

The Durability Properties of High Performance Mortar with HCWA-DSF Supplementary Binder

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ABSTRACT

The study was conducted to investigate the effect of the inclusion of high calcium wood ash (HCWA) and densified silica fume (DSF) on the durability properties of high strength cement mortar. A total of twelve different mix designs of mortar were fabricated with the use of HCWA at various cement replacement levels between 0 % to 20 % combined with 7.5 % densified silica fume (DSF) and subjected to chloride diffusion test. The chloride diffusion assessments was performed based on average soluble chloride content determined at various depth of mortar immersed in 4% sodium chloride solution. Significantly lower chloride diffusivity was observed for cement mortars containing 2 - 20 % of HCWA used in combination with 7.5 % DSF by weight of binder as compared to an equivalent pure cement mortar. Hence, the use of HCWA as a supplementary binder material in concrete was found to enhance its chloride resistance.

Keywords. Durability, chloride diffusion, soluble chloride content, cement replacement material, recycling

INTRODUCTION

The migration of chloride into the reinforced concrete structural member subjected to marine exposure environment or salt contamination are major problem affecting its durability performance and also shorten the serviceability duration of a reinforced concrete structure (Tamimi et al., 2008). This is because the ingress of chloride ions into the reinforced concrete structural member can result in the electro-chemical corrosion of the internal steel reinforcements (usually in the form of pitting corrosion), reducing the effective area of internal steel reinforcements and eventual failure of the structural member. The corrosion of steel reinforcements is an electro chemical process which is influenced by the electrical resistivity of the concrete cover, the pH value of cement paste which is in contact with the steel and the diffusion rate of chloride and oxygen ions into the steel reinforcement zone of a reinforced concrete member (Apostolopoulos and Papadakis, 2008). The diffusion of chloride through the concrete cover occurs due to concentration gradient between the external exposure environment and the internal pore water. Chloride ion diffusion is the most effective when pores in the hardened cement pastes are saturated, but it can also take place in partially saturated concrete or mortar. The time required for chloride ions to diffuse through

the concrete cover to the reinforcing steel in quantities large enough to break down the passivity of the reinforcing steel depends mainly on the permeability of the concrete material (Song et al., 2008). The extent of chloride diffusion is closely related to the quality of concrete and its pore structure (Song and Kwon, 2009), presence of cracks on the surface of concrete (Djerbi et al., 2008) and the provided concrete cover thickness (Conciatori et al., 2008).

Steel reinforcement in concrete is normally protected by a thin layer of iron oxide that is formed on the rebar surface by the high alkalinity of surrounding concrete. The corrosion of internal steel reinforcements does not commence unless the chloride content at the reinforcement surface exceeds a critical value known as the threshold chloride level. Once the threshold value of chloride concentration is exceeded, the passive layer is destroyed and corrosion of rebar is initiated. The threshold chloride level is influenced by several factors namely concrete mix proportion, exposure condition, type of cement or presence of mineral additives. With due consideration on the typical chloride environment exposure, the threshold chloride content for un-cracked normal strength concrete was reported to be in the range of 0.2-0.6% by weight of binder (Jiang et al., 2012).

Hence, an improved cementitious system is required to ensure that the chloride content of the steel reinforcement zone does not exceed the threshold values in order to prolong the service life of reinforced concrete structure exposed to chloride bearing environment. Hence, it is the aim of the study to investigate the effect of the inclusion of HCWA in combination with DSF as a cement replacement material in mortar on its chloride diffusivity behaviour.

MATERIALS AND METHODS

Portland Cement. ASTM Type I Portland cement (PC) was used in this study. Both the physical and chemical properties of cement used comply with specifications in ASTM Standard C150 (ASTM, 1997).

High Calcium Wood Ash. HCWA is a by-product acquired from an industrial scale fully automatic boiler unit (commercially known as Bio-Turbomax boiler) used in the rubber wood timber product manufacturing industry. The wood biomasses used as fuel in the boiler were derived from local rubber wood species dominantly *Hevea Brasiliensis*. The wood biomasses were incinerated under a self-sustained burning condition within an atmosphere with a turbulent air flow supplied by an in-built air pump unit. The temperature of incineration was maintained within the range of $800\pm 10^{\circ}\text{C}$. Raw wood ash extracted from the boiler unit was sieved through a laboratory sieve with an opening size of $150\mu\text{m}$ to remove large agglomerated ash particles and carbonaceous materials. Ash passing the $150\mu\text{m}$ sieve was then ground in a ring mill until a mean particle diameter (d_{50}) of $8.39\mu\text{m}$ was attained. The physical and chemical properties of HCWA were determined and reported in another related study by the authors (Cheah and Ramli, 2011).

Densified Silica Fume. Silica fume used in this study was collected from the precipitator unit of local ferrosilicon industry after it had undergone densification process for enhancement of its bulk density. Densification of raw silica fume was carried out by the air flotation method within the storage silo for 24 hour. The physical and chemical properties of DSF used in this study was determined and reported by the authors in another related study (Cheah and Ramli, 2011).

Aggregates. Fine aggregates used were locally sourced quartzitic natural river sand in uncrushed form with a specific gravity of 2.65 and a maximum aggregate size of 5mm. Fine aggregates were dried to saturated surface dry conditions for use as a constituent material in

mortar mixes. Fine aggregates were graded in accordance to BS812: Part 102 (BSI, 1989) and the grading of fine aggregates used were in compliance with overall grading limits of BS 882 (BSI, 1992). The fineness modulus of the fine aggregates was determined to be 3.26.

Superplasticizer and Mixing Water. An aqueous solution of polycarboxylic ester by the commercial designation of Glenium Ace 388 was used as a superplasticizer in this study. The chemical and physical properties of the superplasticizer was formulated to be in compliance with specifications of Type F and Type G admixtures prescribed in ASTM C 494 (ASTM, 2011). Physical properties of the superplasticizer used are presented in Table 1. The superplasticizer was incorporated into the mortar mixtures at a required dosage in order to maintain a desired level of workability. Potable water from local water supply network was used as mixing water.

Mixture proportioning, mixing, moulding and curing. The binder: sand and water/binder ratios were maintained constant at 1:2.25 and 0.32, respectively for all mortar mixes produced. The Portland cement binder was partially replaced using HCWA at substitution levels of 0, 2, 4, 6, 8, 10, 12, 14, 16, 18 and 20 % by total binder weight. Meanwhile, DSF was used as a partial cement replacement material at a constant replacement level of 7.5 % for all mixes containing HCWA. Superplasticizer was dosed at appropriate dosages to maintain the desired mortar slump of 70±20mm, as prescribed in BS EN 206: Part 1 (BSI, 2000) as S2 (medium workability) slump range. The flow of mortar mixes was maintained within the range of 26±5% to ensure an adequate workability of the mix for proper compaction within the steel moulds. PC was used as the only hydraulic binder in the control mortar mix (C). The mix proportion of mortars are summarized in Table 1.

Table 1. Mixture proportion of mortar mixes

Mix Designation	Cement (kg/m ³)	DSF (kg/m ³)	HCWA (kg/m ³)	Sand (kg/m ³)	Water (kg/m ³)	SP Dosage (%)
C	708	0	0	1593	227	0.5
CS	655	53	0	1593	227	1
W2	588	53	14	1593	227	1
W4	627	53	28	1593	227	1.1
W6	612	53	42	1593	227	1.3
W8	598	53	57	1593	227	1.4
W10	584	53	71	1593	227	1.5
W12	570	53	85	1593	227	1.7
W14	556	53	99	1593	227	2
W16	542	53	113	1593	227	2.6
W18	528	53	127	1593	227	3
W20	513	53	142	1593	227	3

Each batch of mortar was homogenized using an epicyclic type mechanical mixer complying with specifications in ASTM Standard C305 (ASTM, 1994). During the mixing of mortar mixes containing HWCA, Portland cement and HCWA were initially dry mixed at a low mixing speed for 3 minutes prior to the addition of other constituent materials. Further

mixing sequences and durations were performed in accordance to standard procedures prescribed in ASTM Standard C305 (ASTM, 1994). Mortar prisms were moulded using steel mould with internal dimensions of 100 x 100 x 500 mm. Compaction of the mortar mix in the mould was performed in three equal layers with each layer vibrated for 10 s. All the specimens were then cured in the mould for 24 hours. Upon being de-moulded, the test specimens were further cured by immersion in water till 28 days. Following that, the prisms were then immersed in 4 % sodium chloride solution for various immersion durations (28, 90, 182 and 364 days) prior to the soluble chloride content test.

Sampling method and chloride content assessment. The cores were extracted by means of a portable diamond core drill having an internal diameter of 25 mm. The samples were cut through to the full depth of the mortar prisms, removed and washed with distilled water to clean the surface. Locations of coring are shown in Figure 1. The distilled water was used instead of the tap water to avoid traces of chloride ions which are present in the tap water which will affect the chloride test result. The air dried samples are then grinded into fine powder with fineness of 100 % passing 150 μm test sieve using a ring mill.

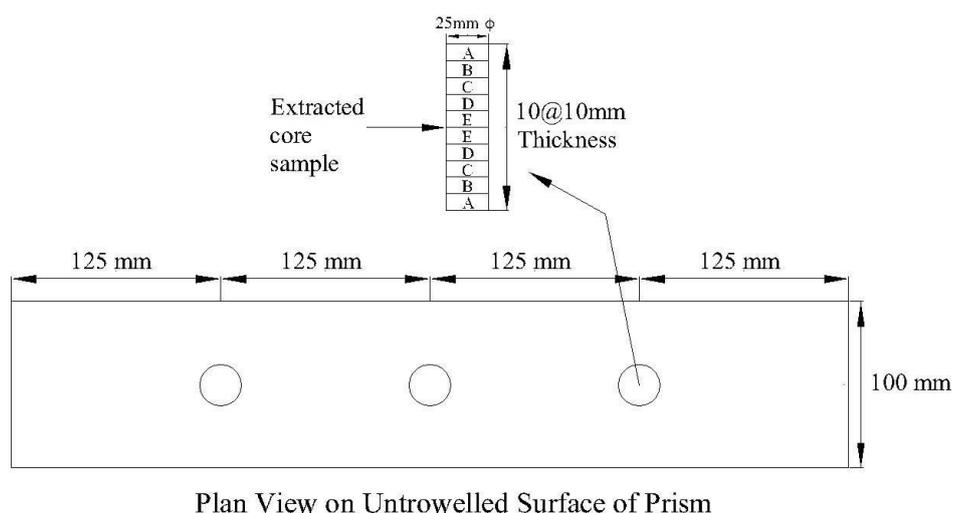


Figure 1. Location of extraction of the 25 mm cores

The chloride content analysis was conducted on all powdered samples by the method of titration in accordance to procedures prescribed in the British Standard BS 1881; Part 124 (BSI, 1988). The chloride content, J , is calculated as a percentage by weight of cement to the nearest 0.01% using Equation 1.

$$J = \left[V_5 - \frac{V_6 m}{0.1} \right] \left[\frac{0.3545}{M_c C_1} \times 100 \right] \quad (1)$$

Where M_c is the weight of sample (g), V_5 is the volume of 0.1mol/L silver nitrate standard solution added, V_6 is the volume of thiocyanate standard solution used (mL), m is the molarity of the thiocyanate standard solution (mol/L) and C_l is the binder content of the sample used.

Chloride Diffusion Analysis. The diffusion of chloride ion into the micropores of concrete or mortar occurs in a non-steady state process whereby the rate of diffusion may vary with the distances along the sections perpendicular to the direction of diffusion. The Fick's second law can be suitably used to predict the concentration of chloride ions at various depth of a concrete weight subjected to uni-directional chloride diffusion (Sun et al., 2012). The mathematical model of Fick's Second law is presented in Equation 2.

$$\frac{\partial C^2}{\partial t^2} = D \frac{\partial^2 C}{\partial x^2} \quad (2)$$

An analytical solution to Equation 2 with the assumption that the flux of chloride at anytime is proportional to the chloride concentration gradient in the concrete of a semi-infinite medium as proposed by Luping and Gulikers(2007) is presented as follows:

Boundary Conditions:

$$C = 0 \text{ at } x > 0 \text{ and } t > 0 \quad [\text{Initial Boundary Condition}]$$

$$C = C_0 \text{ at } x = 0 \text{ and } t > 0 \quad [\text{Boundary condition}]$$

By solving partial differential equation in Equation 3 using the boundary conditions, the following solution can be obtained and used for the calculation of diffusion coefficient of each layer tested:

$$C(x, t) = C_0 \left\{ 1 - \operatorname{erf} \frac{x}{\sqrt{4Dt}} \right\} \quad (3)$$

where, C_0 is the chloride content at the datum layer (taken as first layer tested) (%), erf is the error function, $C(x, t)$ is the chloride concentration (%) at a given depth x (in cm), %, t is the period of exposure (s), D is diffusion coefficient (cm^2/s).

RESULTS AND DISCUSSIONS

Effect of HCWA Content on the Average Chloride Content. For the determination of chloride permeability of a concrete material, two different methods namely the long term immersion tests and electrically accelerated chloride migration test have recently been used (Chahal et al., 2012, Sahmaran et al., 2007). Although the electrically accelerated chloride migration test provide rapid information about the diffusion properties of concrete, the test results may not be reliable due to possible adverse effects of the relatively high voltage imposed on the rebar in concrete (McGrath and Hooton, 1996). The chloride content of the mortar mixes at every 10 mm interval from the exposed surface was examined after exposure

durations of 28, 90, 182 and 364 days. The water soluble chloride content of the HCWA-DSF, DSF-cement and Portland cement mortars at various durations of immersion is presented in Table 2. From the test results, it could be noted that the chloride content reduces with increasing sampling depth into the mortar prisms. The highest difference in chloride content was between average sampling depth of 5 mm and 15 mm whereby there was a drastic drop in chloride content when the average sampling depth was increased to 15 mm from 5 mm for all immersion durations as shown in Table 2.

As referred to Table 2, the inclusion of HCWA at cement replacement levels of 2% up to 20 % in combination with 7.5 % DSF by binder weight had resulted in a significant reduction in the chloride content of the mortar mixes produced especially for the average sampling depth of 5 mm at all durations of immersion in salt water as compared to the Portland cement mortar. After immersion in 4 % Sodium Chloride solution for a total duration of 364 days, the water soluble chloride content of all the HCWA-DSF and DSF-cement mortars at the sampling interval of 20-30 mm was still observed to be lower than the maximum allowable content of 0.15 % as prescribed in the ACI Building Code 318 (ACI, 1992). Meanwhile the water soluble chloride of Portland cement mortar at the specified interval and immersion duration was determined as 0.599 % which exceeded the allowable limit prescribed. The sampling depth interval of 20-30 mm was considered as it is equivalent to the typical depth of concrete cover provided for reinforced concrete structural element as prescribed in the British Standard BS 8110 (BSI, 1985).

In a comparison made between various duration of immersion, it was also observed that chloride diffusion is a time dependent process. This is indicated by the increasing concentration of chloride in all the mortar mixes on prolonged salt water immersion duration from 28 days up to 365 days. The average chloride content of the HCWA-DSF mortar mixes was observed to be lower as compared to the Portland cement mortars as indicated in Table 2. The percentage reduction in average chloride content in the mix is also presented in the same table.

In a comparison made between the average chloride content between the HCWA-DSF mortar and DSF-cement mortar indicated that mortars with HCWA content of between 2% and 14% in combination with 7.5 % of DSF had lower average chloride content as compared to the DSF-cement mortar (CS) for all immersion durations considered. This could be attributed to the refined pore structure of the cement paste matrix in the presence of secondary C-S-H mineral from the hydration reaction between Portlandite component of HCWA and amorphous silica of DSF within the capillary pores.

Table 2 Chloride content in mortar prism (% by weight of binder)

Immersion Duration	Mix Design	Sampling Depth (mm)					Average Chloride Content (%)	% Reduction in average chloride content
		0-10	10-20	20-30	30-40	40-50		
28 DAYS	C	1.521	0.369	0.115	0.069	0.023	0.419	
	CS	1.152	0.138	0.092	0.046	0.046	0.295	29.7
	W2	0.576	0.115	0.092	0.046	0.046	0.175	58.2
	W4	0.300	0.046	0.023	0.000	0.000	0.074	82.4
	W6	0.484	0.092	0.023	0.000	0.000	0.120	71.4
	W8	0.507	0.092	0.046	0.000	0.000	0.129	69.2
	W10	0.484	0.115	0.023	0.000	0.000	0.124	70.3
	W12	0.507	0.046	0.046	0.000	0.000	0.120	71.4
	W14	0.645	0.115	0.023	0.000	0.000	0.157	62.6
	W16	0.922	0.161	0.092	0.023	0.023	0.244	41.8
	W18	1.129	0.138	0.092	0.023	0.023	0.281	33.0
W20	1.222	0.207	0.138	0.046	0.023	0.327	22.0	
90 DAYS	C	2.674	0.691	0.161	0.069	0.046	0.728	
	CS	2.051	0.161	0.092	0.046	0.046	0.479	34.2
	W2	0.715	0.138	0.092	0.046	0.046	0.207	71.5
	W4	0.530	0.046	0.046	0.023	0.023	0.134	81.6
	W6	0.715	0.115	0.046	0.023	0.023	0.184	74.7
	W8	0.668	0.115	0.069	0.000	0.000	0.170	76.6
	W10	0.576	0.138	0.046	0.023	0.000	0.157	78.5
	W12	0.530	0.069	0.069	0.000	0.000	0.134	81.7
	W14	1.199	0.115	0.092	0.000	0.000	0.281	61.4
	W16	1.844	0.161	0.092	0.046	0.046	0.438	39.9
	W18	2.144	0.161	0.092	0.046	0.046	0.498	31.6
W20	2.236	0.230	0.138	0.069	0.046	0.544	25.3	
182 DAYS	C	2.766	1.176	0.254	0.069	0.069	0.867	
	CS	2.121	0.161	0.092	0.069	0.069	0.502	42.0
	W2	0.829	0.138	0.092	0.069	0.046	0.235	72.9
	W4	0.673	0.092	0.046	0.046	0.046	0.181	79.2
	W6	0.985	0.138	0.092	0.069	0.046	0.266	69.3
	W8	0.922	0.207	0.092	0.069	0.069	0.272	68.6
	W10	0.668	0.161	0.115	0.046	0.046	0.207	76.1
	W12	1.268	0.254	0.092	0.092	0.092	0.360	58.5
	W14	1.775	0.300	0.138	0.069	0.069	0.470	45.7
	W16	2.213	0.161	0.092	0.069	0.046	0.516	40.4
	W18	2.305	0.207	0.092	0.069	0.069	0.549	36.7
W20	2.397	0.277	0.138	0.092	0.069	0.595	31.4	
364 DAYS	C	2.996	1.222	0.599	0.115	0.069	1.000	
	CS	2.190	0.392	0.092	0.069	0.069	0.562	43.8
	W2	1.683	0.254	0.092	0.069	0.046	0.429	57.1
	W4	1.613	0.507	0.046	0.046	0.046	0.452	54.8
	W6	1.152	0.184	0.092	0.069	0.046	0.309	69.1
	W8	1.014	0.207	0.092	0.069	0.069	0.290	71.0
	W10	0.738	0.184	0.138	0.069	0.069	0.240	76.0
	W12	1.360	0.254	0.115	0.092	0.092	0.383	61.8
	W14	1.844	0.461	0.138	0.069	0.069	0.516	48.4
	W16	2.305	0.553	0.092	0.069	0.069	0.618	38.2
	W18	2.420	0.711	0.092	0.069	0.069	0.672	32.8
W20	2.512	0.780	0.138	0.092	0.069	0.718	28.2	

Influence of HCWA on Chloride Diffusivity of Mortar. By using Equation 3, the calculated values of soluble chloride content at all the intervals were averaged to obtain the average chloride diffusion coefficient at a given immersion duration as shown in Table 3.

Table 3 Average chloride diffusion coefficient of mortar mixes

Mix Design	Average Chloride Diffusion Coefficient (10^{-7} cm ² /s)							
	Immersion Durations (days)							
	28	% Reduction	90	% Reduction	182	% Reduction	364	% Reduction
C	2.994	-	1.208	-	0.711	-	0.437	-
CS	2.905	3.0	0.954	21.0	0.516	27.4	0.269	38.4
W2	2.848	4.9	0.893	26.1	0.458	35.5	0.241	44.8
W4	1.161	61.2	0.734	39.3	0.422	40.6	0.235	46.2
W6	1.206	59.7	0.752	37.7	0.460	35.3	0.233	46.6
W8	1.273	57.5	0.419	65.3	0.491	31.0	0.246	43.7
W10	1.220	59.2	0.537	55.5	0.449	36.8	0.249	42.9
W12	1.239	58.6	0.408	66.3	0.535	24.8	0.271	37.9
W14	1.230	58.9	0.446	63.1	0.526	26.0	0.270	38.1
W16	2.556	14.7	0.938	22.3	0.495	30.3	0.279	36.2
W18	2.560	14.5	0.963	20.3	0.530	25.4	0.290	33.6
W20	2.814	6.0	1.040	13.9	0.568	20.1	0.310	29.0

From the chloride diffusion coefficient results in Table 3, The inclusion of only DSF in the Portland cement mortar at 7.5 % by weight of binder was observed to result in the reduction of the chloride diffusion coefficient of the mortar mix produced (CS) as compared to the pure Portland cement mortar (C). It was also observed that the inclusion of HCWA at cement replacement level of 2 % up to 16 % in combination with 7.5% DSF by weight of binder seems to have effect on lowering the chloride diffusion coefficient of the mortars further for all immersion durations considered in the study. The percentages of reduction in chloride permeability by the inclusion of HCWA at various immersion durations as compared to the Portland cement mortar are also indicated in Table 3. It could be observed that the inclusion of HCWA at cement replacement level between 4-10 % in combination with 7.5% DSF by weight of binder had resulted in the most significant reduction in the chloride permeability of the mixes at all durations of immersion. From the chloride diffusion results, it could be noted that the inclusion of HCWA at high level of cement replacement up to 20 % by weight of binder had contributed significantly to reduction in the chloride permeability of mortar mix as compared to the Portland cement mortar. This is most probably due to the effect of refined capillary pore structure in the presence of secondary pozzolanic reaction (Antiohos et al., 2008, Antiohos et al., 2006, Gleize et al., 2003). The low chloride diffusion coefficients of the HCWA-DSF mortars justify the low average chloride content of the mixes as described earlier.

CONCLUSIONS

The average water soluble chloride ion present in the HCWA-DSF mortar mixes with HCWA content of 0-20% and DSF content of 7.5 % by mass of binder was found to be lower as compared to the pure Portland cement mortar for all chloride exposure durations up to 364 days. Besides, the HCWA-DSF mortars were also found to have lower coefficient of

chloride permeability as compared to pure Portland cement mortar. The lower chloride permeability of the HCWA-DSF mixes could be attributed to the refined pore structure of the mortar mixes by the secondary hydration product formed from the Portlandite-silica secondary hydration reaction. Hence, it can be concluded that the inclusion of HCWA in combination with DSF as a partial cement replacement material can contribute towards a significant enhancement of the chloride resistance of concrete and mortar.

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