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Influence of the C/S and C/A ratios of hydration products on the chloride ion binding capacity of lime-SF and lime-MK mixtures

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Abstract

The mechanisms of chloride ion binding in cementitious systems when supplementary cementing materials are present are not completely understood, although it is believed to relate to the alumina content of the mixture. This relationship is investigated through the use of lime–silica fume and lime–metakaolin mixtures. It was found that while the alumina content does have an important influence, the chloride binding capacity was also controlled by the calcium-to-alumina and calcium-to-silica ratios. At a high C/A ratio, the formation of monocarboaluminate is favoured, which has a high ability to form Friedel's salt, and does so at low chloride concentrations (less than 0.1 M). With a low C/A ratio, the formation of stratlingite is favoured, with little formation of monocarboaluminate. If alumina is not present, chloride is bound by the C–S–H phase. The binding capacity of the C–S–H was found to depend on its calcium-to-silica ratio, C–S–H with a higher C/S having a greater binding capacity.

Keywords: Hydration products (B); Chloride (D); Blended cement (D); X-ray diffraction (B)

1. Introduction

The ability of concrete to bind chloride ions and retard their rate of penetration is an important factor in determining the service life of concrete structures with regards to chloride-induced corrosion. As such it has been extensively studied, and some of its mechanisms are beginning to be understood. For plain Portland cement mixtures, the primary mechanism is the formation of Friedel's salt and related complexes from the aluminate phases [1–7], although there is evidence that C–S–H can bind chloride ions as well [3,8–11]. However, its contribution is normally considered secondary.

In blends of Portland cement and supplementary cementitious materials (SCM), the influence of the SCM on chloride binding is believed to be a function of the aluminate content. While this has generally proven to be the case [12–14], there is some evidence to the contrary [15]. More importantly, however, the effect of inclusion of SCM's is more significant than that which would be expected solely from the change in alumina content [16]. Nilsson et al. [17] suggested that the partial replacement of cement with silica fume will have three main effects which will influence the binding capacity: 1) a reduction in the pH of the pore solution which will increase chloride binding, 2) a dilution of C_3A which will reduce binding, and 3) an increase in the amount of the C–S–H which should increase binding. It is also known that this replacement results in the formation of C–S–H with lower C/S than the C–S–H formed without the presence of silica fume [18]. It is not likely that the dilution of the C_3A can solely explain the observed reduction in the binding capacity as a result of the partial replacement of cement with silica fume.

To isolate the effect of silica fume and metakaolin, a series of experiments were conducted using lime mixtures. Lime was used rather than portland cement so as to isolate the binding mechanisms that occur with the hydrated silica fume or

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metakaolin. The influence of SF and MK when mixed with Portland cement were investigated in a separate study reported elsewhere [19].

2. Experimental procedures

To investigate the effect of varying alumina and silica proportions, two supplementary cementing materials were used. Silica fume (SF) contains greater than 90% silica, but almost no alumina. Metakaolin (MK) contains both silica and alumina in approximately equal proportions. The oxide compositions of the silica fume and metakaolin used are shown in Table 1. Mixtures of SF–lime and MK–lime were tested for their chloride binding capacity. Three different SCM/lime proportions were used — 2/1 (SF21), 1/1 (SF11), and 1/2 (SF12) by mass. Since up to 30% SF replacement is needed to react with all the $Ca(OH)_2$ produced as a result of hydration, a 2/1 ratio of SF to lime was an upper limit in the amount of SCM that could be included. A greater proportion of silica fume would result in unreacted particles. The SCM/lime ratios were then varied so that the resulting C–S–H hydrates would have different C/S ratios. A w/cm ratio of 2.0 was chosen to obtain workable mixes without the addition of a superplasticiser. The mix water contained 85 mmol/L NaOH and 345 mmol/L KOH to simulate alkali concentrations previously determined in a control, 100% Portland cement mixture [19]. The mixes were cured for 2 months at 38 °C to accelerate the pozzolanic reactions prior to testing.

The equilibrium procedure proposed by Tang and Nilsson [9] to establish chloride binding isotherms of cement pastes was followed in this work. At the end of the curing period, the pastes were demolded and the central portion was saw-cut into approximately 3-mm thick discs using a wet diamond blade lubricated with distilled water. The sliced samples were vacuum dried for three days in a desiccator containing silica gel and soda lime. They were then stored for a month in a glove box kept at 11% RH (using saturated lithium chloride solution). Soda lime was used to remove the carbon dioxide from the air inside the glove box. It has been reported that only a monolayer of water remains on the surface of cement hydrates at 11% RH [20], and this has been assumed to apply to the SF–lime and MK–lime hydrates studied here. After storage, 25 g samples were stored in 125 ml plastic bottles and placed under vacuum for about two hours. The bottles were filled with a known volume (approximately 60 mL) of NaCl solutions of varying concentrations (0.1, 0.3, 0.5, 0.7, 1.0, 2.0, 3.0 M Cl). The chloride solutions were saturated with calcium hydroxide (3 g/L, pH = 12.5) to prevent the leaching of calcium hydroxide from the samples during storage. The bottles were sealed and stored in the open laboratory atmosphere (22 °C), for 5–6 weeks to allow equilibrium to be established by diffusion of the chloride ions into the paste samples. This period of time was selected based upon experience with similar mixtures in identical experimental conditions. After equilibrium between the pore solution of the samples and the host solutions was reached, the host solutions were analyzed for chloride concentration, after appropriate dilution, by means of potentiometric titration with a Metrohm DMS760 automatic titrator versus 0.01 molar $AgNO_3$ titrant with a silver electrode.

Table 1
Oxide compositions of silica fume and metakaolin (mass %)

	SiO_2	Al_2O_3	TiO_2	P_2O_5	Fe_2O_3	CaO	SrO
Silica fume	94.48	0.24	0.01	0.14	0.63	0.44	0.02
Metakaolin	52.01	44.72	1.6	0.09	0.58	0.00	0.02

	MgO	Mn_2O_3	Na_2O_3	K_2O	$(Na_2O)_{eq}$	SO_3	LOI
Silica fume	0.38	0.03	0.16	1.01	0.82	0.36	2.87
Metakaolin	0.00	0.01	0.32	0.19	0.45	0.12	0.9

It is assumed that after equilibrium is reached between the external solution and the pore solution of the sample, the reduction in the concentration of the host solution is due solely to chloride being bound by the cement. Then, knowing the initial and final concentration, the volume of the external solution and the dry mass of the sample, the amount of bound chloride can be calculated according to the following formula:

$$C_b = 35.453V(C_i - C_e)/W_d \tag{1}$$

Where:

C_b	amount of bound chloride in mg Cl/g of sample.
V	volume of the external solution in mL.
C_i	initial chloride concentration of the external solution in mol/L,
C_e	free chloride concentration at equilibrium of the external solution in mol/L.
W_d	dry mass of the sample in g, and
35.453	is the molar mass of the chloride ion.

The W_d mass is calculated using the formula:

$$W_d = W_{11}(1 - \zeta_{11}) \tag{2}$$

Where:

W_{11}	mass of the sample at 11% RH in g,
ζ_{11}	evaporable water content at 11% RH.

The free chloride ion concentrations were then plotted versus the bound values for each mixture to obtain the isotherms.

After equilibrium had been established, samples for XRD testing were taken out of the chloride solutions and wiped with a dry cloth to removes excess solution. They were then vacuum dried for three days in a dessicator containing silica gel and soda lime. After drying, the samples were removed to a low (11%) relative humidity environment that contained soda lime (to absorb the CO_2 in the air) where they were ground to powder and sealed in vials. The vials were returned to the dessicator to await testing. The X-ray diffraction patterns were obtained on a Siemens D5000 X-ray diffractometer using filtered CuKα radiation with a wavelength $\lambda = 15.418$ nm.