Chloride Diffusion in Cementitious Pastes: Comparative Study between OPC and Blended Cements Containing Natural Pozzolana and Slag

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ABSTRACT Chloride apparent diffusion coefficient (D_{app}) of a porous media is an indicative of its capacity to resist chloride ingress. It is used to predict the service life of reinforced concrete structures. This paper presents experimental study to measure the effect of blended cement paste containing Sudanese Natural Pozzolana (SNP) from Bayuda Desert in the Northern State on D_{app} by using Bulk Diffusion Test (Nord-Test NT-Build 443). Three mixes are investigated, each mix contains 3 specimens, the first mix is a reference mix with 100% Ordinary Portland Cement (OPC) compared with second mix having another containing 75%OPC:25%NP, third mix having 50%OPC:50%GGBS. All pastes have water binder ratio of 0.55. The D_{app} of 50%OPC:50%GGBS is found to be 1.794×10^{-6} mm²/s which is lowest among the pastes. The D_{app} for 75%OPC:25%NP is 2.80×10^{-6} mm²/s and the D_{app} for 100%OPC is 3.145×10^{-6} mm²/s which is the highest.

Keywords: Chloride, Diffusion, Natural Pozzolana, Slag.

1. INTRODUCTION

In modern days, concrete takes an enormous role around the globe in the usage of man-made construction material. It offers many characteristic such as: appropriate mechanical and durability. Furthermore, it can be transformed into various shapes and sizes easily. Although concrete illustrates many advantages, its disadvantages ought to be in our consideration. Environmental problem may arise from manufacture of Portland cement as component of concrete.

Individually, the cement industry is estimated to be responsible consequently, lowering the consumption of cement is presumably a solution towards sustainable development [1]–[5].

Natural pozzolans (NP) has been extensively used as a supplementary cementing materials, particularly in regions which lacks other industrial pozzolans such as pulverised fuel ash (PFA) known as fly-ash, ground granulated blastfurnace slag (GGBS) and silica fume (SF). The Industrial pozzolanas have proven to

improve durability and strengths, however, they are not produced locally in Sudan [6]. Usually the use of NP involves technical benefits, energy preservation and emission compatible with sustainable development [2].

NP have become important because of their role in concrete durability [3] specially if need to improve resistance to chloride ingress.

The Sudan has many resources of NP materials that are not used so cements manufacturers in Sudan must utilize more amounts to produce Portland Pozzolanic Cement [7].

The NP of Bayoda desert in Northern Sudan [8] when mixed as partial replacement of cement, Mechanical strength tests confirmed the actual behavior of the Bayoda pozzolana blended cement substitution of OPC with the samples, gave better strength development results in comparison with OPC specimen. There are several short-term investigation on Sudanese Natural Pozzolanas (SNP) [8]–[10] most of them are limited to compressive strength, also there are

classification respect to shrinkage, physical and chemical properties of the SNP.

There is a need to investigate the NP role in durability of concrete, namely, resisting chloride and sulphate attacks on concrete, especially there are no local industrial pozzolanic materials to improve durability in materials in Red Sea coastal structures, as well as, some effluent sewer works in Industrial Khartoum area. Concrete durability is characterized by its resistance to weathering action, chemical attack, and other degradation processes.

The aim of this paper is to measure the effect of chloride diffusion in blended cement paste containing the SNP and compare, it with reference pastes containing Ordinary Portland Cement (100% OPC) and 50%OPC:50%GGBS.

2. CHLORIDE DIFFUSION: A BRIEF REVIEW OF THE UNDERLYING THEORY

Chloride diffusion into concrete, like any diffusion process, is controlled by Fick's First Law, which, in the one-dimensional situation normally considered, states in Equ. 1:

$$J = -D_{eff} \frac{dC}{dx} \quad \text{Equ 1}$$

Where:

J = is the flux of chloride ions (mole/m³.s) or (kg/m³.s),

D_{eff} = is the effective diffusion coefficient (m²/s),

C = is the concentration of chloride ions (kg/m³) or (%mass) and x is a position variable.

In practical terms, this equation is only useful after steady-state conditions have been reached, i.e. there is no change in concentration with time. It can be used, however, to derive the relevant equation for non-steady conditions (when concentrations are changing), often referred to as Fick's Second Law [12] as shown in Equ 2,:

$$\frac{\partial C}{\partial t} = D_{eff} \frac{\partial^2 C}{\partial x^2} \quad \text{Equ 2}$$

which includes the effect of changing concentration with time (t). This has been solved using the boundary condition $C(x=0, t > 0) = C_0$ (the surface concentration is constant at C_0), the initial condition $C(x > 0, t = 0) = 0$ (the initial concentration in the concrete is zero) and the infinite point condition $C(x = \infty, t > 0) = 0$ (far

enough away from the surface, the concentration will always be zero) [13].

The solution is given by Equ 3:

$$C(x, t) = C_s - (C_s - C_i) \cdot \text{erf} \left(\frac{x}{\sqrt{4 \cdot D_a \cdot t}} \right) \quad \text{Equ 3}$$

where:

$C(x, t)$ = chloride concentration, measured at depth x and exposure time t , mass %,

C_s = projected chloride concentration at the interface between the exposure liquid and test specimen that is determined by the regression analysis, mass %,

C_i = initial chloride-ion concentration of the cementitious mixture prior to submersion In the exposure solution, mass %,

x = depth below the exposed surface (to the middle of a layer), m,

D = apparent chloride diffusion coefficient, m²/s,

t = the exposure time, s, and

erf = the error function defined by Equ 4.

$$\text{erf}(Z) = \frac{2}{\sqrt{\pi}} \int_0^Z \exp(-u^2) du \quad \text{Equ 4}$$

Non-linear Regression Analysis Perform the regression analysis by minimizing the sum given in Equ 5.

$$S = \sum_{n=0}^N \Delta C^2(n) = \sum_{n=0}^N (C_m(n) - C_c(n))^2 \quad \text{Equ 5}$$

Where:

S = sum of squares to be minimized, (mass %) ²,

N = the number of layers ground off,

$\Delta C(n)$ = difference between the measured and calculated chloride concentration of the n th layer, mass %,

$C_m(n)$ = measured chloride concentration of the n th layer, mass %, and $C_c(n)$ = calculated chloride concentration in the middle of the n th layer, mass %.

3. MATERIAL AND METHODS

A. Material

Cement:

Ordinary Portland cement (OPC) produced by Atbara cement Co., Grade 42.5 conforming to BS EN197-1:2000 was used for casting all the specimens.

Natural Pozzolana:

Powdered SNP in this study was obtained from Bayuda Desert in the Northern State, some 63Km South of Merowe city. Its chemical properties are listed in Table I.

TABLE I: CHEMICAL PROPERTIES OF NATURAL POZZOLANA

Compounds	(Silicon dioxide) SiO ₂	(Aluminum oxide) Al ₂ O ₃	(Iron III Oxide) Fe ₂ O ₃	Loss on Ignition	Moisture content
Percentage %	51.51	16.47	11.86	5.4	0.975

Ground Granulated Blastfurnace Slag (GGBS):

Its imported from Egypt and has been used to cast foundation for Comb-Cycle Power Station in Port Sudan, its chemical properties are listed in Table II.

TABLE II: CHEMICAL PROPERTIES OF GGBS.

Compounds	Result %Wt.
Magnesium Oxide (MgO)	4.110
Aluminum oxide (Al ₂ O ₃)	10.056
Silicon dioxide (SiO ₂)	30.699
Phosphorus Pent oxide (P ₂ O ₅)	0.070
Sulfur Trioxide (SO ₃)	1.854
Chloride (Cl)	0.075
Potassium Oxide (K ₂ O)	0.368
Calcium Oxide (CaO)	50.651
Titanium Dioxide (TiO ₂)	1.1015
Chromium III Oxide (Cr ₂ O ₃)	0.0031
Manganese III Oxide (Mn ₂ O ₃)	0.278
Iron III Oxide (Fe ₂ O ₃)	0.708
Strontium Oxide (SrO)	0.085

Sodium chloride (NaCl):

Sodium chloride technical grade manufactured by Extra Pure (S.D. Fine-Chem Limited (SDFCL), India).

Epoxy:

Epoxy (SIKA, UAE) that is made of two packs (Resin & Hardener) was used as a sealant applied on all sides of the paste cylinder except the face exposed to 3% NaCl solution.

Deionized water:

Used for casting, curing and preparing NaCl solution and all standardized solutions.

Standard Solutions:

Sodium Hydroxide Na(OH)₂, Nitric Acid (HNO₃), Silver Nitrate (AgNO₃), Ammonium Thiocyanate (NH₄SCN), Ferric Ammonium Sulphate NH₄Fe(SO₄)₂ according to BS EN 1744-5:2006 (Volhard's method).

B. Methods

Preparation of specimens

Three mixes were made as listed in Table III. Three replicates of each mix were cast using cylindrical mold 10 cm diameter * 75 cm height

TABLE III: MIX PROPORTION

Mixes	Water/Binder ratio	Ordinary Portland Cement (OPC) (kg)	Sudanese Natural Pozzolan a (SNP) (kg)	Ground Granulated Blast furnac Slag (GGBS) (kg)	Water (kg)
100% OPC.	0.55	8.478	-	-	4.663
75%OPC:25 %NP.	0.55	6.358	2.120	-	4.663
50%OPC:5 0%GGBS	0.55	4.239	-	4.239	4.663

Casting:

Cement pastes were made up by mixing cement with deionized water to required w/c (0.55). Then, the paste was mixed for 3 munities by laboratory Hobart concrete mixer. After being mixed, the speciemen were cast and into the cylindrical molds and compacted manually. The specimens were sealed and demolded for 24 hours.

Curing:

The specimens were cured into deionized water for 14 days at 27°C, and saturated with limewater (Ca(OH)₂ 3 g/l) for 28 days, to prevents any initial sorption effects when the chloride solution is introduced.

Salt Ponding:

All cured specimens' sides were coated using the Epoxy sealant expect one face exposed to air as shown in Figure 1. The only uncoated face was then exposed to a 2.8 M NaCl solution, (165 g/l), they were soaked for extra period of 35 days.

Fig. 1: specimen after coated with Epoxy (Dia.10 cm *75 cm)

Slicing:

The powder obtained by grinding off specimen by lathe machine into 8 layers parallel to the exposed surface after being dried for 2 days as shown in Figure 2 The slicing recommended to be done accordance to ASTM C1152/1152M [11] for the short duration the depth intervals were moderated as shown in Table IV.

Chemical analysis:

From grinding; 72 powder samples were collected (24 samples for each mix) in plastic pages and they had been digested as shown in Figures 3-(A,B) and titrated as shown in Figure 3-(C) according to BS EN 1744-5:2005 (Volhard's method).

4. RESULTS AND DISCUSSION

The average results represented by the volume of SCN^- ions from a burette are shown in Figure 4.

Concentration of chloride ion Cm (% mass) calculated according to BS EN 1744-5:2005: (Volhard's method) are shown in Figure 5.

The volume of SCN^- ions as shown in Figure 4 increase with increasing the depth from surface which mean there is more excess of silver ion reacting with SCN^- and, Cl^- decrease with increasing the Ag^+ ions and depth.

Concentration of chloride ion Cm (% mass) calculated according to BS EN 1744-5:2005 (Volhard's method) are shown in Figure 5. The chloride ions concentration, as shown in Figure 5, decrease with increasing the depth.

Fig. 2: grinding off specimen by Lathe machine.

TABLE IV: RECOMMENDED BY ASTM C1152/1152 AND ACTUAL DEPTH INTERVALS (IN MM) FOR POWDER GRINDING

W/C (0.55)	Recommended depth (mm)	Actual depth (mm)
Depth 1	0-1	0- 0.5
Depth 2	1-3	0.5-1
Depth 3	3-5	1-1.5
Depth 4	5-8	1.5-2
Depth 5	8-12	2-3
Depth 6	12-16	3-4
Depth 7	16-20	4-5
Depth 8	20-25	5-6

Fig. 3-(a); sample during digestion

Fig. 3-(b); sample after digestion and during filtration

Fig. 3-(c); sample after titration (equivalent point).

Fig. 4: the volume of SCN⁻ ions for OPC, 25%NP, and 50%GGBS.

Also it has been found that the concentration of chloride in the same layer at any depth for GGBS is lower than NP, and the NP is lower than OPC. That means the GGBS and NP have a higher resistance to chloride ingress. This maybe due to improvement of microstructure attributed to hydration of GGBS and NP in later ages and also has a good resisting characteristic to chloride ingress [16].

Fig. 5: Concentration of chloride ion C_m , (mm)

The chloride concentrations C_m (mass%) and corresponding depths were entered into Microsoft Excel®, 2010 and a polynomial best fit regression was carried out to predict chloride concentration at surface of specimens (C_s) as shown in Figure 6.

The correlation Equations are displayed in Figure 6 as well as :

For 100%OPC $y = 0.0025x^2 - 0.0301x + 0.1175$ & $R^2 = 0.9602$

For 75%OPC : 25%NP $y = 0.0015x^2 - 0.0221x + 0.0861$ & $R^2 = 0.9784$

For 50%OPC : 50%GGBS. $y = 0.0023x^2 - 0.0266x + 0.0846$ & $R^2 = 0.9754$

The value of $X = 0$ was substituted into the chart Equations for each mix and the resulting C_s values are :

C_s for OPC 0.1175 %mass, for 25%NP 0.0861 %mass and for 50%GGBS 0.0846 %mass.

After determining C_s for each mix the C_m value and the depths and concentration of profiles are fed in Microsoft Spreadsheet prepared by Strategic Highway Research Program [14] the depth should be changed according to moderated depth in Table IV, and using Eqs 3 and 5 to obtain the D_{app} . As shown in Figures 7, 8 and 9 and the D_{app} Values are shown in Figure 10.

The apparent chloride diffusion coefficients (D_{app}) for OPC, 25%NP and 50%GGBS in Figure 10 are $D_{app.OPC} = 3.145 \times 10^{-12} \text{m}^2/\text{s}$ this agree with Andrade [15]. $D_{app.NP} = 2.800 \times 10^{-12} \text{m}^2/\text{s}$ and $D_{app.GGBS} = 1.793 \times 10^{-12} \text{m}^2/\text{s}$ this agree with Higashiyama, and Saeki [16], [17]. $D_{app.GGBS}$ is lower than $D_{app.NP}$, and $D_{app.NP}$ higher than $D_{app.OPC}$.

$$(D_{app.GGBS})/(D_{app.OPC}) = 0.57$$

$$(D_{app.NP})/(D_{app.OPC}) = 0.89$$

Fig. 6: Chloride concentration at the surface (C_s) for OPC, NP and GGBS.

It can be seen that the OPC are more likely to undergo chloride induced corrosion at an early stage in their service life, 25%NP reduce the chloride ingress by 11% and for replacement OPC by 50%GGBS reduce the chloride ingress by 43%. Shown that 25%NP clearly ranking between 100% OPC and 50%GGBS.

5. CONCLUSIONS

- ❖ In the three systems the performance of 25%NP in resisting of chloride ingress is higher than the performance of 100%OPC and lower than the performance of 50 % GGBS, NP performed in between GGBS and OPC.
- ❖ Value of D_{app} for 100%OPC is $3.145 \times 10^{-12} \text{m}^2/\text{s}$, 75%O:PC25%NP is $2.80 \times 10^{-12} \text{m}^2/\text{s}$ and 50%OPC:50%GGBS is $1.793 \times 10^{-12} \text{m}^2/\text{s}$.
- ❖ Further analysis and use of other test of chloride diffusion test should be conducted to explore the performance of SNP in Sudan, as well.

Fig. 7: Chloride Profile for OPC and Dapp.

Fig. 8: Chloride Profile for 25% NP and Dapp.

Fig. 9: Chloride Profile for 50% GGBS and Dapp.

Fig. 10: The Apparent Chloride Diffusion Coefficients ($D_{app,c}$) for OPC, 25NP and 50GGBS

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