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Chloride Ion Penetration Performance of Biogenic Pozzolanic Cement Concrete

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Abstract: *Concrete is a pervious material whose durability depends mostly on the constituent materials. Penetration of water, oxygen, CO_2 and aggressive ions, such as chlorides and sulphates into reinforced concrete can cause the passive layer on reinforcing steel to break down thereby making it susceptible to corrosion. Use of pozzolanic materials reduces the permeability of concrete due to conversion of calcium hydroxide into calcium silicate hydrates which in turn increases the concrete durability in terms of corrosion resistance. In this work, permeability of chloride ion was determined for various mixes of concrete specimens (50 mm thick and 100 mm in diameter) when the cement content was partially replaced with some selected biogenic pozzolans using Rapid Migration Test. The result shows that groundnut shell ash, locust bean pod ash, sugarcane bagasse ash and bamboo leaf ash can be effectively used in partial replacement of OPC in concrete up to 12% with added advantage of better durability in terms of resistance to chloride ion penetration.*

Keywords: *Chloride ion, Permeability, Durability, Pozzolan, Corrosion.*

1. INTRODUCTION

Concrete is a composite construction material composed primarily of aggregates, cement and water. Concrete is the most widely used construction material on earth. Over the years it has been used in vast quantity for the construction of buildings, bridges, roads, dams and many other civil infrastructures. According to Glavind and Munch–Petersen [1], its worldwide annual consumption in 2002 was about 5 billion m^3. Moreover, it has been predicted that its demand would double every decade [2]. Hence its performance and effects on the environment are of great importance.

Durability of concrete is the ability of a concrete to withstand to a satisfactory degree the effects of service conditions to which it will be subjected such as weathering, chemical action and wear. The current provisions for durability in the standards outline the exposure conditions, concrete mix requirements, cover depth provisions and execution of concrete practices [3, 4]. These standards based the quality control in concrete on the compressive strength measurement using standard cube or cylinder specimen. However, strength is an inadequate measure of the quality of a reinforced structure with regards to durability which is dependent on the permeability of the concrete cover [5]. Durability can be measured in terms of chloride ion ingress, shrinkage, carbonation, sulphate attack etc. Permeability implies that the pores are sufficiently interconnected for gases or liquids to be able to pass through [6]. Use of pozzolanic materials reduces the permeability of concrete due to conversion of calcium hydroxide {$Ca(OH)_2$}otherwise soluble and leachable into cementitious compounds [6]. Rukzon and Chindaprasirt [7] discovered that incorporation of palm oil fuel ash and rice husk ash decreases the chloride penetration of mortar by increasing nucleation sites for precipitation of hydration products, reducing $Ca(OH)_2$ and improving the permeability of mortar.

Corrosion is the loss of material that occurs as a result of the interaction between chemical and biological agents when metals are exposed to the environment [8]. Corrosion of reinforced steel will affect the service life of concrete reinforced structures through metal lost in the reinforced steel rods which leads to reduction of the mechanical properties of the structure. Also, corrosion products occupy a higher volume than the base metal and this produces internal stresses, which may cause the concrete to crack. Degradation of concrete structures by corrosion processes is a serious problem and has major economic impact. In service conditions, the concrete covering the steel bars gives physical and chemical protection to the reinforcement. The concrete cover provides an alkaline environment surrounding the steel, resulting in the formation of an oxide layer, called a passive film, which protects the steel from corrosion. But, the passive layer does not provide a perfect and permanent barrier in aggressive environments containing initiators of corrosion (primarily aggressive ions like chlorides, humidity, carbon dioxide, and oxygen) [9].

Exposure of reinforcing steel to these primary aggressive ions, together with inadequate construction practices in difficult environmental conditions will lead to de-passivation of the steel which in turn will cause corrosion of the reinforcing steel [10]. Therefore, reinforced concrete structures need to be durable. One of the main forms of attack from the environment is the ingress of chloride ions, which leads to corrosion of steel reinforcement and subsequent reduction in the resistance, utility, and aesthetics of the structure [11]. Chlorides can be introduced into concrete during batching or from the environment during service through contact with sea water. Reinforced concrete structures that are exposed to harsh environments are often expected to last with little or no repair or maintenance for long period of time (100 years or more). In order to achieve this, there is need for durable structures to be produced. For reinforced concrete bridges, one of the major forms of environmental attack is chloride ingress which may lead to dilapidation of the structure thereby leading to early repair and premature replacement of the structure. A common method of preventing such deterioration is to prevent chlorides from penetrating the structure to the level of reinforcing steel bar by using relatively impenetrable concrete which can be achieved through the use of cement pozzolans.

Therefore, this research work aims at making durable concrete through the inhibition of chloride ion penetration by pozzolanic action. The effects of some pozzolanic materials on chloride ion penetration in concrete were studied by partially replacing cement with these pozzolans in order to determine the degree in which their presence will affect the durability of concrete.

1.1 Research Significance

Various researches have been carried out on the ability of pozzolans to increase the compressive strength of concrete and their optimum percentage replacements were obtained. Some researchers have also reported the ability of pozzolans to improve the durability of concrete in well-established pozzolans like slag, rice husk ash, silica fume among others. The pozzolans in this research work are new emerging pozzolans which suitability to improve compressive strength has been established [12-14]. Therefore, knowing their durability property in term of chloride ion penetration will further enhance their suitability as reliable admixture in concrete.

2.0 MATERIAL AND METHODS

The materials used in this research work were groundnut shell ash (GSA), locust beans pod ash (LBPA), bamboo leaf ash (BLA), sugarcane bagasse ash (SBA), sand (fine aggregate), granite (coarse aggregate), cement (Dangote Portland Cement) and clean water as the curing medium. GSA was produced from groundnut shell by drying the shell and burning it in an incinerator and later put in a furnace at a temperature of 500ºC and sieved with 50μm sieve size. LBPA was obtained from locust beans pod of the African locust bean tree (*Parkia Biglobosa*). SBA was produced by burning sugar cane bagasse at 650ºC while BLA was produced by drying and burning Bamboo leaf to a temperature of 650ºC. Ordinary Portland cement (OPC) was partially replaced with pozzolans at the dosage of 12% by volume of concrete materials. 12% percentage replacement has been obtained as the optimum percentage replacement for GSA, LPBA, BLA and SBA in term of compressive strength evaluation [15-17]. The chemical composition of the major oxides of GSA, LBPA, SBA, BLA and OPC obtained using Minipal 4 Energy Dispensing X-Ray Fluorescence Spectrometer are shown in Table 1. The results of the chemical composition for these pozzolans show that they belong to the group of pozzolanic material; they satisfy most of the requirements specified by ASTM C618 [12]. The particle size distributions for the GSA, LBPA, BLA and SBA are shown in Figures 1 to 4 respectively while that of the sand used is shown in Figure 5. Water cement ratio of 0.6 was used, while the densities of the cement, sand and coarse aggregates were 38 kg/m^3, 2180 kg/m^3 and 2650 kg/m^3 respectively

Table 1: Chemical composition of the major required oxides of pozzolans

Constituent	**% Composition**				
	(GSA)	**(LBPA)**	**(BLA)**	**(SBA)**	**OPC**
Ferrous oxide (Fe_2O_3)	8.20	7.19	11.5	6.64	4.65
Silica (SiO_2)	49.0	18	53	53	22.00
Calcium Oxide (CaO)	5.00	-	3.4	4.1	62
Aluminum Oxide (Al_2O_3)	12.00	-	21	22	5.03
Magnesium Oxide (MgO)	6.74	0.48	0.88	-	2.06
Sodium Oxide (Na_2O)	9.02	-	-	-	0.19
Potassium Oxide (K_2O)	2.04	61.8	1.3	0.5	0.40
Sulphite (SO_3^{2-})	6.21	3.6	-	-	1.43
Loss on ignition (LOI)	4.0	4.0	2.0	5.0	

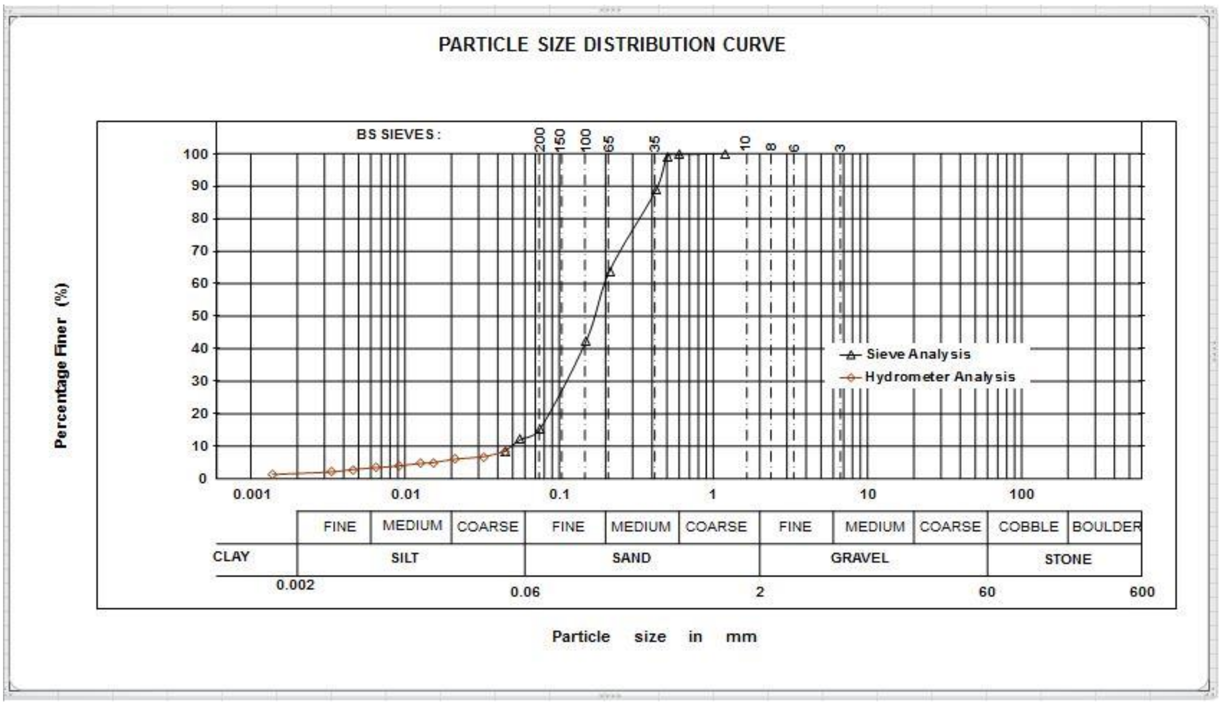

Figure 1: Particle size distribution curve for GSA

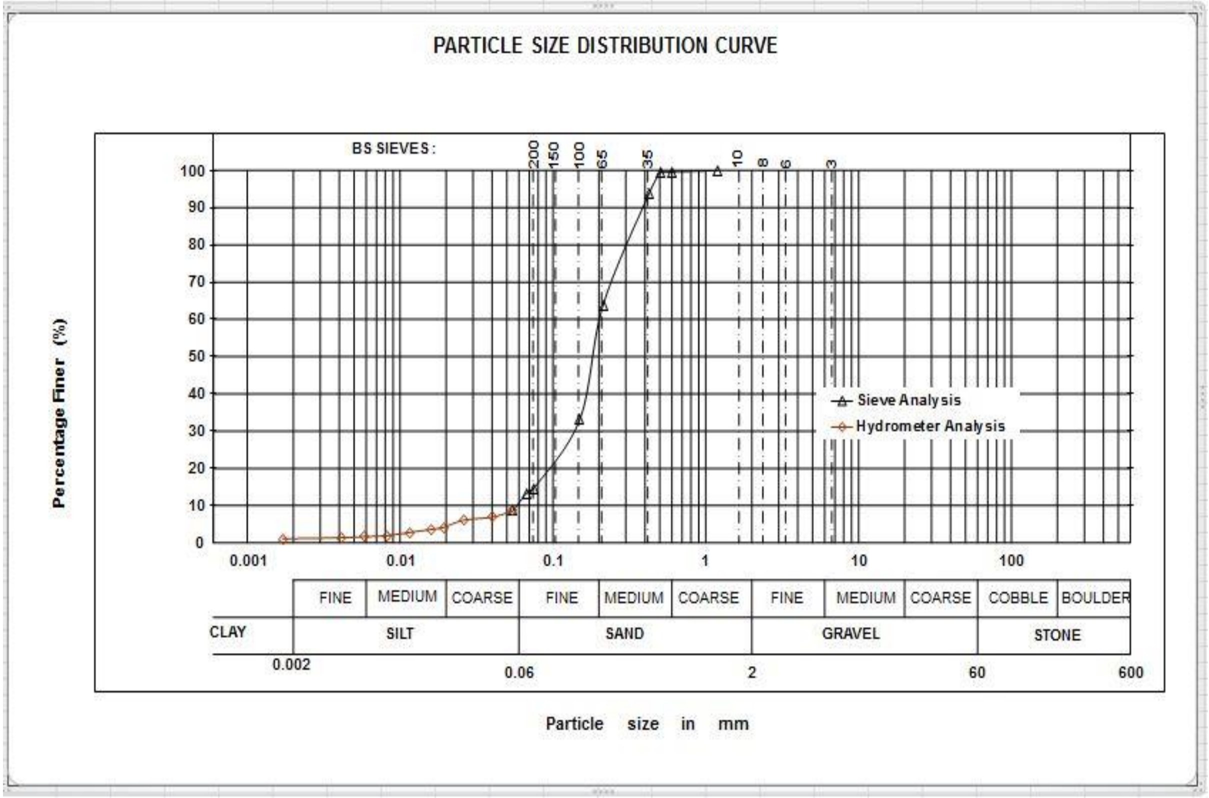

Figure 2: Particle size distribution curve for LBPA

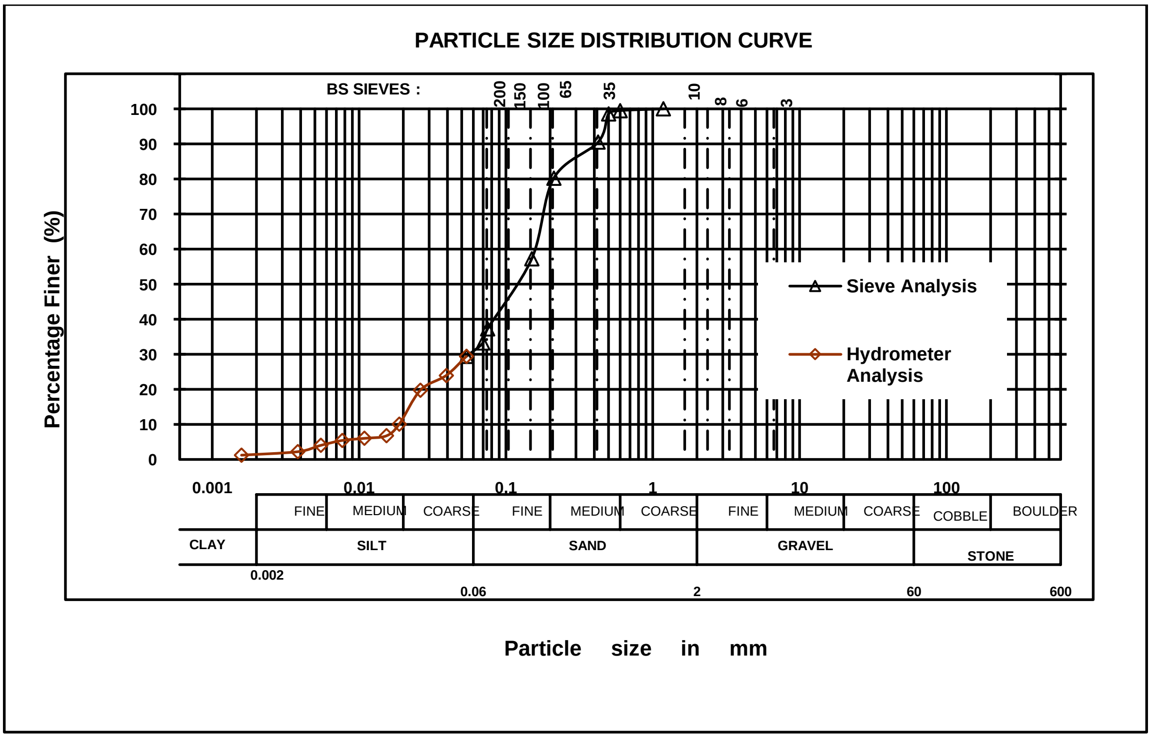

Figure 3: Particle size distribution curve for BLA

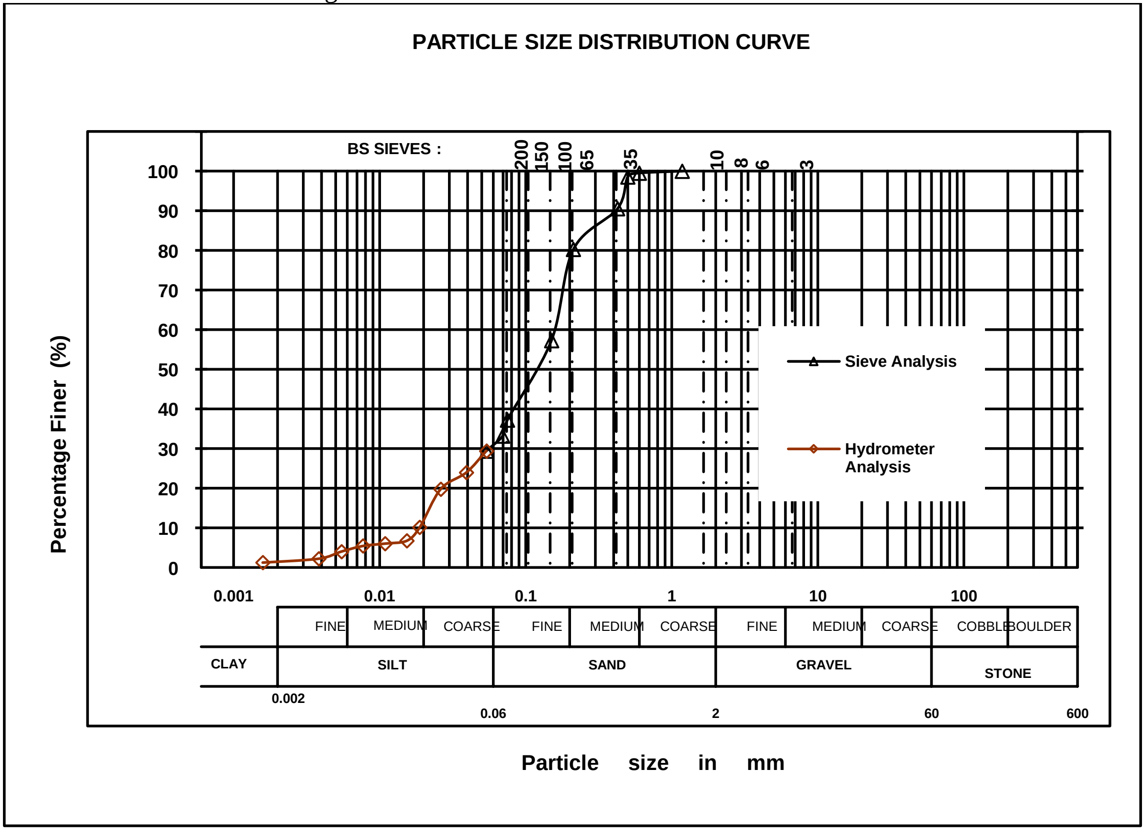

Figure. 4: Particle size distribution curve for SBA

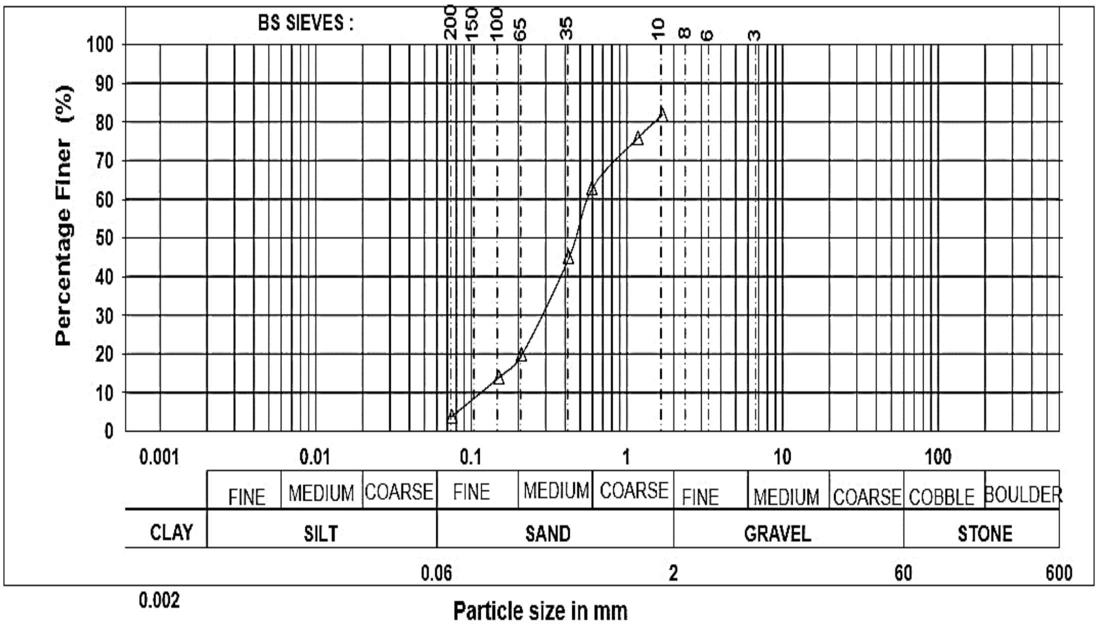

Figure 5: Particle size Distribution Chart for sand

2.1 Specimens

The dosage of the pozzolans used is based on the dosage by which optimum compressive strength has been achieved [16]. The concrete constituents were thoroughly mixed in the proportion shown in Table 2. A total of six treatments (TR) were used with the OPC as the control treatment. A mix ratio of 1:2:4 for cement, sand and coarse aggregates respectively was used with and slump values of 60±5 mm. Concrete specimens of 50 mm thick and 100 mm in diameter were cast for the various mix proportion stated in Table 2. Six specimens were cast and tested for each of the mix proportion at either 30days or 56days. A total of 72 specimens were cast, tested and recorded. The cast specimens were covered with a polyurethane sheet and in a 23±2°C chamber and moist cured until the test ages.

Table 2: Concrete mix proportions between ordinary Portland cement (OPC) and some pozzolans

S/N	Concrete Mix Proportions	Treatment Name
1.	100% OPC	OPC*
2.	96% OPC + 4% GSA	GSA4
3.	88% OPC + 12% GSA	GSA12
4.	88% OPC + 12% LBPA	LBPA12
5.	88% OPC + 12% BLA	BLA12
6.	88% OPC + 12%SBA	SBA12

*Control, GSA is groundnut shell ash, LBPA is locust beans pod ash, BLA is bamboo leaf ash and SBA is sugarcane bagasse ash.

2.2 Experimental Investigation

Permeability of chloride ion was determined for various mixes of concrete when OPC was partially replaced with groundnut shell ash (GSA), locust bean pod ash (LBPA), sugarcane bagasse ash (SBA) and bamboo leaf ash (BLA) using Rapid Migration Test (RMT). A migration cell was set up with a concrete specimen 50 mm thick and 100 mm in diameter with an applied voltage of 10V as shown in Figure 6. The volume of the 10%NaCl solution was 750 ml and that of 0.1NaOH was 300 ml. After 8 hours the specimen was removed and split and the depth of chloride penetration was determined in one half of the specimen using colorimetric technique in which 0.1N Silver Nitrate was used as colorimetric indicator similar to the procedure of Otsuki *et al*. [13] and Tang and Nilsson [14].

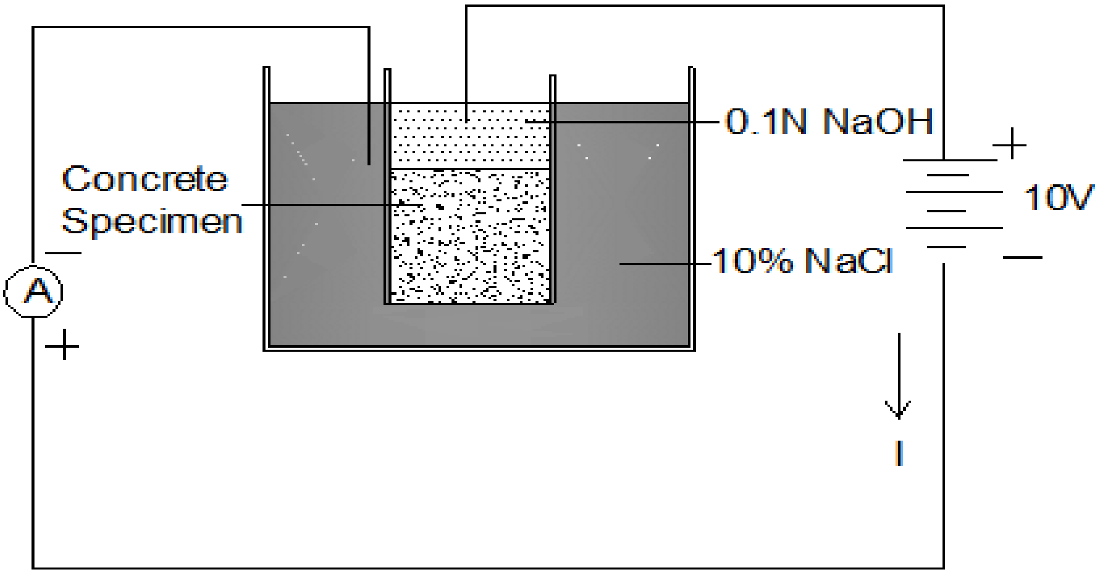

Figure 6: Rapid Migration Test Set up [14]

At the age of 30 and 56 days the concrete specimen were removed and tested for the depth of the chloride ion penetration. The current across each cell as well as the temperature change were also recorded.

2.3 Analytical Investigation

The Results of the chloride ion penetration depths for 56 day curing for the various mix proportions were compared using analyses of variance (ANOVA) and least significant different (LSD) tests as post hoc test with the aid of SPSS 16.0 software package.

3.0 RESULTS AND DISCUSSION

3.1 Current and Temperature Profile Across Cells

The current across each cell (Figure 6) prepared for the various mix proportions and the temperature of NaOH solution were recorded during the experiment. The variation over time in the current across each cell is shown in Figure 7 for all mixes at 56 days. Measurements of initial current (I_c), intermediate current (Ip), final current (I_f), initial temperature (T_o) and final temperature (T_f) for each specimen are presented in Table 3 for 56 days. The difference between current variations before and after chloride-ion passes through specimen illustrates that the effect of other ions in the pore solution on the current is not significant (or it is assumed that the ratio of chloride-ion to the other ions in the pore solution is constant) after the passage of the chloride-ion.

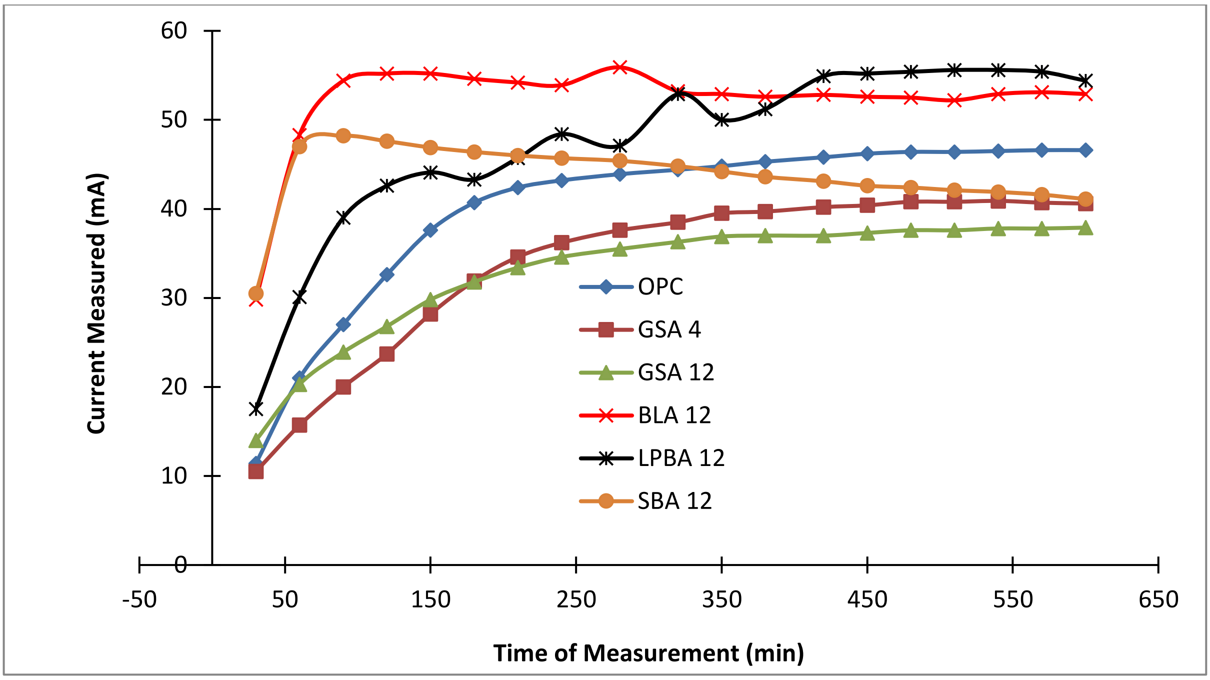

Figure 7: Measured current and the corresponding time for OPC and other pozzolans at 56 days.

The temperature variations for the specimens at 56 days curing vary from 1.0 to 2°C as shown in Table 3. The result in Table 3 shows that the temperature change during the chloride ion penetration test using RMT for 56 days curing is minimal.

Table 3: Measurement of current and temperature for various pozzolans at 56 days

	I_c (mA)	I_p (mA)	I_f (mA)	$[\frac{(I_P-I_c)}{I_c}]$ (100%)	$[\frac{(I_f-I_p)}{I_p}]$ (100%)	T_o, °C	T_f, °C	Change in Temperature, °C
OPC	11.4	44.4	46.6	289	4.95	27.5	29.0	1.5
GSA-4%	10.5	38.5	40.6	267	5.45	27.5	29.0	1.5
GSA-12%	14.0	36.3	37.9	159	4.41	27.0	29.0	2.0
BLA-12%	29.8	53.2	52.9	78.52	-0.56	26.0	27.0	1.0
SBA-12%	17.5	52.9	54.4	202.29	2.84	27.0	29.0	2.0
LBPA-12%	30.5	44.8	41.1	46.89	-8.26	28	29.0	1.0

3.2 Chloride Ion Penetration Profile

The chloride ion penetration depth obtained after 30 days of curing concrete specimen with OPC, GSA4, GSA12, BLA12, LPBA12 and SBA12 is shown in Fig 8. It is shown that GSA4 has a final depth of 18 mm followed by SBA12 with final depth of 20 mm and then GSA 12 with a final depth of 21 mm. The addition of these three pozzolans is expected to improve the permeability resistance of their corresponding concrete beyond that of OPC. It is also clear that BLA12 has the same permeability resistance as that of OPC with the final depth of 24 mm whereas permeability of LPBA12 is lower than that of OPC with a final depth of 26 mm.

The result of the depth of penetration of chloride ion obtained for 56 days after curing the concrete specimen with OPC, GSA4, GSA12, BLA12, LPBA12 and SBA12 is shown in Figure 8, specimen SBA12 and GSA12 emerged the most durable with the same final penetration depth of 15 mm, followed by BLA12 with a final penetration depth of 16 mm and then LBPA12 with final penetration depth of 17 mm and GSA4 has a final depth of 18 mm, OPC (control) has a final depth of 20 mm.

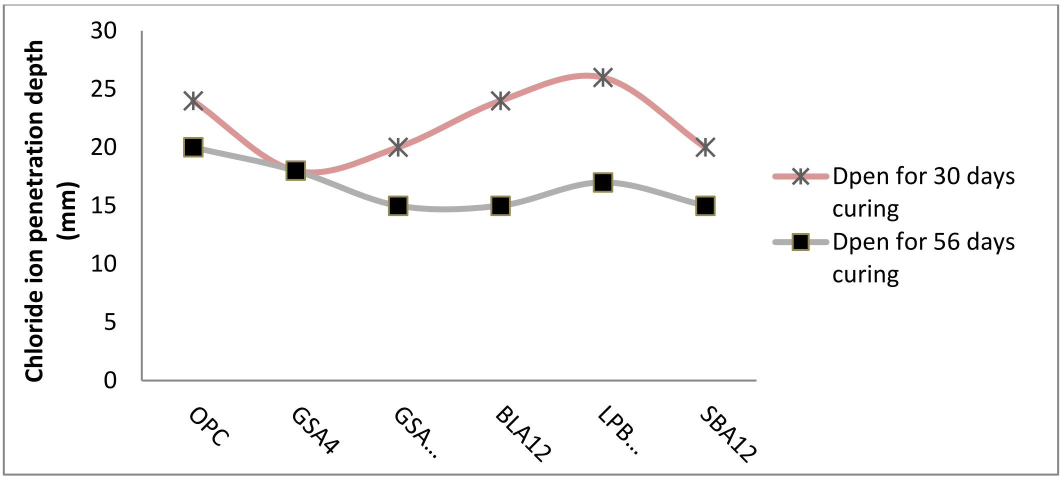

Figure.8: Depth of chloride ion penetration for the blended mixes at different curing days

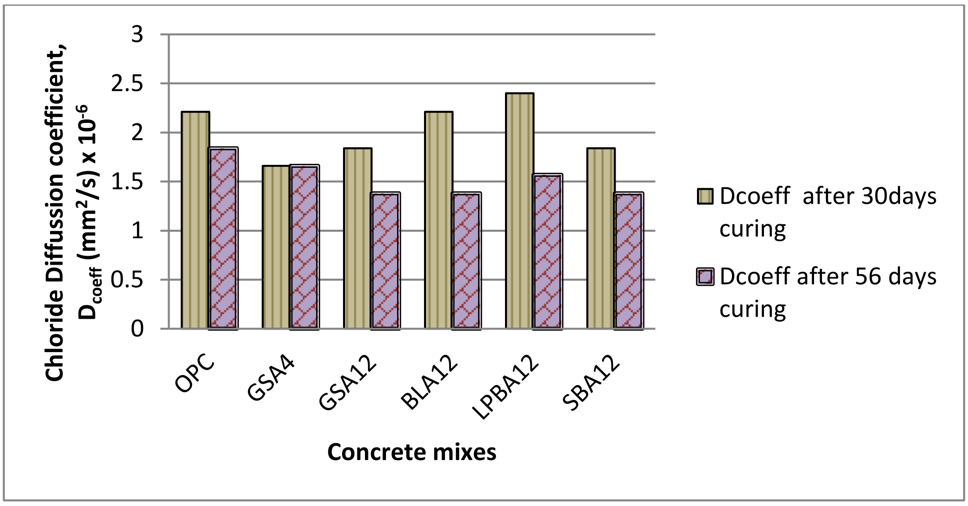

Figure 9: Diffusion coefficients for various concrete mixes and curing days

This result shows that all the pozzolanic blended concrete have better penetration resistance to chloride ion than the OPC and are therefore more durable. The partial replacement of cement with any of them in concrete production will improve the durability properties. It was observed that the results of chloride ion penetration as well as that of the diffusion coefficient for both 30days and 56 days curing (Figures 8 and 9) showed that for all the specimens, there was increase in resistance to penetration as the curing days increased; implying that durability of concrete could increase with increasing curing days. Past research works carried out on chloride ion penetration obtained similar result for different pozzolans; there was a significant improvement in the concentration of chloride ion at different depth of concrete generated by inclusion of fly ash (20%) and slag (60%) (QCL, 1999) as well asf rice husk ash at 20% replacement of OPC at 90 days [18].

The increased chloride penetration resistance is due to reduced average pore size of the concrete and the improved interfacial zone. The relatively high resistance of the concrete (with pozzolanic materials) to chloride penetration can be partly explained by its expected lower median pore diameter and porosity values. Furthermore, normal OPC concrete will have a higher $Ca(OH)_2$ content in the hydrated structures. The reaction of the pozzolans with the available $Ca(OH)_2$ from OPC facilitates full hydration of the binder to achieve a high quality concrete structure and least possible permeability [19].

These test data, and those from many other researchers, highlight the benefits to be obtained in terms of reducing chloride ion penetration by incorporating pozzolans in concrete exposed to aggressive conditions.

3.3 Comparison of Experimental Results

The comparison of the experimental results from the chloride ion penetration depths for 56-day curing using ANOVA and LSD tests for the various mix proportions are shown in Tables 4. The result in Table 4 shows that when OPC was compared with GSA4, with GSA12 and with LPBA12 there were significant differences ($p < 0.05$) between the permeability of OPC and these three pozzolans; durability property of GSA4, GSA12 and LPBA12 is significantly higher than that of OPC and therefore will perform better in terms of durability than OPC and therefore could replace OPC in concrete production giving a better durability. Whereas no significance difference between OPC and BLA12 or OPC and SBA12; consequently, BLA12 and SBA12 could be substituted for OPC without significantly altering the permeability property of the concrete.

Table 4: LSD test for chloride ion penetration depth for 56-day curing

i	j	MD(i-j)	p	Remark
1	2	2.1	0.043	*
	3	3.1	0.004	**
	4	1.1	0.283	NS
	5	2.2	0.035	*
	6	1.4	0.174	NS
2	3	1.0	0.329	NS
	4	-1.0	0.329	NS
	5	0.1	0.922	NS
	6	-0.7	0.493	NS
3	4	-2.0	0.054	NS
	5	-0.9	0.379	NS
	6	-1.7	0.100	NS
4	5	1.1	0.283	NS
	6	-0.3	0.769	NS
5	6	-0.8	0.434	NS

**Mean Difference is significant at $p < 0.01$,*Mean Difference is significant at $p < 0.05$, NS= Not Significant, 1-OPC (control), 2-GSA4, 3-GSA12, 4-BLA12, 5-LPBA12, 6-SBA12

4.0 CONCLUSIONS

Based on the result obtained from the chloride ion penetration test for OPC, GSA4, GSA12, LBPA12, BLA12 and SBA12 using RMT, it can be concluded that:

1. partial replacement of OPC with GSA, LPBA BLA and SBA at 12% will give a better durable concrete in terms of resistance to chloride ion provided the curing age is not less than 56 days.
2. chloride ion penetration resistance of GSA and LPBA blended concrete mixes at 12% partial replacement of OPC is significantly higher than that of OPC mix.
3. GSA and LPBA blended concrete mixes at 12% partial replacement of OPC is a potential supplementary materials for cement in concrete production especially in aggressive or marine environment. Their natural sustainability is ecofriendly and will contribute positively to the global greenhouse effect as well as the overall sustainability of construction materials.

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