Chloride diffusivity, chloride threshold, and corrosion initiation in reinforced alkali-activated mortars: Role of calcium, alkali, and silicate content

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The aim of this study is to investigate systematically the chloride diffusivity and chloride threshold of a wide range of calcium-rich and fly ash-dominated alkali-activated samples in light of their compositional differences. To this end, the effects of various fly ash (FA)-to-slag ratios, of alkali concentrations and of silicate content in the activator were investigated. The electrochemical aspects of the passive samples were also assessed. Results show the prominent role of calcium in the matrix to reduce the chloride diffusivity. While higher alkali concentration increased the porosity and chloride diffusivities in general, lower modulus ratios provided considerably better performance in the FA-dominated samples. Chloride threshold values range between 0.19 (wt% binder mass) for calcium-rich mortars fabricated at low levels of alkalinities and 0.69 for FA-dominated mortars fabricated with highly alkaline activators. Half-cell potential and polarization resistance of alkali-activated samples were in general lower than their Portland cement counterparts.

1. Introduction

Corrosion of reinforcement is one of the main causes of premature failure in concrete structures; it shortens the designated service life of buildings and infrastructures, leading to huge economic losses annually [1, 2]. Chloride-induced corrosion of reinforcement, which usually takes place in marine environments or as a consequence of using de-icing salts, can be studied in two separate phases. During the initiation phase, the chloride ions penetrate the concrete and reach the surface of the reinforcement in considerable amounts, breaking down the passive layer around the bars which is otherwise stable in highly alkaline environments [3]. After depassivation and during the propagation phase, corrosion starts and rust products accumulating around the bars can lead to such structural damage as concrete spalling, delamination, loss of ductility of the bars, etc. While the reinforced concrete members can still sustain the applied loads during the initial stages of the propagation phase [4], it is common practice and more conservative to limit the service life of the structure to the end of the initiation phase, i.e. the point when the reinforcement depassivates and corrosion starts.

Several factors determine the duration of the initiation phase (i.e. the service life). This includes the rate of chloride ion diffusion, which is influenced by the permeability (physical absorption capacity) of the concrete/mortar and the chloride binding capacity of the matrix, as well as the stability of the passive film around the reinforcement, which is indirectly measured by the concentration of chloride ions required to break it down (chloride threshold). While a considerable amount of research has been conducted in the past to study various factors involved in the initiation phase of corrosion of ordinary Portland cement (OPC) binders, there is still some uncertainty regarding topics such as the chloride threshold, the passivation/depassivation mechanism and the effect of chloride binding in these binders (see for example [5, 6]). For new binders such as alkali-activated binders, there is comparatively little data available regarding their durability in marine environments, as these materials have only recently gained momentum as viable alternative construction materials [7, 8].

Apart from relatively limited previous research studies on the corrosion initiation of alkali-activated binders, variabilities of these binders in terms of both precursors and the properties of the final product are other factors that widen the consensus gap among researchers with regards to durability performance. Alkali-activated binders are produced by the reaction of solid precursors such as metakaolin, fly ash (FA), and ground granulated blast-furnace slag (GGBS) with an alkali metal hydroxide or silicate solution; in addition, the carbon emissions attributed to their production is less than their Portland cement counterparts [9, 10]. Depending on the precursor used, the final products can have considerably different nano/microstructures with different

transport properties. Alkali-activation of aluminosilicate sources such as metakaolin and FA results in an amorphous aluminosilicate network (also called geopolymer, as first coined by Davidovits [11]) with an intrinsically porous nano/microstructure [12]. On the other hand, alkali activation of slag binders with a considerable amount of calcium in the matrix leads to the production of some form of calcium silicate hydrates notable for the partial substitution of alkalis and aluminium [13–16] with a finer pore structure than those of aluminosilicate networks [17]. The type and concentration of the activator and the ratio of silicates to alkalis play an important role in developing the pore structure and stability of the passive layer, as has been reported in a number of previous research studies [18–21]. The involvement of all the variables mentioned above can explain the often contradictory results on the corrosion performance and transport properties of alkaliactivated and geopolymer-type materials reported in the literature.

With regards to the chloride penetration in geopolymer-type binders, only a limited number of studies can be found in the literature; at the same time, some researchers have reported a higher resistance to chloride penetration and a lower rate of corrosion of reinforced samples (see for example [22, 23]). A quick review of the sample compositions in those studies, however, reveals that in almost all cases these samples were synthesized using very highly alkaline solutions with low modulus ratios (= molar ratio of silicates to alkalis), increasing the risk of efflorescence [24], and raising safety concerns regarding the application of a caustic solution at very high pH levels during the manufacturing process. On the other hand, the requirement for calcium in the matrix to form a finer gel structure to reduce the rate of chloride penetration is suggested in a number of previous studies, based on the observed superior performance of alkali-activated slag binders, or blended fly ash and slag binders, compared with geopolymer-type or even OPC binders in chloride-contaminated environments [8, 17, 18, 25–28].

Although previous studies provide valuable information regarding various aspects of durability performance of alkali-activated materials during the initiation phase of corrosion, they lack a systematic approach that both incorporates all the different influential parameters and investigates their correlations. The variability of the sources for raw precursors as well as the experimental techniques used in the previous studies add another layer of difficulty to interpreting the results available in the literature. Thus, the current study aims to investigate systematically the effects of binder composition, including the FA/GGBS ratio, the alkali concentration and the modulus ratio on the chloride diffusivity and chloride threshold values of a wide range of alkali-activated mortar samples. The results are discussed in light of the pore structure development in various compositional conditions. Chloride binding is also studied through assessment of free and total chloride content of chloride contaminated mortar samples. The electrochemical aspects of samples before depassivation are studied and the results are discussed accordingly.

2. Experimental program

2.1. Materials and mix proportions

Gladstone fly ash (Gladstone FA) from the Gladstone power stations in Queensland, Australia, and ground granulated blast-furnace slag (GGBS) supplied by Australian Steel Mill Services (ASMS), Port Kembla, New South Wales, Australia, were used as solid precursors to fabricate alkali-activated samples. To prepare Portland cement-based reference samples, Australian general-purpose cement manufactured at the Boral Berrima Cement Works (NSW, Australia) was used. A 7.5% limestone mineral addition had been used to produce the cement. The chemical compositions of the aluminosilicate raw precursors as determined by X-ray fluorescence (XRF) analysis are shown in Table 1. The amorphous content of the raw materials used for alkali-activated paste fabrication was also measured through the X-ray diffraction (XRD) test using the spike method (5 wt% zinc oxide was used).[1] The amorphous content of

Table 1
Chemical compositions of Gladstone FA, and GGBS by X-ray fluorescence (XRF) analysis.

	Gladstone fly ash (wt%)	GGBS (wt%)
SiO_2	47.9	35.0
Al_2O_3	25.7	14.1
Fe_2O_3	14.7	0.36
CaO	4.11	40.9
MgO	1.36	5.51
Na_2O	0.81	0.29
K_2O	0.67	0.30
TiO_2	1.39	0.59
P_2O_5	1.21	0.02
Mn_3O_4	0.19	0.55
SO_3	0.19	1.15
Loss on ignition (LOI)	0.69	NA

NA: not available.

Gladstone FA and GGBS was 79.1% and 100% respectively. The crystalline phases in fly ash samples consist of mullite ($Al_{2.17}O_{4.89}Si_{0.78}$), quartz ($SiO_2$), magnetite ($Fe_3O_4$), and hematite ($Fe_2O_3$). The only crystalline phases in GGBS were traces of quartz. Particle size distribution of the solid precursors was determined using the laser diffraction technique with a Malvern Mastersizer 2000 instrument (Fig. 1). The powders were dispersed in water and ultrasonication at 20 kHz was used before the analysis. As can be seen, Gladstone FA is finer than the GGBBS, and the bulk of particles were about 5–6 μm in the Gladstone FA, as opposed to 14–15 μm in the GGBS.

A mixture of sodium hydroxide (NaOH), or sodium hydroxide (NaOH) + potassium hydroxide (KOH) solution, and grade D sodium silicate solution were used as the activator. Technical grade NaOH pellets supplied by Ajax Finechem were dissolved in tap water to prepare the NaOH solution. KOH flakes were supplied by Recochem Inc. and dissolved in tap water as a partial replacement of NaOH in some mixes. The waterglass solution was provided by PQ Australia (Na_2O = 14.7%, SiO_2 = 29.4% and H_2O = 55.9% (by mass)). The NaOH or NaOH + KOH and waterglass solutions were mixed in proportions to form alkaline solutions at different concentrations and modulus ratios (M_s = molar ratio of SiO_2/M_2O, M = Na or Na + K), as shown in Table 2. After mixing, the alkaline activator was allowed to cool to ambient temperature and equilibrate for 24 h prior to fabrication of the specimens.

Four OPC mortars with water-to-cement ratios similar to the water-to-binder ratios of alkali-activated mixes were also fabricated so that the chloride diffusivities and electrochemical performance of the alkaliactivated samples could be compared with those of the OPC samples.

For the FA-dominated samples (75% FA – 25% GGBS), a minimum alkali content of 5% was used to enhance the early-age strength development, which occurs mainly through the formation of the aluminosilicate network. By increasing the GGBS content to 50% or more, lower alkali contents could be used as a combination of the aluminosilicate network and some form of calcium silicate hydrate gel (with a higher probability of formation at lower alkalinity levels [16, 29]) in these binders is responsible for strength development and providing greater early-age strength as a result.

2.2. Mixing procedure and manufacturing mortar samples

Alkali-activated mortars were manufactured in a Hobart planetary-type mixer. The FA and GGBS were first introduced into the bowl and dry mixed to achieve a uniform dispersion. The activator solution was then added and the pastes mixed for 2 min at low speed. Mixing then stopped to scrape down the bowl and the blade, followed by another

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[1] Refer to Section 2.5 for XRD test conditions