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## Research Article

# Chloride Ingress in Chemically Activated Calcined Clay-Based Cement

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Chloride-laden environments pose serious durability concerns in cement based materials. This paper presents the findings of chloride ingress in chemically activated calcined Clay-Ordinary Portland Cement blended mortars. Results are also presented for compressive strength development and porosity tests. Sampled clays were incinerated at a temperature of 800°C for 4 hours. The resultant calcined clay was blended with Ordinary Portland Cement (OPC) at replacement level of 35% by mass of OPC to make test cement labeled PCC35. Mortar prisms measuring 40 mm × 40 mm × 160 mm were cast using PCC35 with 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution as a chemical activator instead of water. Compressive strength was determined at 28th day of curing. As a control, OPC, Portland Pozzolana Cement (PPC), and PCC35 were similarly investigated without use of activator. After the 28th day of curing, mortar specimens were subjected to accelerated chloride ingress, porosity, compressive strength tests, and chloride profiling. Subsequently, apparent diffusion coefficients ( $D_{app}$ ) were estimated from solutions to Fick's second law of diffusion. Compressive strength increased after exposure to the chloride rich media in all cement categories. Chemically activated PCC35 exhibited higher compressive strength compared to nonactivated PCC35. However, chemically activated PCC35 had the least gain in compressive strength, lower porosity, and lower chloride ingress in terms of  $D_{app}$ , compared to OPC, PPC, and nonactivated PCC35.

## 1. Introduction

Steel reinforced cement based materials are susceptible to degradation when exposed to chloride-laden environments [1]. Chlorides ingress in these materials mostly from chloride contaminated waters such as industrial effluents, mixing waters, and sea water [2]. They are also deliberately introduced as admixtures to modify certain properties of cement [3]. Deicing salts such as NaCl (sodium chloride) usually added to clear the ice on roads also acts as a rich source of chlorides in cement based materials [2]. When chlorides ingress into the mortar/concrete to the level of rebars, if their amounts are beyond the critical threshold concentration, they induce and propagate pitting corrosion. Chloride-induced corrosion causes premature deterioration of cement based structures hence reducing their service life [4].

Chlorides ingress in cement based materials mainly through capillary absorption, permeation, and diffusion.

Capillary absorption occurs when the surface moisture and liquids are introduced to the cement based materials through capillary action as a result of wetting and drying cycles. Permeation occurs due to buildup of hydraulic pressure gradient that causes liquids/ions to penetrate the mortar/concrete networks. High pressure is essential for permeation process to occur and therefore the process is of concern in instances such as deep sea oil rigs, tunnel linings, and hydrothermal wells. Diffusion involves movement of molecules in form of gas or a liquid from a high concentration to a low concentration in order to achieve system equilibrium [5]. Diffusion is the most predominant method through which chlorides ingress in cement based materials [6]. Chloride ingress also occurs through a combination of two or more aforementioned processes.

Chlorides penetration in cementitious materials is majorly dependent on cement type and binding capacity [7]. Cementitious materials have the potential to bind a

proportion of chlorides to them. When chlorides penetrate cement based structures, some are either bound physically by the calcium silicate hydrate (CSH) phase or chemically by the alumina-ferric oxide-monosulphate (AFm) phase, while some remain as free chlorides in the pore solution. The free chlorides in pore solution cause depassivation of rebar [8]. They also lower the pH of the mortar/concrete surrounding the embedded steel reinforcement, leading to pitting corrosion. Binding of chlorides results in their immobilization and subsequently reducing their amount in mortar/concrete matrix. It is generally agreed that blended cements exhibit higher chloride binding ability due to higher amount of alumina and CSH phases that result from the incorporated pozzolana.

Blended cement exhibits low porosity as a result of increased amount of secondary cementitious materials due to pozzolana reaction [9]. Low porosity has been found to greatly reduce the penetration of chlorides in mortars. Other research work shows that chloride diffusion coefficient is dependent on pore structure since pore can be both room for holding chloride ion and route for ion diffusion [5]. Pozzolana materials increase nucleation sites for precipitation of hydration products resulting in pore refinement. Low porosity can also be achieved by use of mortars with high compressive strength [10]. Incorporation of pozzolanic materials in blended cements has been found to lower the permeability of aggressive ions such as chlorides. Reduced penetration of chloride ions in hydrated cements has been found to lower the susceptibility of rebars to pitting corrosion [11]. This has been found to improve the durability of cement based structures.

Calcined clay has been used as pozzolanic materials for strength enhancement and improvement of durability in cement based structures [12]. Previous studies conducted by the same authors [13] involved blending of calcined clay at 35% replacement of the mass of Ordinary Portland Cement (OPC) to make a test cement labeled PCC35. It was established that PCC35 and Portland Pozzolana Cement (PPC) exhibited similar performance in terms of chloride ( $\text{Cl}^-$ ) ingress, apparent diffusion coefficient ( $D_{\text{app}}$ ), and strength development before and after exposure to  $\text{Cl}^-$  media. In addition, it was found that PCC35 met the minimum standard requirements of compressive strength for pozzolana based cement mortars as specified in the EAS 148-1:2000 standard. However, the 28-day compressive strength of PCC35 was lower compared to OPC mortars. The present study therefore aims to improve the 28-day compressive strength of PCC35 to match or exceed that of OPC by using sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) solution as an activator and evaluating its performance in chloride rich media. In this study, chloride ingress in chemically activated PCC35 (PCC35-0.5 M  $\text{Na}_2\text{SO}_4$ ) and nonactivated PCC35 (PCC35- $\text{H}_2\text{O}$ ) vis-à-vis with commercial OPC and PPC was investigated. Additionally, the influence of compressive strength and porosity on chloride ingress resistance was also evaluated.

## 2. Materials and Methods

**2.1. Materials.** OPC (42.5 N) and standard sand used in this work were supplied by East Africa Portland Cement

TABLE 1: Binder characteristics of the mortars.

Binder label	Main binder characteristics
PCC35- $\text{H}_2\text{O}$	Cast using PCC35 and water
PCC35-0.5 M $\text{Na}_2\text{SO}_4$	Cast using PCC35 and 0.5 M $\text{Na}_2\text{SO}_4$
PPC- $\text{H}_2\text{O}$	Cast using PPC and water
OPC- $\text{H}_2\text{O}$	Cast using OPC and water

Company—Athi River, Kenya. Raw clay was sampled from three different places within Ugweri region (longitude  $37^\circ 34' 19.47''\text{E}$ , latitude  $0^\circ 25' 20.44''\text{S}$ ) in Embu County, Kenya. In each place, three clay samples were obtained from a depth of 0.9 meters. Clay sampled from a given place was mixed mechanically to obtain a homogenous mixture and stored in labeled polythene bags.

### 2.2. Methods

**2.2.1. Calcination of Clay.** The sampled clay was dried to a constant weight at  $105^\circ\text{C}$  in an oven. 5 kg of the dried clay, in a platinum trough, was placed in an electrical muffle furnace and allowed to heat for 4 hours at  $800^\circ\text{C}$ . The resultant clay was cooled and ground in a laboratory ball mill until 95% of the calcined clay particles were below  $45\ \mu\text{m}$  size.

**2.2.2. Binder Formulations.** PCC35 was prepared by mechanically blending 35% of calcined clay and 65% of OPC by mass to make a 6 kg of PCC35 binder in an automatic mixer for 1 hour. The pioneering research conducted by the same authors [13] showed that PCC35 exhibited lower 28-day compressive strength compared to OPC mortars. To overcome this limitation, 0.5 M  $\text{Na}_2\text{SO}_4$  solution was used as a chemical activator during casting of PCC35 to accelerate its 28-day compressive strength. The composition of different binders used in this work is given in Table 1.

**2.2.3. Compressive Strength Determination.** Mortar preparation, curing, and compressive strength were done in accordance with EAS 148-1:2000 standard. However, slight modifications were adopted. First, a water/binder ( $w/b$ ) ratio of 0.55 was used to obtain a workable mix. Secondly, 0.5 M  $\text{Na}_2\text{SO}_4$  solution was also used in place of water as a chemical activator.

**2.2.4. Determination of Porosity.** The porosity of the mortars was calculated using

$$P = \frac{W_a - W_b}{W_a - W_c} \times 100, \quad (1)$$

where  $P$  is the porosity,  $W_a$  is the specimen weight in the saturated surface-dry condition,  $W_b$  is the specimen dry weight until reaching constant weight in oven, and  $W_c$  is the weight of saturated specimen.

**2.2.5. Chloride Ingress.** For each category of cement, three prisms, cured for 28 days, were subjected to chloride profiling using a method prescribed by ASTM C1202-97 (2001) standard. Cathode compartment of an electrochemical setup

was filled with 500 cm<sup>3</sup> of the 3.5% NaCl solution. The anode compartment cell was filled with 500 cm<sup>3</sup> of the sodium hydroxide (NaOH) solution. A mortar prism was firmly placed in the assembled test cell using epoxy coating. A stainless steel rod was dipped in each cell such that they were in contact with the periphery faces of the specimen. The rods were fastened with a clamp at both ends to hold the whole assembly together. An external voltage cell was used to apply a voltage difference of 12 ± 0.1 V between the electrodes. After the whole assembly was completed and the solutions in both the anode and cathode compartments were in place, the power was switched on. The top of the container was covered with a polyethylene paper and the entire model was maintained at 22 ± 1°C. Both solutions in the anode and cathode compartments were stirred at intervals of 30 minutes for a period of 36 hours by use of a glass rod to maintain a relatively uniform concentration throughout the compartment depth. After the exposure duration, mortar prisms were removed from the electrochemical setup and they were packed and sealed in plastic bags. A mortar prism, from the plastic bag, was polished from all sides using sand paper. The prism was cut into 10 mm slices along the length using 2 mm thick water lubricated saw. The slices were dried to a constant mass in an oven at 105°C. The dried slices were pulverized and ground to pass through 76 μm sieve. Between each grinding or pulverization, the grinder or pulverizer was thoroughly cleaned to avoid cross-sample contamination. The ground samples were kept in a sealed plastic bags awaiting chloride analysis.

**2.2.6. Chloride Profiling.** The chlorides at each depth of cover were analyzed using Mohr titration procedure in all the mortars considered. A similar study was conducted by the same authors [13]. However, in the present case, mortars were separately cast using water and 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution as an activator.

The diffusion of chloride in mortar was approximated from the solution to Fick's second law of diffusion where chloride ion diffusion into mortar was estimated in one direction only (*x*-axis) given as [14]

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

where *D* is the chloride diffusion coefficient of mortar, *C* is the chloride concentration at any time, and *t* is a function of depth, *x*. The estimation of apparent chloride diffusion coefficients was achieved under nonsteady state conditions assuming boundary conditions  $C_{(x,t)} = 0$  at  $t = 0, 0 < x < \infty$ ,  $C_{(x,t)} = C_s$  at  $x = 0, 0 < t < \infty$ , constant effects of coexisting ions, linear chloride binding, and one-dimensional diffusion into semi-infinite solid [2]. Crank's solution to Fick's second law of diffusion is given by [14]

$$C_{(x,t)} = C_s \left[ 1 - \operatorname{erf} \left( \frac{x}{\sqrt{4D_{\text{app}}t}} \right) \right], \quad (3)$$

where  $C_{(x,t)}$  is concentration of Cl<sup>-</sup> at any depth *x* in the concrete bulk at time *t*, *C<sub>s</sub>* is the surface concentration, and

*D<sub>app</sub>* is the apparent diffusion coefficient. The error correction function, erf, is the Gaussian error function obtained from computer spreadsheets. The chloride profiles were obtained by fitting (3) to experimentally determined chloride profile concentrations, thus determining the values of *D<sub>app</sub>* and *C<sub>s</sub>* mathematically.

The penetration of chloride ions in mortar is a slow process [2]. Therefore, in order to assess chloride penetration, a test method that accelerates the process was employed [15]. The movement of chlorides was accelerated through the use of an electrical field. The movement of ions in a solution under an electrical field is governed by the Nernst-Planck equation [15] given by

$$-J_i = D_i \frac{\delta C_{i(x)}}{\delta x} + \frac{Z_i F}{RT} D_i C_i + \frac{\delta E(x)}{\delta x} + C_i V_{i(x)}, \quad (4)$$

where *J<sub>i</sub>* is the flux of the ionic species *i*, *D<sub>i</sub>* is the diffusion coefficient of the ionic species *i*, *C<sub>i</sub>(*x*)* is the concentration of ionic species *i* as a function of location *x*, *Z<sub>i</sub>* is the valence of ionic species *i*, *F* is Faraday's constant, *R* is the universal gas constant, *T* is the temperature, *E*(*x*) is the applied electrical potential as a function of *x*, *V<sub>i</sub>(*x*)* is the convection velocity of *i*, and  $\delta E_{(x)}$  is change in applied potential difference with distance. Since there was no convection (i.e., no pressure or moisture gradients) the term  $C_i V_{i(x)}$  reduces to zero. Further, it was assumed that pure diffusion term is negligible compared to the effect of electrical migration, which is reasonable for a sufficiently strong applied voltage (at least 10–15 V) [16], and the term  $D_i (\delta C_{i(x)} / \delta x)$  reduces to zero. Equation (4) was thus reduced to

$$J_i = \frac{Z_i F}{RT} D_i C_i \frac{\delta E(x)}{\delta x} \quad (5)$$

Equation (6) allows the solution for *D* once the chloride ion flux is determined assuming that the voltage drop across the cell is linear, the chloride concentration is constant in the cell (steady state conditions have been reached), and the heating of the solution and concrete is negligible [15, 16].

The calculation of *D<sub>app</sub>* (apparent diffusion coefficient) from chloride profiles is a common practice since this parameter depicts the mortar/concrete's ability to resist chloride penetration in a natural environment. The most common present practice to measure the amount of chlorides versus penetration depth is to use chloride profile after a predetermined time of exposure [2, 14, 17–19]. The fitting of this profile to the error function equation enabled the calculation of the diffusion coefficient, *D<sub>mig</sub>*. *D<sub>mig</sub>* is the diffusion coefficient in an accelerated laboratory setup; it was therefore necessary to compare the diffusion of these chlorides in a natural setup. *D<sub>mig</sub>* was, therefore, converted to *D<sub>app</sub>* using

$$D_{\text{app}} = \frac{RT}{Z_i F} D_{\text{mig}} \frac{\ln t^2}{\Delta \phi}, \quad (6)$$

where *R* is the universal gas constant, *T* is the temperature in *K*, *Z<sub>i</sub>* is the charge of the ionic species *i*, *F* is the Faraday's constant, *t* stands for the time taken for the ionic species to penetrate in mortar, and  $\Delta \phi$  represents the voltage applied, normally about 12 ± 1 V [15, 16].

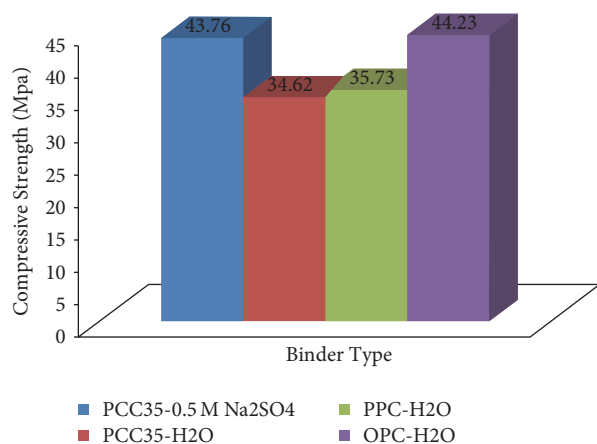


FIGURE 1: Compressive strength of mortars versus binder type.

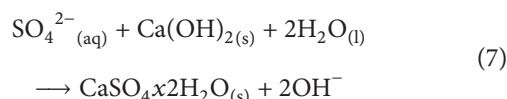
### 3. Results and Discussion

#### 3.1. Compressive Strength

**3.1.1. Compressive Strength Test Results before Exposure to Chloride Rich Media.** The 28-day compressive test results are given in Figure 1.

It was observed that 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution greatly increased the compressive strength of PCC35 compared to nonactivated PCC35 on the 28th day of curing. This can be attributed to sulphate activation. Sulphate activation is based on the ability of sulphates to react with aluminium oxide in the glass phase of pozzolana to form ettringite [20]. Presence of ettringite has been found to contribute to strength at early ages [21]. More ettringite formation results in a significant solid volume increase, hence forming a less porous structure and subsequently leading to higher early strength [20]. The lower compressive strength exhibited by nonactivated PCC35 is likely due to presence of large amount of unactivated and/or undissolved pozzolana in the mortar matrix. High early compressive strength in 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution activated mortars is possibly due to acceleration of pozzolana reaction and formation of more AFt phase.

According to [20] during sulphate activation, the pH of pore water in cement matrix is greatly increased by sulphate through ion exchange as shown in



Presence of increased content of OH<sup>-</sup> raises the pH of mortar matrix. High pH has been reported to increase the dissolution of pozzolana materials hence improving pozzolanic reaction [22, 23]. This subsequently increases the early compressive strength of cement mortars due to increased formation CSH that is responsible for strength [24].

**3.1.2. Compressive Strength Test Results after Exposure to Chloride Rich Media.** The results for percent gain in compressive strength after exposure of the mortar in 3.5% NaCl are given in Figure 2.

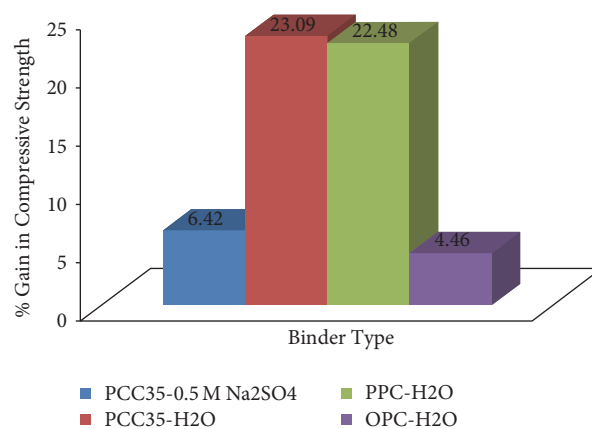


FIGURE 2: Percentage gain in compressive strength versus binder types.

All the test cement showed an increase in compressive strength after exposure to the chloride rich media. This could be attributed to the ingress of sodium and chloride ions in the cement matrix. Na<sup>+</sup> and Cl<sup>-</sup> are known to activate or initiate residual cement hydration or pozzolanic reaction and thus increase strength of mortar/concrete [25].

Blended cement (PCC35-0.5 M Na<sub>2</sub>SO<sub>4</sub>, PCC35-H<sub>2</sub>O, and PPC-H<sub>2</sub>O) exhibited higher gain in compressive strength than OPC-H<sub>2</sub>O. This could be attributed to the fact that in blended cements ingressed chlorides activate the pozzolana reaction resulting in increased compressive strength. The slight increase in compressive strength observed in OPC-H<sub>2</sub>O is possibly due to the ingressed chlorides initiating hydration reaction of residual OPC-H<sub>2</sub>O at 28 days of curing.

PCC35-0.5 M Na<sub>2</sub>SO<sub>4</sub> exhibited the lower gain in compressive strength compared to PCC35-H<sub>2</sub>O. This could be attributed to low chloride ingress in PCC35-0.5 M Na<sub>2</sub>SO<sub>4</sub> due its low porosity. PCC35-0.5 M Na<sub>2</sub>SO<sub>4</sub> exhibited high 28-day compressive strength leading and low porosity. Low porosity in PCC35-0.5 M Na<sub>2</sub>SO<sub>4</sub> mortars is responsible for reduced ingress of aggressive chlorides ions. Chloride ions activate pozzolanic reaction [13]. Reduced ingress in PCC35-0.5 M Na<sub>2</sub>SO<sub>4</sub> therefore could have resulted in low gain in compressive strength. Another possible explanation for low gain in compressive strength of PCC35-0.5 M Na<sub>2</sub>SO<sub>4</sub> mortars is that the presence of the chemical activator (0.5 M Na<sub>2</sub>SO<sub>4</sub>) in PCC35-0.5 M Na<sub>2</sub>SO<sub>4</sub> might have accelerated the pozzolanic reaction to a large extent leading to limited reactants (pozzolana-alumina and silica) on the 28th day of curing to be acted upon by the ingressed chlorides. However, PCC35-H<sub>2</sub>O exhibited higher porosity hence higher amount of chlorides penetrated the mortar bulk. The ingressed chlorides activated the pozzolanic reaction resulting in higher gain in compressive strength.

**3.2. Porosity.** The porosity of 28-day cured mortar prisms for different binders is given in Figure 3.

It was observed that blended cement exhibited lower porosity than OPC-H<sub>2</sub>O. The low porosity in blended cement mortars can be attributed to the fact that pozzolana materials



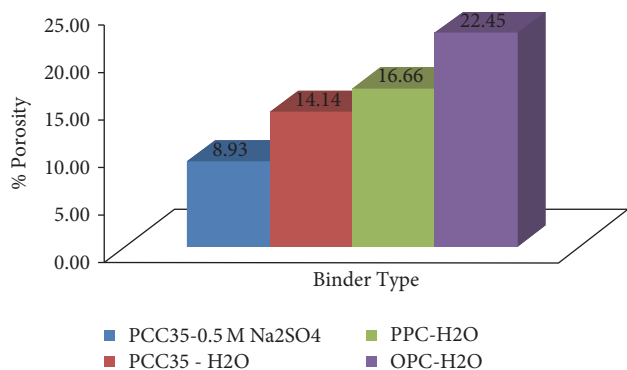


FIGURE 3: Porosity of 28-day cured mortar prisms versus binder types.

such as calcined clays increase nucleation sites for precipitation of hydration products resulting in pore refinement thus lowering the porosity [26]. CH produced during hydration of OPC-H<sub>2</sub>O consumed in pozzolanic reaction forming secondary CSH and CAH [27]. However, in OPC-H<sub>2</sub>O, the pozzolana reaction does not occur; hence CH produced during hydration leads to formation of voids in the mortar matrix thus increasing its porosity [24].

PCC35-0.5 M Na<sub>2</sub>SO<sub>4</sub> exhibited lower porosity compared to PCC35-H<sub>2</sub>O. This is possibly due to low high early compressive strength in 0.5 M Na<sub>2</sub>SO<sub>4</sub> activated mortars. The addition of 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution might have resulted in accelerated pozzolana reaction and formation of more Aft phase thus causing the PCC35-0.5 M Na<sub>2</sub>SO<sub>4</sub> mortars to be denser than PCC35-H<sub>2</sub>O.

**3.3. Chloride Ingress.** In this study, chloride diffusion coefficients were used as a measure of chloride ingress in mortar and they were approximated from the solution to Fick's second law of diffusion.

**3.3.1. Chloride Diffusivity.** Chloride profile analysis entailed determination of the concentration of the ions (Cl<sup>-</sup>) at different depths of cement mortar bulk of PCC35-H<sub>2</sub>O, PCC35-0.5 M Na<sub>2</sub>SO<sub>4</sub>, OPC-H<sub>2</sub>O, and PPC-H<sub>2</sub>O. Chloride profiles for the amount of chlorides against depth of penetration for each category of the cement mortar are presented in Figure 4.

It was observed that the amount of chlorides decreased with increase in depth of penetration in all cement categories considered. In addition, the amount of chlorides at the shallow depths of cover (<20 mm) decreases sharply. This is possibly due to chloride binding capacity of the cement mortars. All cement binds a proportion of the chloride present [7]. Chlorides can be chemically or physically bound in the mortar matrix [5]. Chloride binding reduces diffusion rates of chlorides into the bulk of the cement mortars involved. Chloride binding at the surface of mortar can be attributed to increased CSH content [1]. The increased CSH bound Na<sup>+</sup> in NaCl solution and hence retarded the ingress of the chlorides.

Blended cement exhibited lower chloride ingress compared to OPC-H<sub>2</sub>O. Blended cements exhibit low porosity as a result of increased amount of CSH and CAH gels due

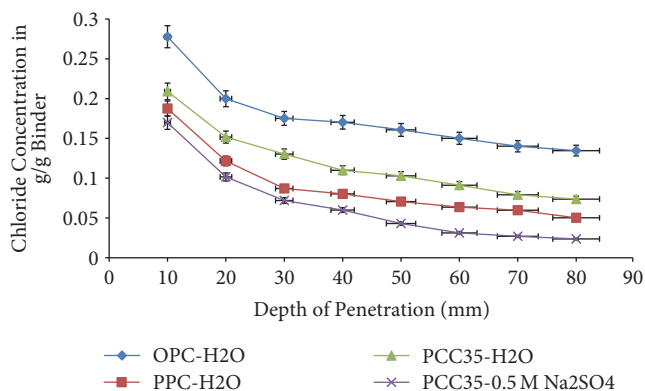


FIGURE 4: Concentration of chloride ions (g/g of cement) mortar versus depth (mm).

TABLE 2:  $D_{app}$  and  $r^2$ -values for different cement mortars at  $w/c = 0.55$ .

Binder type	$D_{app}$ (m <sup>2</sup> /s) × 10 <sup>-12</sup>	$r^2$ -values
PCC35-H <sub>2</sub> O	6.914	0.964
PCC35-0.5 M Na <sub>2</sub> SO <sub>4</sub>	5.948	0.969
PPC-H <sub>2</sub> O	6.932	0.969
OPC-H <sub>2</sub> O	18.069	0.942

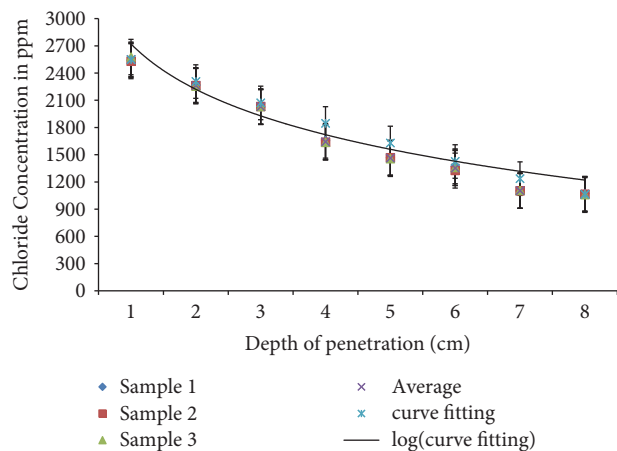
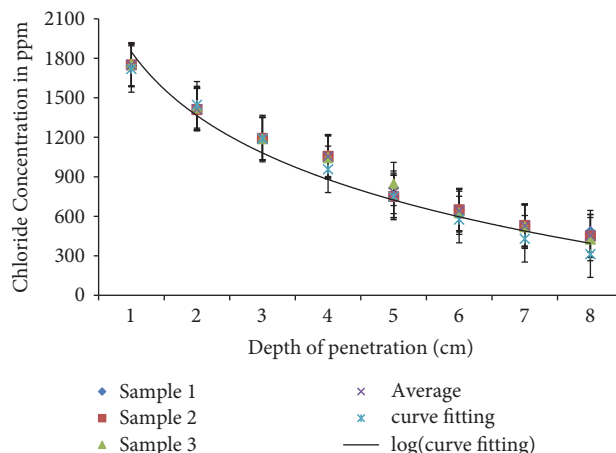
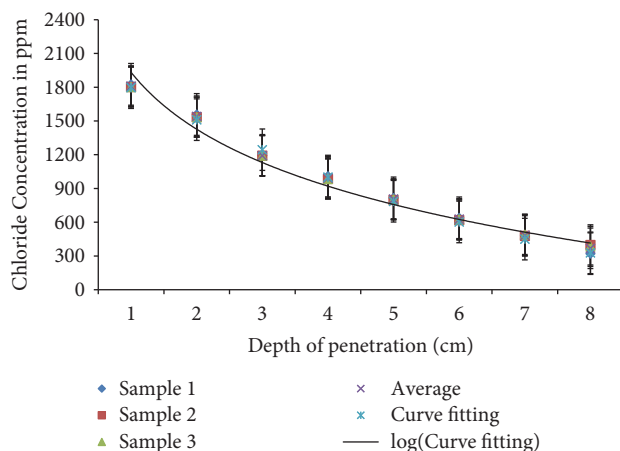
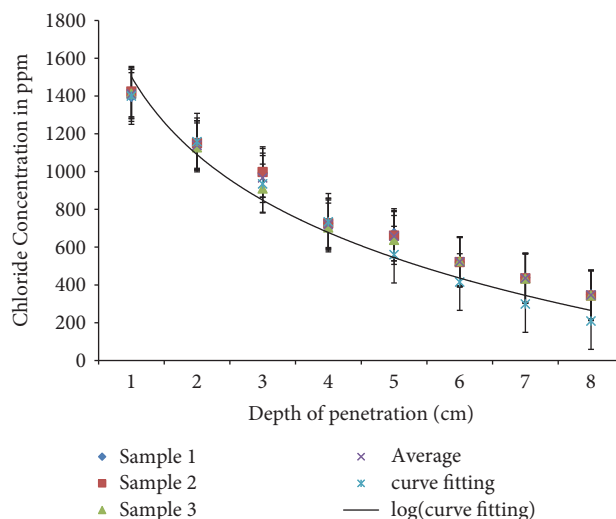
to pozzolana reaction [28]. Low porosity greatly reduces the ingress chlorides in mortars [29]. As observed, OPC-H<sub>2</sub>O had high porosity due to large amount of CH produced during hydration. It is therefore apparent that the high porosity in OPC-H<sub>2</sub>O provided the pathway for the ingress of chlorides in mortar. Moreover, blended cements have higher binding capacity as a result of incorporated pozzolana materials and increased hydration products [18, 19]. Hydrated blended cement has been reported to contain higher content of CSH content than hydrated OPC-H<sub>2</sub>O [30]. This could have further offered more chloride binding sites resulting in increased immobilization of chloride ions into the blended cement mortars.

PCC35-0.5 M Na<sub>2</sub>SO<sub>4</sub> exhibited the lower chloride ingress compared to PCC35-H<sub>2</sub>O. This can be attributed to higher compressive strength in PCC35-0.5 M Na<sub>2</sub>SO<sub>4</sub> mortars as a result of accelerated pozzolana reaction and formation of more Aft phase. High compressive strength results in reduced spaces in mortar matrix hence greatly reducing the penetration of chloride ions [31]. PCC35-0.5 M Na<sub>2</sub>SO<sub>4</sub> also exhibited lower porosity compared to PCC35-H<sub>2</sub>O. Low porosity has been reported to greatly reduce the ingress of aggressive ions chloride ions included.

**3.3.2. Apparent Chloride Diffusion Coefficients ( $D_{app}$ ).** The error fitting curve for determination of  $D_{app}$  for the test cement (PCC35-H<sub>2</sub>O, PCC35-0.5 M Na<sub>2</sub>SO<sub>4</sub>, PPC-H<sub>2</sub>O, and OPC-H<sub>2</sub>O) mortars is presented in Figures 5–8.

$D_{app}$  and  $r^2$ -values for different cement mortars obtained from the error fitting curves are presented in Table 2.

OPC-H<sub>2</sub>O exhibited higher apparent diffusion coefficient ( $D_{app}$ ) values than blended cements. This could be attributed

FIGURE 5: Error function fitting curve for OPC-H<sub>2</sub>O.FIGURE 7: Error function fitting curve for PCC35-H<sub>2</sub>O.FIGURE 6: Error function fitting curve for PPC-H<sub>2</sub>O.FIGURE 8: Error function fitting curve for PCC35-0.5 M Na<sub>2</sub>SO<sub>4</sub>.

to high porosity in OPC-H<sub>2</sub>O mortars. The connectivity of the pore system depends on the degree to which it has been filled with hydration products [19]. Therefore low diffusion coefficients in blended cements are expected due to the fact that blended cements has more cementitious materials in the mortar matrix [6]. Low  $D_{app}$  values in blended cements compared to OPC-H<sub>2</sub>O could be due higher chloride binding capacity in blended cements than in OPC-H<sub>2</sub>O mortars. Blended cement has been found to bind more chlorides than OPC-H<sub>2</sub>O [32]. High chloride binding ability effectively removes a large proportion of chloride ions in the pore structure of a cement mortar. This possibly led to low chloride ingress in the cement mortar characterized by low  $D_{app}$  as observed in this study.

PCC35-0.5 M Na<sub>2</sub>SO<sub>4</sub> exhibited the lower apparent diffusion coefficient ( $D_{app}$ ) values compared to PCC35-H<sub>2</sub>O. This can be attributed to lower chloride ingress in PCC35-0.5 M Na<sub>2</sub>SO<sub>4</sub> mortars due to low porosity of the mortar specimens. Low porosity provides high resistance chloride ingress mortars. This can also lead to lower apparent diffusion coefficient ( $D_{app}$ ) values in PCC35-0.5 M Na<sub>2</sub>SO<sub>4</sub> mortars.

## 4. Conclusion

Based on the study, it can be concluded that chemically activated mortars (PCC35-0.5 M Na<sub>2</sub>SO<sub>4</sub>) exhibited higher compressive strength compared to nonactivated PCC35 on the 28th day of curing. However, chemically activated PCC35 had the least gain in compressive strength when exposed to chloride rich media, lower porosity, and lower chloride ingress in terms of  $D_{app}$ , compared to OPC, PPC, and nonactivated PCC35.

## Conflicts of Interest

The authors declare that there are no conflicts of interest.

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## References

- [1] M. U. Khan, S. Ahmad, and H. J. Al-Gahtani, "Chloride-induced corrosion of steel in concrete: An overview on chloride diffusion and prediction of corrosion initiation time," *International Journal of Corrosion*, vol. 2017, Article ID 5819202, 9 pages, 2017.
- [2] E. P. Nielsen and M. R. Geiker, "Chloride diffusion in partially saturated cementitious material," *Cement and Concrete Research*, vol. 33, no. 1, pp. 133–138, 2003.
- [3] B. Pacewska and I. Wilińska, "Comparative investigations of influence of chemical admixtures on pozzolanic and hydraulic activities of fly ash with the use of thermal analysis and infrared spectroscopy," *Journal of Thermal Analysis and Calorimetry*, vol. 120, no. 1, pp. 119–127, 2015.
- [4] T. Woubishet Zewdu and S. Esko, "Service life prediction of repaired structures using concrete recasting method: State-of-the-art," in *Proceedings of the 11th International Scientific Conference on Modern Building Materials, Structures and Techniques, MBMST 2013*, pp. 1138–1144, Lithuania, May 2013.
- [5] T. J. Gardner, *Chloride transport through concrete and implications for rapid chloride testing*, Msc [Thesis], University of Cape Town, Cape Town, South Africa, 2006.
- [6] J. Wang, P. M. Basheer, S. V. Nanukuttan, and Y. Bai, "Influence of compressive loading on chloride ingress through concrete," in *Proceedings of the Civil Engineering Research Association of Ireland (CERAI)*, 2014.
- [7] M. V. A. Marinescu and H. J. H. Brouwers, "Chloride binding in OPC hydration products," in *Proceedings of 17th Ibausil International Conference on Building Materials*, H. B. Fischer and K. A. Bode, Eds., Bauhaus-Universität Weimar, Weimar, Germany, 2009.
- [8] M. V. A. Florea and H. J. H. Brouwers, "Chloride binding related to hydration products: Part I: Ordinary Portland Cement," *Cement and Concrete Research*, vol. 42, no. 2, pp. 282–290, 2012.
- [9] P. Chindaprasirt and S. Rukzon, "Strength, porosity and corrosion resistance of ternary blend Portland cement, rice husk ash and fly ash mortar," *Construction and Building Materials*, vol. 22, no. 8, pp. 1601–1606, 2008.
- [10] O. S. B. Al-Amoudi, W. A. Al-Kutti, S. Ahmad, and M. Maslehuddin, "Correlation between compressive strength and certain durability indices of plain and blended cement concretes," *Cement and Concrete Composites*, vol. 31, no. 9, pp. 672–676, 2009.
- [11] Z. H. Dong, W. Shi, and X. P. Guo, "Initiation and repassivation of pitting corrosion of carbon steel in carbonated concrete pore solution," *Corrosion Science*, vol. 53, no. 4, pp. 1322–1330, 2011.
- [12] M. Antoni, *Investigation of cement substitution by blends of calcined clays and limestone [Ph.D. thesis]*, École Polytechnique Fédérale de Lausanne, 2013.
- [13] J. M. Marangu, J. Muthengia, and J. Wa-Thiongo, "Performance of potential pozzolanic cement in chloride media," *IOSR Journal of Applied Chemistry (IOSR-JAC)*, vol. 7, no. 2, pp. 36–44, 2014.
- [14] J. Crank, *The Mathematics of Diffusion*, Clarendon Press, Oxford, UK, 2nd edition, 1975.
- [15] E. Samsonl, J. Marchandl, and K. A. Snyder, "migration test results," *Materials and Structures*, vol. 36, pp. 156–165, 2003.
- [16] M. Castellote, C. Andrade, and C. Alonso, "Phenomenological mass-balance-based model of migration tests in stationary conditions. Application to non-steady-state tests," *Cement and Concrete Research*, vol. 30, no. 12, pp. 1885–1893, 2000.
- [17] J. Bai, S. Wild, and B. B. Sabir, "Chloride ingress and strength loss in concrete with different PC-PFA-MK binder compositions exposed to synthetic seawater," *Cement and Concrete Research*, vol. 33, no. 3, pp. 353–362, 2003.
- [18] D. K. Mutitu, J. K. Karanja, and J. M. Wachira, "Diffusivity of chloride ion in mortar cubes made using ordinary portland and portland pozzolana cements," *IOSR Journal of Applied Chemistry*, vol. 7, no. 2, pp. 67–73, 2014.
- [19] R. A. Patel, Q. T. Phung, S. C. Seetharam et al., "Diffusivity of saturated ordinary Portland cement-based materials: A critical review of experimental and analytical modelling approaches," *Cement and Concrete Research*, vol. 90, pp. 52–72, 2016.
- [20] C. Shi and R. L. Day, "Comparison of different methods for enhancing reactivity of pozzolans," *Cement and Concrete Research*, vol. 31, no. 5, pp. 813–818, 2001.
- [21] A. M. Rashad, Y. Bai, P. A. M. Basheer, N. B. Milestone, and N. C. Collier, "Hydration and properties of sodium sulfate activated slag," *Cement and Concrete Composites*, vol. 37, no. 1, pp. 20–29, 2013.
- [22] A. Allahverdi and J. Ghorbani, "Chemical activation and set acceleration of lime-natural pozzolan cement," *Ceramics - Silikaty*, vol. 50, no. 4, pp. 193–199, 2006.
- [23] C. Shi and R. L. Day, "Chemical activation of blended cements made with lime and natural pozzolans," *Cement and Concrete Research*, vol. 23, no. 6, pp. 1389–1396, 1993.
- [24] A. Tironi, M. Trezza, A. Scian, and E. Irassar, "Incorporation of Calcined Clays in Mortars: Porous Structure and Compressive Strength," *Procedia Materials Science*, vol. 1, pp. 366–373, 2012.
- [25] E. A. Kishar, D. A. Ahmed, M. R. Mohammed, and R. Noury, "Effect of calcium chloride on the hydration characteristics of ground clay bricks cement pastes," *Beni-Suef University Journal of Basic and Applied Sciences*, vol. 2, no. 1, pp. 20–30, 2013.
- [26] J. Sarfo-Ansah, E. Atiemo, K. A. Boaky, D. Adjei, and A. A. Adjaottor, "Calcined clay pozzolan as an admixture to mitigate the alkali-silica reaction in concrete," *Journal of Materials Science and Chemical Engineering*, vol. 02, no. 05, pp. 20–26, 2014.
- [27] S. Abo-El-Enein, M. Amin, F. El-Hosiny, S. Hanafi, T. ElSokkary, and M. Hazem, "Pozzolanic and hydraulic activity of nano-metakaolin," *HBRC Journal*, vol. 10, no. 1, pp. 64–72, 2014.
- [28] M. R. Karim, M. M. Hossain, M. N. N. Khan, M. F. M. Zain, M. Jamil, and F. C. Lai, "On the utilization of pozzolanic wastes as an alternative resource of cement," *Materials*, vol. 7, no. 12, pp. 7809–7827, 2014.
- [29] D. M. Roy, W. Jiang, and M. R. Silsbee, "Chloride diffusion in ordinary, blended, and alkali-activated cement pastes and its relation to other properties," *Cement and Concrete Research*, vol. 30, no. 12, pp. 1879–1884, 2000.
- [30] I. Janotka, L. Krajci, P. Uhlík, and M. Bacuvčík, "Natural and calcined clayey diatomite as cement replacement materials: microstructure and pore structure study," *International Journal of Engineering Research and Technology*, vol. 3, no. 13, pp. 20–26, 2014.
- [31] L. Zingg, M. Briffaut, J. Baroth, and Y. Malecot, "Influence of cement matrix porosity on the triaxial behaviour of concrete," *Cement and Concrete Research*, vol. 80, pp. 52–59, 2016.



- [32] D. H. Kim, K. Shimura, and T. Horiguchi, "Effect of tensile loading on chloride penetration of concrete mixed with granulated blast furnace slag," *Journal of Advanced Concrete Technology*, vol. 8, no. 1, pp. 27–34, 2010.



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