Performance of Potential Pozzolanic Cement in Chloride media

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Abstract: *The paper presents finding of the pozzolanic activity of calcined clays from selected regions of Embu County – Kenya. The results are also presented for the compressive strength development and Chloride ingress resistance of the blend of the calcined clays with Ordinary Portland Cement (OPC), vis a vis commercial OPC and Portland Pozzolana cement (PPC). The objective of the study was to investigate the viability of using locally available materials to make affordable cementitious materials. Sampled clays were activated at different temperatures and time and blended with OPC at different replacement levels. The blends were subjected to accelerated chloride ingress. The blended cement and commercial PPC showed lower chloride ingress, in terms of apparent diffusion coefficients, compared to OPC with the blended cement exhibiting least chloride ingress*

Keywords: *Pozzolana, Calcined Clays, Blended Cement*

I.   Introduction

There is an inherent desire by most people to own decent and affordable houses. On average, the cost of building materials for a housing structure comprises about 50 percent of the total cost of the building (Jones and Dhir, 2000). For lower income shelters this percentage could rise to as much as 80 percent depending on the country where the construction occurs (Laban and Benedetti, 2002; Jones and Dhir, 2000). The high cost is normally attributed to the high prices of cement. A majority of the citizens in developing countries, especially where the Government do not have an established housing and shelter system, cannot afford the cement, which is a major building binder for housing and construction in general (Muthengia, 2008). This has lead to the mushrooming of slums such as Kibera in Nairobi-Kenya. There is an increasing demand for decent housing as the shanty houses poses various health challenges (Ghebreyesus *et al.*, 2000).

The cost of construction materials is increasing day by day because of high demand, scarcity of raw materials and high price of energy. Portland cement is the most common type of cement used in construction. It is an expensive binder due to the high cost of production associated with the high energy requirements of its manufacturing process (Neville, 1995). From the standpoint of energy saving and environmental conservation, the use of alternative constituents in construction materials is now a global concern.

Other relatively low cost materials with cementitious properties are natural pozzolana such as volcanic tuff, clay and waste products from industrial plants such as slag, fly ash and silica fume. They can be used as a partial replacement for Portland cement to make blended cements. In addition, to reduce the cost of binder, there are potential technological benefits from the use of pozzolanic materials as those blended with Portland cement in concrete applications. These include decreased permeability of aggressive ions and increased ultimate strength and durability of concrete. These benefits have lead to an increased demand for pozzolanic materials for use in making pozzolanic cements. The objective of this study was to investigate the potential use of calcined clays from Runyenjes in Kenya as pozzolana.

II.   Materials and methods

Sampling

In this study raw clays were sampled from three different places within Ugweri region (longitude 37 ^{0} 34' 19.47'' E, latitude 0^0 25' 20.44'' S) in Eastern province in Kenya. In each place, three clay samples were obtained from a depth of 3 feet. Clays sampled from a given place were mixed mechanically. The samples were labeled UC1, UC2 and UC3.

Chemical analysis of clays
X-ray Fluorescence Analysis

X-ray Fluorescence Spectroscopy, (XRFS) method was used for the chemical analysis in the usual manner using a sequential X-ray spectrophotometer model number PW4025. The results were presented as percentage oxide.

Flame Photometry and Atomic Absorption Spectroscopy (AAS)

Analysis of the oxides of Na and K were done using a flame photometer model number 410 series .The amount of CaO, MgO, Fe_2O_3, and SiO_2 were determined using AAS model number 6200 – SHIMADZY series. The absorption measurement signal was recorded sequentially each time a new standard solution was used. Calibration curve of concentration of standard solutions versus signal was done. Similar volumes of digested clay sample which corresponded to those of standard solutions were run the on the flame photometer or Atomic Absorption Spectrometer following the instruction manual using standard calibration method.

Calcination of clay

The sampled clay was dried to a constant weight at 110 ^{0}C to a constant weight using an Electrical Muffle furnace model number OSK 9540-MK-SP 38351. 1 kg of the dried clay, in 18 cm by 27 cm clay trough, was put in the furnace and allowed to heat for two hours at 700 ^{0}C. The procedure was repeated at 700 ^{0}C for one hour and at 800 ^{0}C for one hour. The resultant clay was cooled, finely ground using laboratory ball mill to 90 μm mesh size and subjected to pozzolanicity test.

Pozzolanicity test

Pozzolanicity test was carried out following the method prescribed by Luxán *et al.* (1989). Calcium hydroxide solution was prepared in a 250-ml conical flask by addition of 200 mg of analytical-grade $Ca(OH)_2$ in a 200 ml of de-ionized water. The conical flask was then placed in a magnetic plate and the temperature of the solution maintained at 40 ±1 °C. The solution was continuously stirred using a magnetic stirrer. Electrical conductivity of the solution was continuously monitored by a digital conductivity-meter (Oakton CON 510 Series model). After the lime–water system reached a constant conductivity, 5 g of pozzolanic material was added to the solution in the conical flask. Conductivity values of the solution were recorded at thirty minutes intervals after adding the calcined clays for 270 minutes.

The same procedure was repeated for the pozzolana–water systems without lime. Corrected conductivity–time values for lime – pozzolana system were obtained by subtracting the contribution of pozzolana – water from lime – pozzolana system.

Preparation of PCC

Requisite amounts of calcined clay and OPC were mechanically mixed using trowels on a tray to make PCC's at 25, 30, 35, 40, 45 and 50 per cent substitution of OPC. They were labeled PCC25, PCC30, PCC35, PCC40, PCC45 and PCC50 respectively.

Sand

The sampled sand was washed with de-ionized water and sun-dried for two days to a constant weight to remove mud and other soluble substances. The dry sand was sieved to remove coarse material through a 5 mm sieve.

Compressive Strength Determination

This was done in accordance with EAS 148-1(2000). Three mortar prisms each having dimensions of 160 mm × 40 mm × 40 mm were prepared at a go. This was done by mixing 450 g of OPC and 1350 g of sand with two trowels on a non – porous plate for one minute. Requisite amount of water was added to make cement mortars with water /cement ratios of 0.4, 0.55 and 0.63. They were then placed in a curing room with relative humidity above 90 percent and at a temperature of 27 ± 2 ^{0}C for 24 hours ± 30 minutes. After 24 hours ± 30 minutes, they were de – moulded and marked accordingly for identity purpose. The marked prisms were submerged immediately in curing tank maintained at 23 ^{0}C for twenty seven days. On the twenty eighth day, three prisms for each cement category were removed from curing tank and allowed to drain for thirty minutes. The prisms were tested for compressive strength using a Compressive strength machine model number SSC-546.

Chloride profiling

For each category of cement, three prisms, cured for twenty eight days were subjected to chloride profiling using a method prescribed by ASTM C1202-97 (2001). Cathode compartment of an electrochemical set up was filled with 500 cm^3 of the 3.5 percent sodium chloride solution. The anode compartment cell was filled with 500 cm^3 of the 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 $12 \pm 0.1V$ 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 electric current in the test cell was monitored by use of a digital ammeter at intervals of thirty minutes for a period of thirty six hours. The top of the container was covered with a polyethylene paper and the entire model maintained at $22 \pm 1\ ^0C$. Both solutions in the anode and cathode compartments were stirred periodically by use of a glass rod to maintain a relatively uniform concentration throughout the compartment depth.

After exposure duration, the mortar prisms were removed from the electrochemical set up. The mortar prisms 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 $105\ ^0C$.

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.

III.   Results and discussion

Chemical Analysis Results for Sampled Clays
Table 3.1- 3.3 shows the chemical composition in terms of oxides of sampled clays from selected regions within Ugweri region.

Table 3.1: Chemical Composition of the Sampled Clays (XRF Analysis)

Oxide %	UC1	± S.D	UC2	± S.D	UC3	± S.D
Al_2O_3	20.70	±0.02	16.0	±0.01	22.17	±0.02
SiO_2	43.40	±0.36	72.6	±0.00	33.44	±0.05
Fe_2O_3	2.30	±0.57	2.72	±0.01	2.30	±0.60
$Al_2O_3+ SiO_2+ Fe_2O_3$	66.4	±0.89	91.32	±0.02	57.91	±0.59

Table 3.2: Chemical Composition of the Sampled Clays (AAS Analysis)

Oxide %	UC1	± S.D	UC2	± S.D	UC3	± S.D
Al_2O_3	22.01	±0.06	16.4	± 0.65	23.57	± 0.20
SiO_2	44.02	± 0.11	71.26	± 1.68	34.26	± 0.30
Fe_2O_3	1.90	±0.04	2.61	± 0.02	2.52	± 0.17
MgO	0.40	± 0.01	0.2	± 0.02	0.27	± 0.14
CaO	1.90	± 0.26	0.14	± 0.23	1.22	± 0.17
$Al_2O_3+ SiO_2+ Fe_2O_3$	67.93	± 0.438	90.27	± 2.571	60.35	± 0.685

Table 3.3: Chemical Composition of Na_2O and K_2O in the Sampled Clays (Flame photometry   Analysis)
KS 02 1260(1994) and ASTM C618 (2003) prescribes that the sum of Al_2O_3, SiO_2 and Fe_2O_3 should be above

Oxide %	UC1	± S.D	UC2	± S.D	UC3	± S.D
Na_2O	0.05	± 0.01	0.13	± 0.02	0.42	± 0.02
K_2O	0.78	± 0.02	0.72	± 0.07	0.69	± 0.04

70 percent. The sum of these oxides of UC2 surpassed the aforementioned specifications. The oxides are essential in any pozzolana as they provide the siliceous and aluminous material that reacts with lime during the hydration reactions of blended cements.

IV.   Pozzolanicity Test Results

Selected Pozzolanicity test results are presented in figure 3.1. They are presented as percentage loss of conductivity against time.
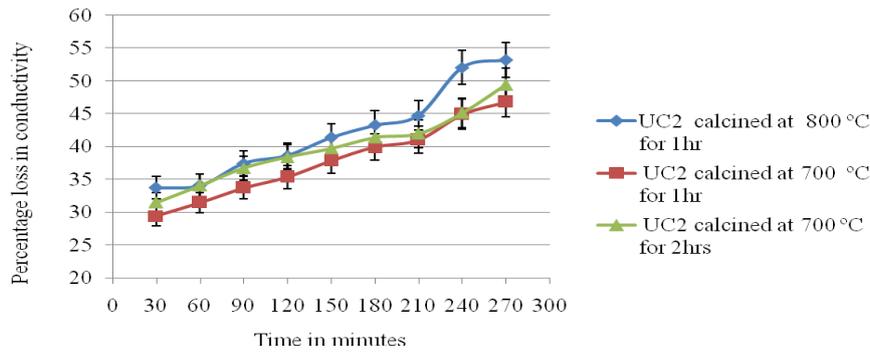
Figure 3.1: Pozzolanicity as a Function of Loss of Conductivity with Time for UC2 Clay Calcined at Different Temperatures and/or Time

It was observed that the calcined clays resulted in decreased conductivity of the water – lime mixture. The loss in electrical conductivity is due to lime fixation as a result of pozzolanic reactivity (Taylor, 1997). The three sample clays, UC1, UC2 and UC3, exhibited pozzolanic properties when calcined at different temperatures. Incinerating the clay samples at temperature of 800 ^{0}C for one hour was observed to be the optimum calcining temperature for all the clay samples. Heating clays at elevated temperatures is necessary to produce a reactive pozzolana (Gathua, 2005). Among the three clay samples, UC2 was observed to exhibit the highest pozzolanic activity. This could be attributed to its higher Al_2O_3, SiO_2 and Fe_2O_3 content than the others. UC2 calcined at 800 ^{0}C for one hour was therefore subjected to further analysis.

Compressive Strength Test Results
4.4.1 Compressive Strength Test Results after 28 Days Curing
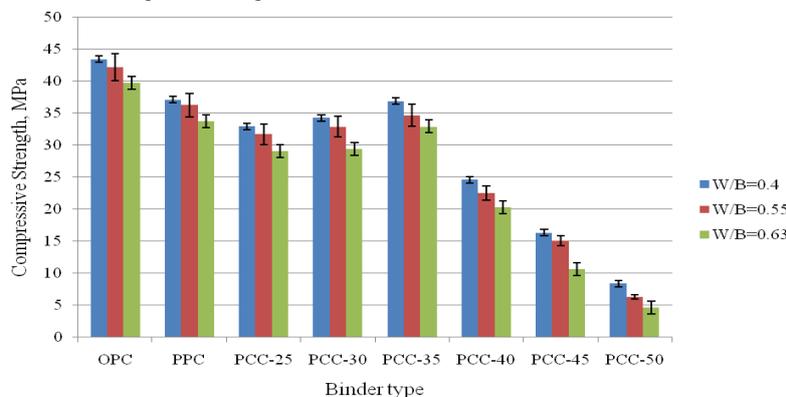The compressive test results are given in figure 4.4

Figure 4.4: Compressive Strength of Test Cements on Verses Binder Type the Twenty Eighth of Curing

It was observed that w/b ratio greatly influenced the strength of all test cements mortars at the twenty eighth day. The strength decreased in the order w/b = 0.4 > w/b = 0.55 > w/b= 0.63. This is because w/b ratio affects the porosity of the hardened paste and the flow or rheology of the mixture as well as cohesion between paste and aggregate (Bentz, 2006).

OPC showed the highest compressive strength as compared to all test cements irrespective of the w/b ratio used. This could be attributed to the fact that OPC contained a higher proportion of C_3S and C_2S that are mainly responsible for the strength development (Rahhal and Talero, 2005). There was notable variation in strength at various replacement levels of OPC with calcined clays. At each w/b ratio, there was increase in compressive strength from PCC25 to PCC 35. When calcined clay is used as part of the cementitious material in a mortar/concrete mix, it reacts with water and $Ca(OH)_2$ to form more CSH. The additional CSH densifies the mortar/concrete matrix enhancing strength (Muller, 2005). The increase in the amount of calcined clays used avails the needed alumino-silicate material to react with the calcium hydroxide produced during the hydration of OPC (Muller, 2005).

There was markedly a progressive decline in compressive strength at increasing replacement levels from 35 percent to 50 percent. Similar observations were made by Darweesh *et al.* (2007) while working with calcined bentonite clays. The worker attributed this to presence of residual inactive or unreacted bentonite minerals as result of low amount of CH. Moreover, the researchers (Darweesh *et al.*, 2007) attributed this to the fact that the high replacement levels of OPC with calcined bentolite clays resulted to a decrease in the primary

binding materials originating from hydration of OPC. More so, the authors attributed this to the fact that although calcined bentonite clays provided the aluminosilicate material for the pozzolanic reaction, the CH produced by hydration of OPC at these replacement levels, was increasingly becoming insufficient for pozzolanic reaction.

The minimum standard requirements of compressive strength for cement mortar prisms by EAS 148-1(2000), specifies a 28 days compressive strength of 32.5 MPa for Portland pozzolana cements. PCC cement met this specification up to 35 per cent replacement of OPC by mass regardless of the w/b used. Compressive strength values for PCC40 - PCC50 did not meet this standard. There was no significant difference in terms of compressive strength gain between PCC35 and commercial PPC at w/b = 0.40, w/b = 0.55, w/b = 0.63 as the T-calculated values were 0.594, 0.354 and 0.499 respectively. The T- calculated values were far below the T-critical value of 6.314. Similarly, there was no significant difference in terms of compressive strength between PCC30 and commercial PPC at w/b = 0.40, w/b = 0.55, w/b = 0.63 as the T- calculated values were 0.303, 0.270 and 0.008 respectively. The T- calculated values were also way below the T- critical value of 6.314.

4.3.2 Compressive Strength Results after Exposure to Chloride Ions Solution
The percent gain in compressive strength results after exposure of the mortar in 3.5 percent sodium chloride solution are given in Figure 4.5
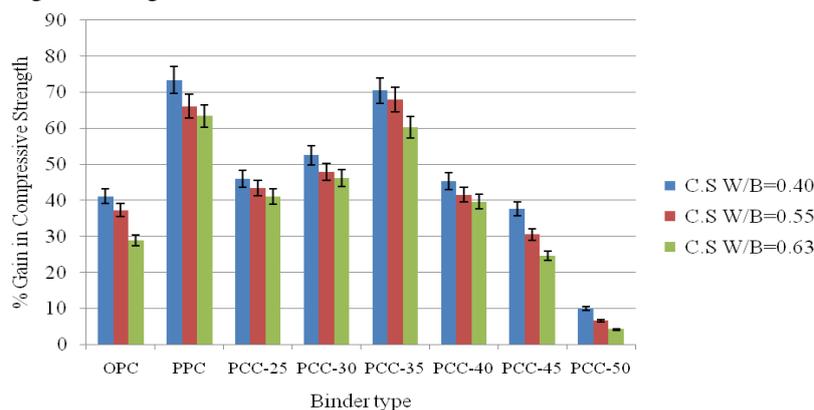

Figure 4.5: Percentage Gain in Compressive Strength verses Binder Types at varying w/b ratios

It was observed that in all cement categories, there was an increase in compressive strength after exposure to the Cl⁻ media. The gain could be attributed to the ingress of sodium and chloride ions in the cement matrix (Luke, 2006). The Na^+ and Cl^- are known to activate or initiate residual cement hydration or pozzolanic reaction and thus increase strength of mortar /concrete (Lorenzo *et al.*, 2003). Lorenzo *et al.* (2003) observed an increase in flexural strength of samples that contained fly ash in marine simulated media. The researchers attributed this to the ingress of Na^+ and Cl^-.

There was marked decrease in compressive strength gain from PCC40 - PCC50. Similar observations were made by Muller (2005) while studying the pozzolanic activity of natural clay minerals with respect to environmental geotechnics. The author observed that at replacement levels above 35 percent of OPC by mass caused a decrease in strength irrespective of the presence of chemical activators. The worker (Muller, 2005) attributed this to low pozzolana –CH reaction. Our results can also be explained in a similar way.

There was notable increase in compressive strength in all categories of cements at various w/b ratios. There was no significance difference in terms of compressive strength gain between PCC35 and commercial PPC at w/b = 0.40, w/b = 0.55, w/b = 0.63 as the T- calculated values were 0.1621, 0.5321 and 0.2871 respectively. The T- calculated values were far below the T- critical value of 6.314. Similarly, there was no significance difference in terms of compressive strength gain between PCC30 and commercial PPC at w/b = 0.40, w/b = 0.55, w/b = 0.63 as the T- calculated values were 0.1697, 0.1329 and 0.1201 respectively. The T-calculated values were also way below the T- critical value of 6.314.

4.5 Ingressed Chloride Profiling
Selected Chloride profiles for the chloride penetration against depth of cover for each category of the cement mortar are presented in Figures 4.6. Chloride profile analysis in this study involved the determination of the concentration of the ions (Cl⁻) at different depths of cement mortar bulk of PCC, OPC and PPC.
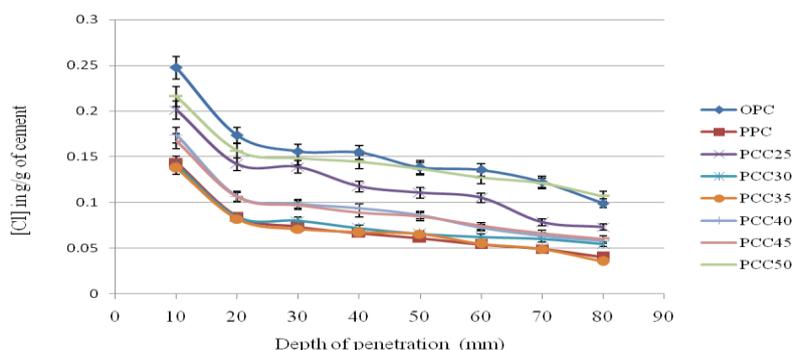
Figure 4.6: Graph of Concentration of Chloride Ions in g/g of Cement Mortar Verses Depth (mm) at 0.4 w/b
It was observed that in all categories of cements, the total chloride decreased with increase in depth of penetration. This was even more pronounced as the w/c ratio reduced. There is sharp decrease in the amount of chlorides at the shallow depths of cover (<20 mm). This could be attributed to chloride binding capacity and diffusivity of chlorides in the cement mortar (Qiang, 2009). All cements bind a proportion of the chloride present (Hirao *et al.*, 2005). Chloride binding reduces diffusion rates of chlorides into the cement bulk of the cement involved (Hirao *et al.*, 2005).

At greater depths of cover (>20mm), it was observed that the OPC exhibited the highest chloride ingress especially at higher w/c ratios. This can be attributed to the fact that blended cements have lower CH than OPC in their pore solution (Bao-min and Li-Jiu, 2004; Hirao *et al.*, 2005). A low amount of CH in blended cements is as a result of pozzolanic reaction (GjØrv and Vennesland, 1979). CH, acts as the main source of OH⁻ hence the decreased amount of OH⁻ leads to a lower exchange capacity between the OH⁻ and the chlorides in the pore water (GjØrv and Vennesland, 1979). These factors clearly explain the low chloride ingress in blended cements used in this study.

Blended cements exhibited lower chloride ingress compared to OPC. The use of pozzolana has been reported to lower the chloride ingress in mortar /concrete (Gonçalves, 2009). The resistance to aggressive attack of PPC's has been attributed to factors such as the pore refinement of its microstructure, the low alkalinity of its pore solution, and the low portlandite, Ca(OH)$_2$, content. These factors, which arise from the pozzolanic reaction, impede diffusion of aggressive ions such as chlorides (Lorenzo *et al.,* 2002).

The presence of pozzolana leads to a greater precipitation of cement gel products than occurs in OPC, which more effectively block the pores more effectively and therefore helping to reduce permeability (Garcı´a *et al.*, 2000). The water-soluble calcium hydroxide liberated by hydrating cement may leach out of hardened concrete and leave voids for the ingress of water. In the pozzolanic reaction, by combining with the Calcium hydroxide (CH) directly reduces the amount of CH, which can reduce the leaching of CH (Garcı´a *et al.*, 2000). The additional products from pozzolanic reaction, C-S-H will close the voids, which result in more dense concrete, and consequently reduce the permeability of concrete arising from a pore refining process (Bai *et al.*, 2003).

Beyond 35 percent replacement of OPC, the amount of chloride ingress in cement mortar gradually increased at all w/b. This is perhaps due to the fact that replacement of OPC beyond 35 percent, the added pozzolana only serves as a filler material with low resultant CSH. Similar observations were made by Khater *et al.* (2010) although studying the Influence of metakaolin on resistivity of cement mortar to magnesium chloride solution. The researchers attributed this to low chloride binding with increase in amount of pozzolana added due to formation of highly porous and less dense cement mortar with low amount of CSH.

As the w/b ratio increased, there was a marked rise in the chloride ingress in all the profile depths of the test cements in the order 0.4 < 0.55 < 0.63. A high w/c ratio is known to contribute to a higher permeability consequently increasing the ingress of chlorides in cement pastes (Page *et al.,* 1986). When the w/b ratio increases, the porosity of the resultant mortar increases (Wild *et al.,* 1996). This results in higher diffusivity of the chloride into the mortar. Vaishali *et al.* (2011) although, studying the chloride ion permeability studies of metakaolin based high performance concrete observed that cement mortar with w/b ratios of 0.3 had a lower chloride content than those cast at a w/b ratio of 0.5. The workers attributed this to the fact that decreased w/b ratio increases the resistance of concrete/mortar by lowering permeability and porosity.
There was no significance difference in terms of chloride ingress between PCC35 and commercial PPC at w/b = 0.40, w/b = 0.55, w/b = 0.63 as the T- calculated values were 0.1621, 0.5321 and 0.2871 respectively. The T- calculated values were far below the T- critical value of 6.314. Similarly, there was no significance difference in terms of compressive strength gain between PCC30 and commercial PPC at w/b = 0.40, w/b = 0.55, w/b = 0.63 as the T- calculated values were 0.1697, 0.1329 and 0.1201 respectively. The T- calculated values were also way below the T- critical value of 6.314.

4.6 Apparent Chloride Diffusion Coefficients

The error fitting curve for determination of apparent chloride diffusion coefficient (D_{app}) for the test cement, PCC50 mortar at w/b=0.63 is presented in figure 4.9. Moreover, the error fitting data for each cement category is presented in table 4.5 - 4.7. Similar error fitting curves were used for determination of the apparent diffusion coefficients for each cement category at w/b=0.40, w/b=0.55 and w/b=0.63.
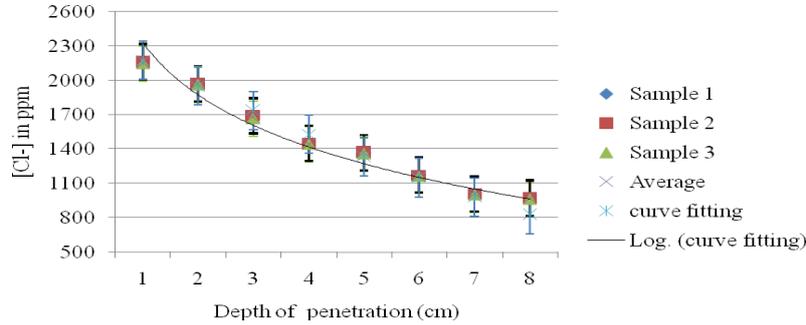

Figure 4.9: Error Function Fitting Curve for PCC50 (w/b = 0.63, D_{app}= 1.832 x 10^{-11} m^2/s, r^2 = 0.954)

Table 4.4: D_{mig}, D_{app} and r^2 - Values for different Cement Mortars at w/b = 0.40

Binder type	W/B=0.40		
	D_{mig} (m^2/s) $\times 10^{-10}$	D_{app} (m^2/s) $\times 10^{-12}$	r^2- values
PCC25	1.559	8.777	0.961
PCC30	1.332	7.499	0.966
PCC35	1.234	6.948	0.969
PCC40	1.552	8.738	0.961
PCC45	1.562	8.795	0.961
PCC50	1.890	10.64	0.955
PPC	1.234	6.948	0.969
OPC	2.773	15.61	0.945

Table 4.5: D_{mig}, D_{app} and r^2 - Values for different Cement Mortars at w/b = 0.55

Binder type	W/B=0.55		
	$D_{mig} \times 10^{-10}$	$D_{app} \times 10^{-12}$	r^2
PCC25	2.609	14.688	0.947
PCC30	1.528	8.602	0.962
PCC35	1.424	8.015	0.964
PCC40	1.597	8.993	0.961
PCC45	1.632	9.192	0.960
PCC50	1.929	10.860	0.955
PPC	1.231	6.933	0.969
OPC	3.210	18.069	0.942

Table 4.6: D_{mig}, D_{app} and r^2 - Values for different Cement Mortars at w/b = 0.63

Binder type	W/B=0.63		
	D_{mig} (m^2/s) $\times 10^{-10}$	D_{app} (m^2/s) $\times 10^{-11}$	r^2- values
PCC25	2.820	1.587	0.945
PCC30	1.964	1.106	0.954
PCC35	1.453	0.818	0.964
PCC40	1.968	1.108	0.954
PCC45	1.968	1.109	0.954
PCC50	3.255	1.832	0.954
PPC	1.259	0.708	0.968
OPC	3.382	1.904	0.941

It was observed that the higher the w/b the higher was the D_{app} across all cement categories. Similar observations were made by Paya *et al*. (2010) and Vaishali *et al*.(2011). The workers attributed this to the fact that high w/b affects porosity mortars. The connectivity of the pore system depends on the amount of original mixing–water filled space and the degree to which it has been filled with hydration products (Wallah *et al.,* 2004). This could explain why increase in w/b ratios resulted to increased diffusion coefficients.

It was observed that the blended cements showed lower D_{app} than OPC at all w/b ratios. Anwar *et al.* (2001) although investigating the influence of RHA in concrete observed a lower ratio of soluble/total chloride ions content than those of OPC concretes. The worker (Anwar *et al.*, 2001) attributed this to the fact that chloride penetration into concrete is affected by the chloride binding capacity of the concrete. Blended cements have been found to bind more chlorides than OPC (Schlangen *at al.*, 2007). High chloride binding ability effectively removes a large proportion of chloride ions in the pore structure of a cement mortar (Schlangen *at al.*, 2007). This leads to low chloride ingress in the cement mortar characterized by low D_{app} as observed in this study. The chloride binding capacity is controlled by the amount of cementing materials used and the C_3A content in the concrete (Hossain, 2005). C_3A content of the cement influences its binding capacity, with increased C_3A content leading to increased binding (Hossain, 2005).

In this study, there was a marked decrease in D_{app} from PCC25 to PCC 35. Similar observations were made by Khan (2010) although investigating the chloride ingress resistance of high performance concrete containing supplementary composites silica fumes, by up to 10 percent replacement level of OPC. The researcher, observed a significant decrease in the chloride diffusion coefficients in binary systems with increase in amount of silica fume. The researcher attributed this to the increased chloride binding with increase in the amount of pozzolana added (silica fume). Vaishali *et al.* (2011), although working on chloride ion permeability studies of metakaolin based high performance concrete, observed that the chloride diffusion coefficients decreased with increase in OPC replacement levels up to 30 percent. The author attributed this to densification of concrete by addition of pozzolana thus lowering porosity. Increased chloride binding and low porosity are therefore the major factors that lead to the decrease in D_{app} from PCC25 to PCC 35.

There was a notable increase in apparent diffusion coefficients from PCC40 – PCC50 at all the w/b ratios considered. This is due to low amount of secondary cementious materials formed as a result of minimal pozzolanic reaction. There was marked decrease in compressive strength development in the said cements as shown in Figure 4.4 and 4.5.

OPC exhibited the highest D_{app} values regardless of the w/b ratio used. This can be attributed to high exchange capacity of OH^- (Qiang, 2009; Poon *et al.*, 2006), low Al_2O_3 phase due to lack of pozzolana inclusion (Balonis and Glasser, 2009). Similar observations were made by Lothenbach and Winnefeld (2006) while studying thermodynamic modeling of the hydration of Portland cement.

There was no significant difference in chloride ingress between PCC35 and commercial PPC at w/b = 0.40, w/b = 0.55, w/b = 0.63 as the T- calculated values were 0.1621, 0.5321 and 0.2871 respectively. The T- calculated values were far below the T- critical value of 6.314. Similarly, there was no significant difference in terms of compressive strength gain between PCC30 and commercial PPC at w/b = 0.40, w/b = 0.55, w/b = 0.63 as the T- calculated values were 0.1697, 0.1329 and 0.1201 respectively. The T- calculated values were also way below the T- critical value of 6.314. From the chloride profiles in figures 4.6 – 4.8, the test cements exhibited similar ingress in chloride ions across all depths of cover. Similarly, from the compressive strength development (figure 4.4), there was no statistical difference between the test cements. Clearly, this shows the test cements PCC30, and PCC35 can be used in similar environments as commercial PPC. This can be attributed to packing of pozzolana grain in hydrated cement (Arya *et al.,* 1990; Guerrero *et al.*, 2000), formation of secondary cementious materials thereby decreasing permeability (Bai *et al.*, 2003; Luke, 2006) as well as inclusion of the Cl^- binding Al_2O_3, from pozzolana (Lorenzo *et al.*, 2003; Barberon *et al.*, 2005).

Acknowledgements

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