.13	14.85
90	13.00	13.89	18.05	16.25
180	13.81	14.09	20.90	19.90
365	14.58	15.57	23.87	22.18
730	15,98	16.38	25.19	23.34

with Wn values of 25.19, 23.34, 16.72, and 15.98 respectively.

The non-evaporable (chemically combined) water content determined for each mix obviously serves as a good indicator of the extent of hydration. It can therefore be expected that the higher the Wn value, the larger the volume of hydration products, which will be available to fill the pores, creating a finer and denser microstructure. In a different study published elsewhere by the Author (21) it was observed that this finer pore structure possessed by the

MTK blends resulted in a corresponding increase in ultimate strength, better resistance to the permeability and/or diffusivity of ions and therefore to improvement in durability performance of concrete.

c) Reaction Rate

Similarly, the K values shown on Fig. (4) indicate that the PC/MTK blends have much higher speeds of hydration. The K values were higher at early ages. The K values of the PC/MTK blends were several folds (about 7-9 times) higher than that of the PFA mix at early ages and

2 - 4 times higher at later ages (see table 3a).

This may be attributed to their higher amorphous content as well as the possession of a higher specific surface area (see table 1).

The slow rate of reaction in PFA/PC blends is a well-known characteristic and has been reported by many previous investigators (21, 22). Hydration in such systems is first retarded (for the first 24 hours) and later accelerated (10, 22, 23). Cabrera and Plowman (24) attributed the retardation to the dilution of the concentration of Calcium (Ca) in solution as well as the preferential formation of hexagonal hydrates, C4AHx, which forms an impervious layer over the Calcium Aluminate, C3A, particles in cement, thus retarding early hydration. They also hypothesized that the hydration of PFA becomes accelerated mostly by amorphous particles acting as nucleation centers for the formation of hydrates[24, 25].

Probably, the fast rate of reaction shown by MTK particles can be partially explained by this hypothesis since they contain even more amorphous silica and alumina as well as finer particles than the PFA.

d) Effect on Porosity and Chloride ion Diffusion

Table 4 shows a perfect correspondence between the hydration rate and the total porosity, chloride ion diffusivity and pore characteristics. The trend observed for total porosity. Capillary pore volume and chloride ion diffusion is as follows:

$$PC > PC/PFA > PC/MTK2 > PC/MTK1 \qquad (7)$$

Considering the degree of hydration and reaction rates, the trend becomes reversed:

$$PC/MTK1 > PC/MTK2 > PC/PFA > PC \qquad (8)$$

In other words, the faster rate of reaction of the pozzolanic blends results in a faster rate of filling of the pore spaces with hydration products, smaller/finer pore volumes and reduced chloride ion diffusivity or permeability[26]. The result from this study is very similar to the result from other works by Khatib and Clay [27]; which showed that there was a systematic reduction in absorption by capillary action with increase in MTK content and by Bai et al [28];

which indicated that the replacement by ultra-fine pozzolans such as MTK and silica fume is much more effective than replacement by PFA, particularly in the early stages of curing.

Here, it is pertinent to note that the results obtained for MTK1 and MTK2 consistently shows a better performance of the former in all respects. The properties of these two materials shown in Table1, does suggest that it is probably the difference in the specific surface characteristics and the amorphous ferri-alumino-silicate content that is responsible for better reactivity of MTK1.

5. Conclusions

Within the limitations of the experimental techniques and methods used, the following main conclusions may be drawn from the results described:

a). The chemically combined water content of the specimen studied gave a good indication of the rates of reaction.

b). PC/Pozzolan blends have much higher combined water content than pure PC pastes as a result of the formation of extra hydration products during the process of pozzolanic reaction.

c). Metakaolinite blend has a much superior reactive potential than the PFA blend used. The k values of the PC/MTK blends were several folds (about 7-9 times) higher than that of the

PFA mix at early ages and 2-4 times higher at later ages. The differences in the rate of reaction seem to be influenced by the mineralogical (e.g, amorphous silica and alumina content), as well as physical characteristics such as the possession of a finer particle size.

d). The faster rate of reaction of the pozzolanic blends results in a faster rate of filling of the pore spaces with hydration products, smaller pore volumes and reduced chloride ion diffusivity.

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