

CONTROLLING ALKALINITY OF CEMENT MATRIX: A KEY APPROACH TO IMPROVE FIBER-CEMENT DURABILITY

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ABSTRACT

Fiber-reinforced mortars may suffer loss of properties due to the long-term durability of fibers in alkaline environment of cement. The objective of the present work was to investigate how the choice of cement type and the use supplementary cementitious materials are able to mitigate degradation of mechanical properties of fiber-cement composites. The cement selection was based on chemical analysis and metakaolin and silica fume were chosen as blend materials. The effect of these materials on the alkalinity of the cement media was evaluated at two stages: the initial pH of pore solution and after 60 days. The first stage experiments were conducted by measurement of pH of pore solution extracts. The second was based on indirect determination of matrix alkalinity through the hydrolysis reaction of poly(ethylene-co-vinyl acetate) added to the composite, characterized via infra-red spectroscopy. The flexural strengths results reflected the importance of the evaluated parameters in the composite resistance.

KEYWORDS

Fiber reinforcement, cement, alkalinity, degradation, supplementary cementitious materials.

INTRODUCTION

Fiber-reinforced mortars (FRM) may suffer loss of properties concerning to the long-term reliability and durability of fibers in alkaline environment of Portland cement. In this sense, cement matrix pH control is crucial to guarantee the stability of the fiber in Portland cement based composites.

In cementitious systems without using alkaline activators the pH is essentially determined by the presence of sulfates, i.e. gypsum and $(\text{Na,K})_2\text{SO}_4$. As the hydration takes place, the pH is gradually reduced, and at this stage, the pore chemical solution is basically controlled by the calcium hydroxide dissolution, which is buffered around 12.5. In the sequence, the pH of the cementitious matrix is a consequence of C-S-H dissolution causing a drastic reduction on alkalinity (Coumes et al, 2006).

Based on that, two approaches were proposed to control cement matrix pH. The first is related to the choice of cements with lesser contents of alkalis and gypsum, evaluated through SO_3 amount and alkaline equivalent ($\text{wt}\% \text{Na}_2\text{O} + 0.658 \text{wt}\% \text{K}_2\text{O}$). The second approach involves the use of supplementary cementitious materials that reduce the pH of the systems by different ways.

The objective of the present work was to investigate how the choice of cement type and the use supplementary cementitious materials are able to mitigate degradation of mechanical properties of fiber-cement composites.

MATERIALS AND METHODS

Materials

Cement selection was based on the chemical composition. The available Portland cements were displayed on Table 1. In order to control alkalis (alkaline equivalent lesser than 0.6) and sulfates contents, cement types CII E 32, CIII 40 RS and CPV ARI RS from supplier 1 were selected.

Table 5 – Chemical compositions of cements from two suppliers.

Oxide composition	Weigth %							
	CII E 32		CIII 40 RS		CP V ARI		CPV ARI RS	
	Supplier 1	Supplier 2	Supplier 1	Supplier 2	Supplier 1	Supplier 2	Supplier 1	Supplier 2
SiO ₂	23.10	22.78	25.85	25.5	19.06	19.69	22.31	21.50
CaO	56.35	60.20	55.00	55.7	63.92	65.00	58.41	61.20
Al ₂ O ₃	7.42	6.34	8.31	8.9	5.22	4.41	6.89	5.63
MgO	2.18	3.04	2.93	4.6	0.81	2.80	1.82	2.93
K ₂ O	0.64	0.79	0.58	NA	0.80	0.98	0.67	0.84
Na ₂ O	0.11	0.30	0.10	NA	0.09	0.31	0.11	0.30
SO ₃	1.43	2.20	2.04	2.1	2.76	3.80	2.45	3.75
Fe ₂ O ₃	2.18	1.81	2.06	1.2	2.90	2.34	2.41	2.16
CO ₂	4.81	NA	1.17	NA	1.74	NA	2.73	NA
RI	1.10	NA	0.62	NA	0.29	NA	0.81	NA
PF	5.71	NA	2.05	2.3	3.36	NA	3.80	NA
Alkaline equivalent	0.53	0.82	0.48	NF	0.62	0.95	0.55	0.85
Date	28/03 2008	18/01 2008	28/03 2008	Dez/07J an/08	28/03 2008	18/01 2008	28/03 2008	18/01 2008

NA = not available.

Among supplementary cementitious materials, white metakaolin (WM) and a silica fume (SF) were chosen. Their chemical characteristics are shown in Table 2.

It is noteworthy, the high values of alkaline equivalent calculated for these materials. However, the ability of the alkalis contributes for the global alkalinity of the system depends on the associated anion. In cement case, the alkalis are associated with sulfates ion that due to their chemical characteristics are promptly dissolved and re-precipitated in the ettringite form. In order to keep the chemical equilibrium from dissolved species, hydroxyl ions are released increasing the pH. As the metakaolin and silica fume shown in Table 2 have limited content of sulfates (< 0.2%), it is assumed that their alkalis are mostly related to material impurities like KCl, clays, and feldspars.

Table 2 – Chemical compositions of supplementary cementitious materials.

Oxide composition	White Metakaolin (WM)	Silica Fume (SF)
SiO ₂	52.7	96.2
CaO	< 0.1	0.26
Al ₂ O ₃	40.8	0.08
MgO	< 0.1	0.36
K ₂ O	1.0	0.75
Na ₂ O	< 0.1	0.17
Fe ₂ O ₃	2.3	0.08
SO ₃	< 0.1	NF
TiO ₂	1.1	NF
PF	2.1	1.59
Alkaline equivalent	< 0.76	0.66
Date	03/01/08	27/04/07

pH Measurements

Pastes were prepared in the 2.12 water to solids (w/s) ratio. The solids were 100wt% cement or mixtures of 70wt% cement and 30wt% metakaolin and 95wt% cement and 5wt% silica fume. Pastes were manually mixed for 5 minutes. After 1 hour from initial contact of cement (or cement and supplementary materials) with water, paste pore fluids were extracted by vacuum filtration using 2 µm filter paper under inert nitrogen atmosphere. pH measurement of the collected pore solution was conducted in a sequential dilution (1:10, 1:100, and 1:1000) using a pH-meter with a hydrogen-ion responsive electrode.

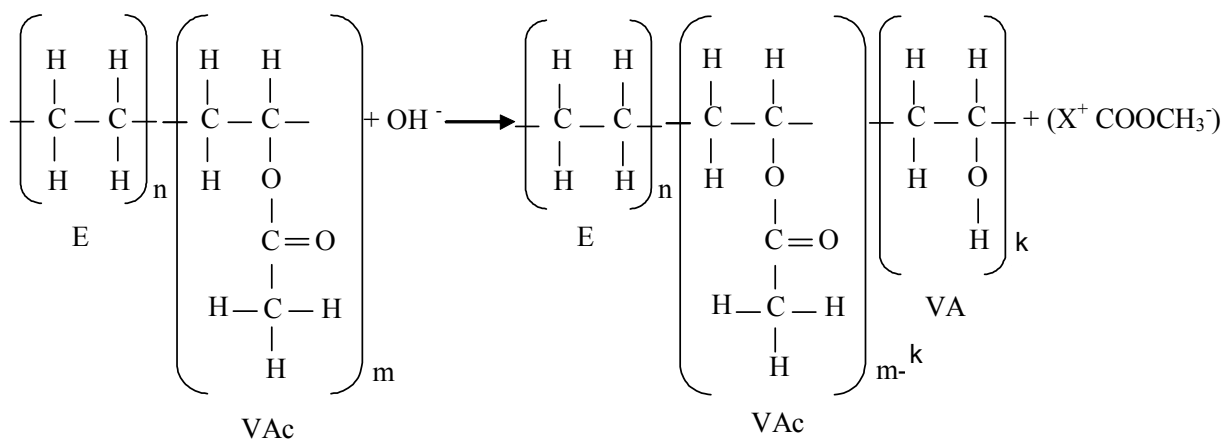
Indirect determination of matrix alkalinity through the hydrolysis of EVA via infra-red spectroscopy

FTIR was used for measuring the extension of hydrolysis reaction (Figure 1) within the poly(ethylene-co-vinyl acetate), EVA, latex. The extension of this reaction depends on the global pH of the cementitious system.

Spectra were obtained for modified pastes with 60 days e range of 4000-400 cm⁻¹ in reflectance-diffuse mode (Perkin-Elmer, Paragon 1000). At the evaluated ages, pastes samples were demolded, crushed and sieved (200 mesh) and blended with KBr. The carboxylate anion region (COO⁻), whose presence is due the alkaline hydrolysis of EVA (Atkins et al, 1991; Silva, 2002), was quantified based on peak area ($A_{\text{carboxylate}}$) in the region of 1556-1562 cm⁻¹. Normalization was performed with the area of the peak centred at 1240 cm⁻¹ (A_{1240} , in the range of 1217-1262 cm⁻¹). The 1240 cm⁻¹ vibration is attributed to C=O and C-O vibrations of carbonyl groups (Fonseca et al, 1991; Silva et al, 2002) of vinyl acetate units, that should reduce or even disappear due EVA saponification. Specifically, extension of hydrolysis (EH) was calculated for Eq. 1 (Mansur, 2008).

$$EH = \frac{A_{\text{carboxylate}}}{A_{1240}} \quad (1)$$

As defined, higher the value calculated for EH higher is the alkalinity of the cementitious system.



where: n = number of ethylene (E) monomers
 m = number of vinyl acetate (VAc) monomers
 k = number of vinyl alcohol (VA) monomers

Figure 12 – Hydrolysis reaction from vinyl acetate units (VAc) to vinyl alcohol (VA) in EVA copolymer chain under alkaline medium.

Flexural Strength

For flexural tests composites were prepared (Table 3) using a non-alkaline resistance fiber as reinforcing material. Three point bend test were carried out with samples of 120 mm x 40 mm x 9 mm.

Table 3 – Composition of samples for flexural tests.

Cement	White Metakaolin	Fiber	Water/solids
100% (control)	0%	6%	2.12
90%	10%	6%	2.12
80%	20%	6%	2.12
70%	30%	6%	2.12

RESULTS AND DISCUSSION

pH measurements

The measured pH values and the corresponding OH⁻ molar concentrations are shown in Figures 2 and 3 for samples under evaluation.

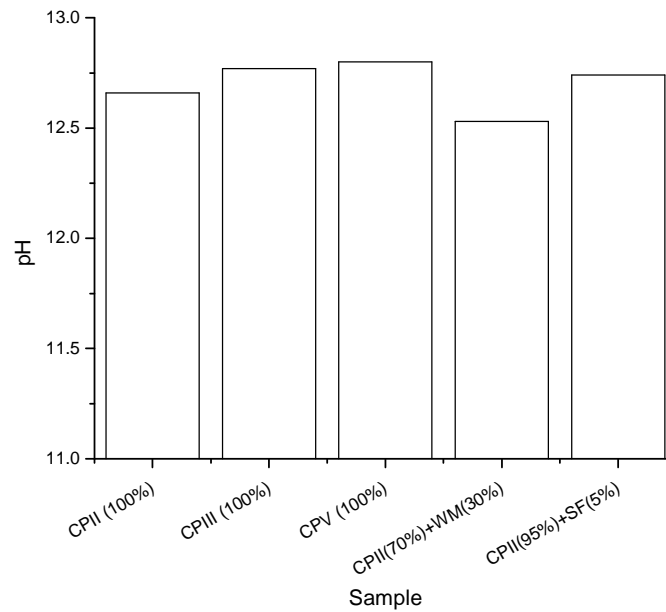


Figure 2 – pH values measured from the cement pastes suspensions under evaluation.

The results have demonstrated the dependence of the initial pore solution chemistry of high soluble alkalis hydroxides and gypsum. When comparing the suspensions of 100% cement, the measured values were a consequence of the alkalis and sulphates content according Table 1: higher values of pH (and $[\text{OH}^-]$) were measured obtained for the cement with higher amounts of these species. The concentration of hydroxyls groups for CPII and CPIII were 27% and 22% respectively lower than the calculated for CPV.

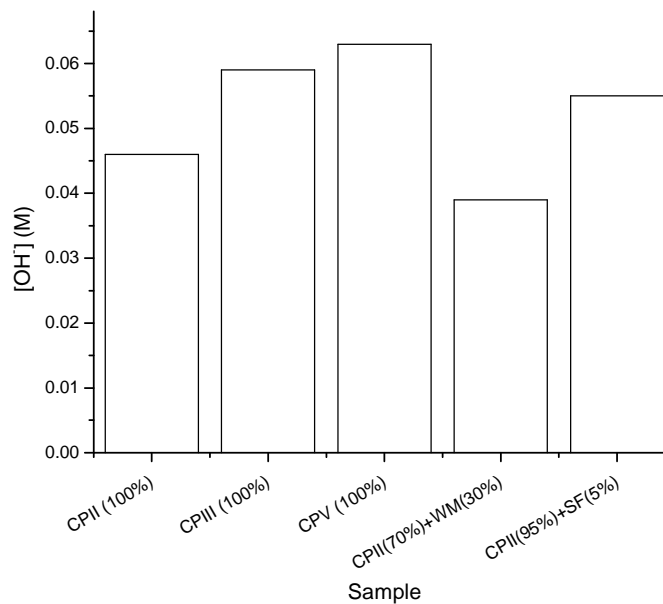


Figure 3 – Molar concentrations of OH^- calculated from measured pHs for the cementitious systems evaluated.

In order to evaluate the effect of additions in the pH, it was necessary to measure the alkalinity of the systems prepared only with the supplementary materials (in the same proportion used in the suspensions) and water (Figure 4).

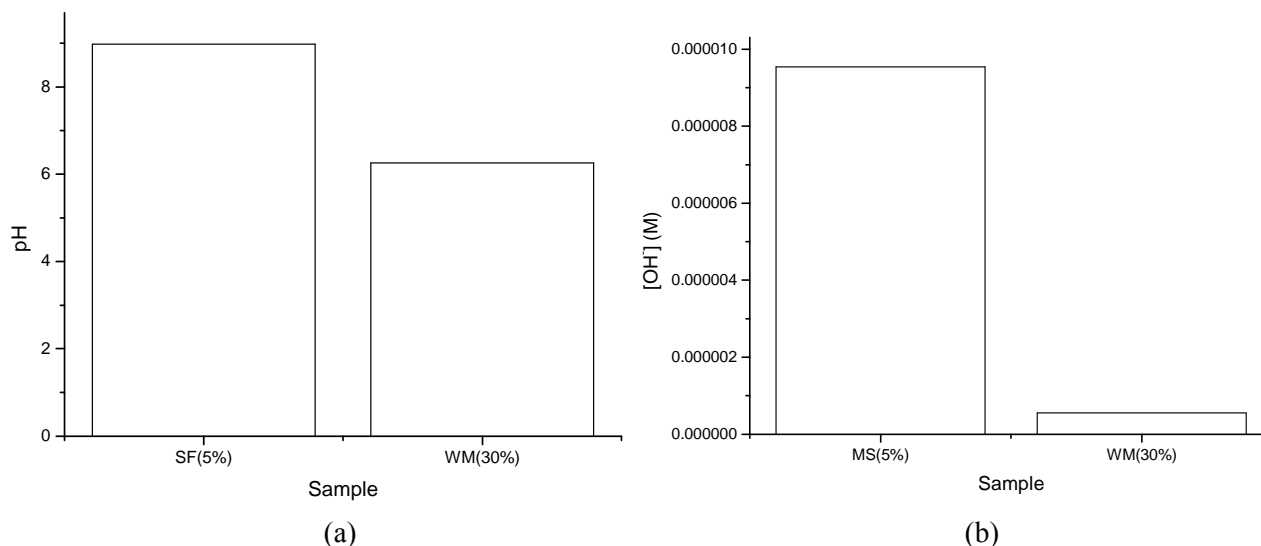


Figure 4 – pH (a) and molar concentrations of OH⁻ (b) from supplementary cementitious materials in water.

Considering the major constituents of the silica fume (SiO_2 and Al_2O_3), the basic pH obtained from this material in water was not expected. However, based on previous explanation, silica fume has presented a high value of alkaline equivalent, which effect was dependent of the associated anion. The result shown that the measured pH was a consequence of this anion associated with the alkaline ions. In this sense, the increasing of the pH measured for the suspension of Portland cement blended with silica fume was a consequence of the sum of hydroxyl species from cement and silica fume. On the contrary, for the metakaolin addition, the both effects favor the pH decrease: the character slightly acid of this material in water and the reduction of cement content in the suspension related to its partial substitution (30%) by metakaolin.

Indirect determination of matrix alkalinity through the hydrolysis of EVA via infra-red spectroscopy

The calculated values for “Extension of Hydrolysis”, EH parameter, are shown in Figure 5. Based on this graphic, it can be seen the effect of substitution of cement for sand, reducing the ions present in the system. Also, the reduction of EVA hydrolysis when the sand was substituted by metakaolin shows the effect of substitution together with the effect of the addition of a non-inert material able to reduce the alkalinity of the cement matrix mostly due pozzolanic activity.

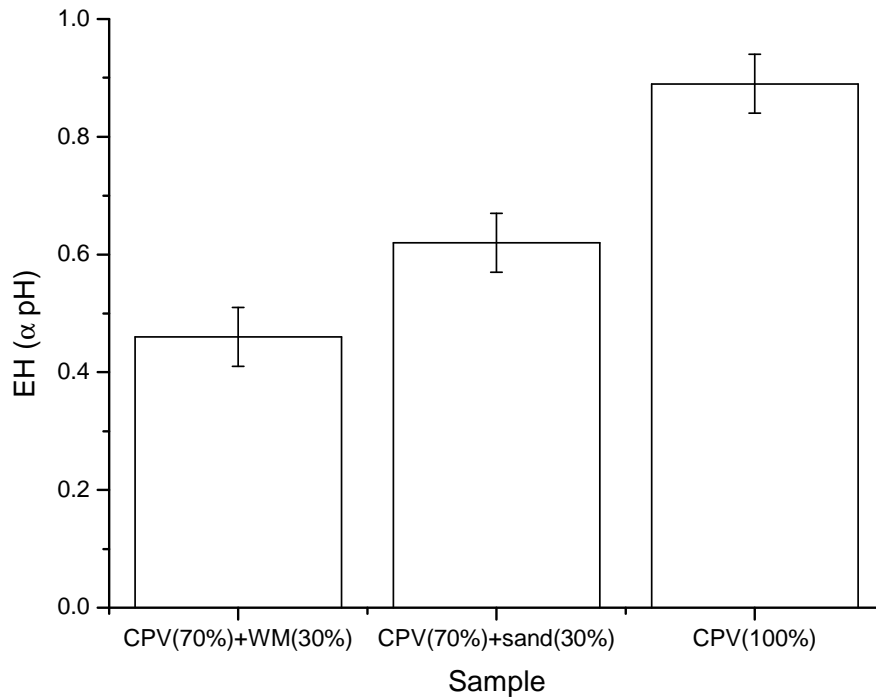


Figure 5 – EH parameter for the cement systems with or without cement substitution.

Flexural Strength

Flexural strength results measured at ages of 3, 7 and 28 days are shown in Figure 6. The measured values clearly demonstrated that at early ages, the effects of the cement content associated with fiber reinforcement are responsible for the composite resistance. At 28 days of age, the resistance of composites with 100% of cement (control) decrease and the flexural strength of fiber-cement samples with metakaolin increase, achieving values higher than that obtained from control samples. Such effect is attributed to the posterior reactions from portlandite with metakaolin and the degradation of fibers by high alkaline medium in 100% cement system.

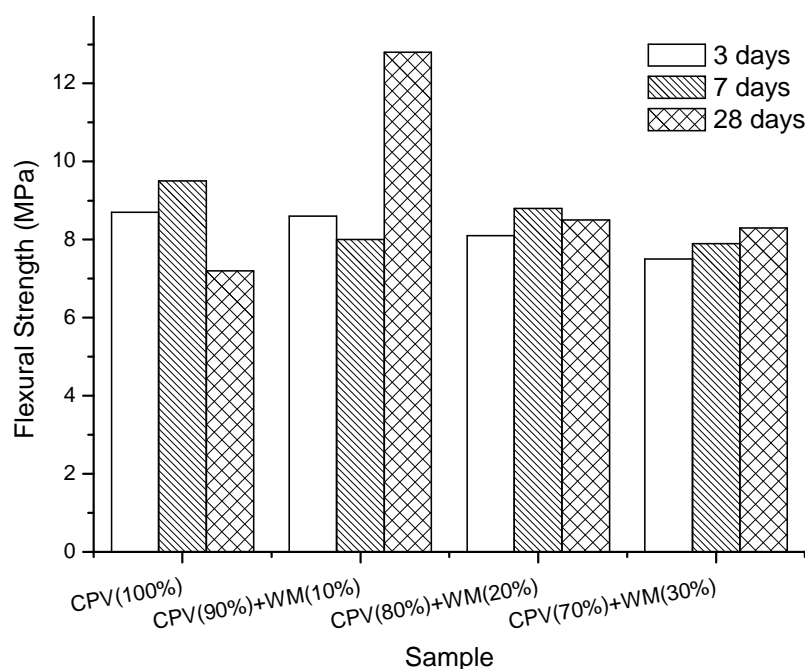


Figure 6 – Flexural strength of composites prepared

CONCLUSION

Based on the results, the composites may be tailored in order to control the alkalinity of the Portland cement inorganic matrix improving the durability of fiber-cement composites. By following an adequate cement selection it is possible to reduce the initial pH of the systems. Furthermore, the incorporation of supplementary cementitious materials may assist on reducing pH at advanced composite ages. The flexural strengths results reflected the importance of the evaluated parameters in the overall composite resistance.

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