Preliminary Investigation of Anticorrosion Effect of Brewer's Spent Grain Ash on Rebar

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***Abstract*—The corrosion behavior of reinforced concrete containing various proportions of admixture Brewer's Spent Grain Ash (BSGA), as replacement for ordinary Portland cement (OPC) in concrete mixes were studied. The admixture was produced by controlled burning of BSGA using a basket burner. X-ray Diffraction (XRD) spectroscopy was performed on the ash to determine its chemical composition and texture (crystalline or amorphous). Concrete samples were made by substituting OPC with BSGA up to 50 weight percent. Corrosion test samples were prepared by centrally placing the reinforcing steels in different concrete mix, leaving 15mm protrusion for electrical connections. The corrosion test samples were partially immersed in sea water sample to simulate chloride induced corrosion of the rebar. The test blocks were connected in parallel to a D.C rectifier set at 6 V to accentuate the rate of corrosion. The amount of current flowing between the bars were measured using high impedance multimeter. Corrosion potential was determined at intervals of 2 days for a period of 28 days after the initial 28 days of conditioning. The results show that ash substitute of 10% substitution of ordinary Portland cement has the optimum corrosion resistance, and ash substitute of up to 20% partial substitution of ordinary Portland cement has superior corrosion resistance compared to conventional concrete.**

Keywords—Rebar; concrete; corrosion; cement substitutes

I. INTRODUCTION

Pozzolanic materials such as fly ash, silica fume, Rice husk ash and some other agro waste ash are being used as partial replacement for ordinary Portland cement (OPC) in several application because of these products capability to enhance the quality of concrete. This effort has created a mutually beneficial condition such that challenges associated with the disposal of agro-waste can easily be eliminated by harnessing this waste for improved concrete structures. Several researchers have studied the replacement of OPC with some of these products, and some of this works have shown that they improve on the quality and durability of the concrete. [1]-[6] reviewed different types of ashes which include rice husk ash (RHA), fly ash, blast furnace slag, cane bagasse ash, they observed that the durability of concrete was improved. A noticeable improvement was observed on the mechanical properties, structural, physical, chemical and resistance to corrosion of rebar in corrosive environments

The durability of reinforced concrete structures is dependent on its resistance to chemical attacks, physical impacts and the ability of the concrete to protect the reinforcing steel bars against corrosion. These are important factors that needed to be considered when choosing materials to be used as partial replacement for cement. Corrosion of reinforcement has been established as the predominant factor causing widespread premature deterioration of concrete structures worldwide, especially of the structures located in the coastal marine environment.

The major cause of corrosion in rebar is the ingress of chloride ions and carbon dioxide to the steel surface. These ions move through the water contained in the pore network, their mobility is defined by the porosity and permeability of the cement matrix. This is direct consequence of the pore structure, porosity and Pore size distribution of the mass of mortar [7]-[14]. The more impermeable the concrete, the greater will be its resistance to deterioration. It has been reported that the replacement of OPC with through the incorporation of pozzolan reduces the average pore size and results in a less permeable paste [9][15]-[22]. Other studies have also shown similar conclusions that permeability of blended cement concrete is less than plain cement paste. Rodriguez et al. [23] observed that the incorporation of RHA in the composites could provide an extensive pore refinement in the matrix and in the interface layer, thereby decreasing water permeability. Agro-waste ash such as Rice hush ash, palm oil fibre ash, bagasse ash, Rice hull ash have been extensively studied and subsequently used for partial replacement of cement in mortar and concrete making [3][21][24][25]. The property of some of these agro waste product that make them amenable for use as cement substitute is known as pozzolanic property of the material.

According to American Society for Testing Materials (ASTM) [26], a pozzolanic materials is defined as a siliceous or siliceous and aluminous materials which in themselves possess little or no cementitious value but which in finely divided form, in the presence of moisture and calcium, they react with calcium hydroxide to form calcium silicate. Pozzolans are commonly used as an addition to cement concrete mixtures to increase the long-term strength and other material properties of Portland cement concrete. A pozzolanic reaction occurs when a siliceous or aluminous material get in touch with calcium hydroxide in the presence of humidity to form compounds exhibiting cementitious properties [27]-[29]. In the cement hydration development, the calcium silicate hydrate (C-S-H) and calcium hydroxide ($Ca(OH)_2$, or CH) are released within the hydration of two main components of cement namely tricalcium silicate (C3S) and dicalcium silicate (C2S) where C, S represent CaO and SiO_2 [30]. Hydration of C3S, C2S also C3A and C4AF (A and F symbolize Al_2O_3 and Fe_2O_3) respectively, is important. Equations 1 – 4 show the pozzolanic reaction reactions mechanism [31]:

$2(3CaO\text{-}SiO_2) + 6H2 \rightarrow 3CaO.2SiO_2.3H_2O + 3Ca(OH)_2$ (1)
$2(2CaO.SiO_2) + 4H_2O \rightarrow 3CaO.2SiO_2.3H2O + Ca(OH)_2$ (2)

$3CaO.A1_2O_3 + 31H_2O + 3CaSO_4 \rightarrow 3CaO.A1_2O_3.3CaSO_4.31H_2O$ (3)

$4CaO.A1_2O_3.Fe_2O_3 + 10H_2O + 2Ca(OH)_2 \rightarrow 6CaO.AI_2O_3.Fe_2O_3.12H_2O$ (4)

Brewers dried grain is the dried extract residue of barley malt alone or in mixture with other cereal grains from the manufacture of malt or beer. It may contain pulverized dried spent maize in an amount not to exceed 3%, evenly distributed. The breweries use more than 400 million tons of grains annually. Left behind after brewing operations are heaps of wet, soggy grains, often called spent or brewers' dried grains-4.5 million tons of them, and that poses a problem. Barley husk represents about one fifth the weight of the dried barley crop. It is a challenging problem to dispose or utilize this low-value by-product, because of the tough, woody, abrasive nature of the husks, their low nutritive properties, resistance to weathering, great bulk and high ash content.

This present work evaluated the corrosion resistance property rebar embedded in concrete made from Brewer's Spent Grain Ash (BSGA) blended with OPC. Structure of barley husk was studied since 1940 by many researchers [32]-[37]. The constituents of barley husks are both organic and inorganic compounds. Analysis reported in literature that the organic matter present in the husks is generally, protein, fat, carbohydrate and crude fibre and very small traces of organic acids are also reported. The inorganic constituents comprise about 6-34% of the husk [38]. The predominant compound of ash is silica. The silica value represents about 90% by weight of the ash [39].

X-Ray Diffraction (XRD) analysis and Infrared (IR) analysis revealed that silicon atoms are assimilated in the barley plant and form part of the plant tissue, probably replacing part of the carbon atoms in the organic compounds [39]. Silicon atoms are first transformed by the combustion process into amorphous silica. In this case they are found attached to oxygen atoms in two ways: either to two oxygen atoms forming a siloxane group Si-O or to oxygen and hydrogen forming a silanol group Si-O-H. Both groups exist up to 700°C but in varying proportions depending on the firing temperature. The siloxane groups unite by the corners to produce low form cristobalite. Barley husk ash silica lost its OH group early. The impurities present enter the lattice forming a kind of solid solution and favor the formation of tridymite these are the views of [40].

II. METHODOLOGY

A. Basket Burner Set Up

The main problem in producing active silica from brewers dried grain ash is to burn them at a temperature below 800°C to stop the silica forming inactive crystals. But it is also necessary to burn them for long enough so that all the cellulose burns away and leaves a white or grey colored ash. Allen designed a simple basket-burner and prescribed its use for incineration of rice husk. He certifies that the designed basket-burner ensures that these conditions will occur [41]. The equipment made comprises of two baskets one large and one small. The larger basket was 600 mm in diameter and about 900 mm high and the smaller basket 250 mm diameter and 750 mm depth. The smaller basket was positioned concentrically inside the larger basket as shown in Fig. 1. Both baskets are made from steel mesh net of hole size 2 mm. The basket was placed in a 200-liter drum and fitted with a cover as wind blowing on the basket can increase the local temperature. To ensure that sufficient air can get to the rice-husks in the basket, 10 holes of 5cm diameter was bored in the base of the drum as shown in Fig. 2.

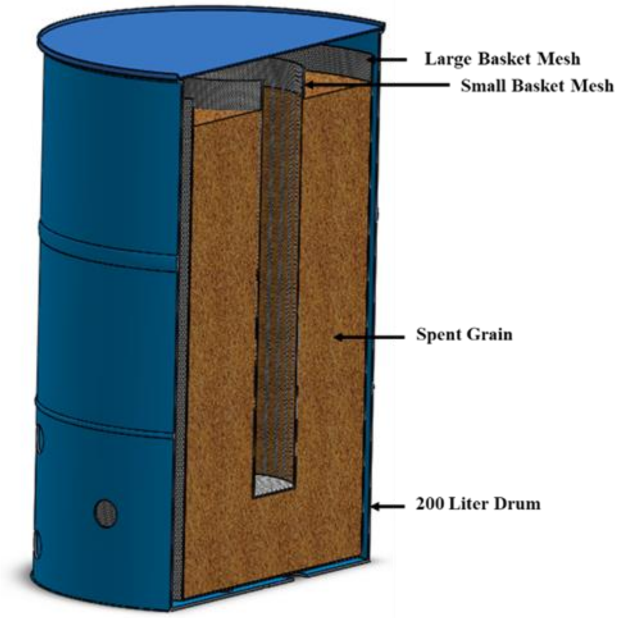

Fig. 1. Basket burner set up

Fig. 2. 200 Liter Drum with Bored Base

B. Concrete Preparation

The chemical composition of ordinary Portland cement (elephant brand) used is shown in table 1 below.

TABLE 1 CHEMICAL COMPOSITION OF PORTLAND CEMENT

Composition	C_3S	C_2S	C_3A	C_4AF	Na_2O	CaO	Others
Quantity(%wt)	55	18	11	7	0.21	0.4	8.39

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Brewer's dried grain was obtained, well sun dried and burnt to ashes using Basket burner, the burnt ashes were sieved through British Standard sieve of 65 microns after grinding. Chemical analysis of the ash was carried out at X-ray diffraction (XRD) Spectroscopy Laboratory of Centre for Energy Research and Development (CERD), OAU, Ile Ife, Nigeria. In this study, Fig. 3 below shows the XRD pattern for BSGA sample from the Figure it can be observed that there is no identifiable peak on the pattern

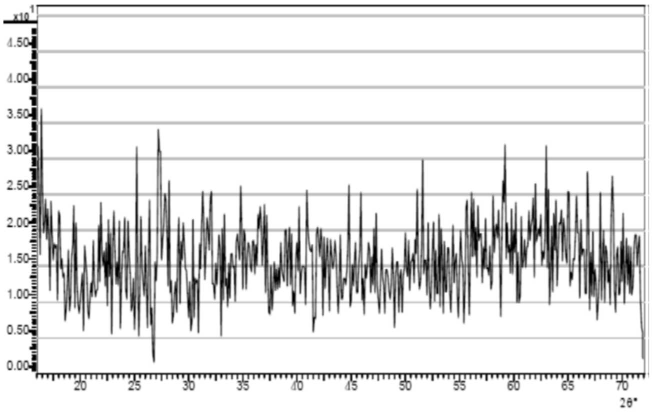

Fig. 3. X-Ray Diffraction test of BDGA

X-ray Diffraction (XRD) enables identification of different chemical composition that constitute the ash and also determine the nature of its silica form. From the XRD pattern of BSGA shown in Fig. 3, the ash is in amorphous state, this is indicated by non-existence of peak on the graph. The identified group include phases of SiO_2, Al_2O_3, CaO, Na_2O, Fe_2O_3, MgO, K_2O, TiO_2 were identified from the 2θ values of the diffraction.

The freshly prepared ash was mixed with ordinary Portland cement in the ratio by weight of Portland cement / ash: 9/1, 4/1, 7/3, 3/2, 1/1. The mixture was placed inside a covered container and thoroughly mixed to ensure proper distribution of the particles of ash and Portland cement. Medium concrete workability and mix ratio of 1:2:4 (cement: sand: coarse aggregate) by mass was adopted. The water/cement ratio of 0.6 was used for all batches. The coarse aggregates used are crushed granite of size 12.5mm.

C. Sample Preparation

The reinforcement steel bars used were collected and analyzed at universal steel limited Lagos. They were cut out from the same stock. The chemical composition of the steel is provided in percentages as C, 0.52; Mn, 0.59; Si, 0.294; Cr, 0.212; Ni, 0.9, Mo, 0.0064; Fe, 97.48. The bars were polished and degreased using methyl ethanol, the dimensions were 100 mm long and 11mm diameter. They were centrally placed in the molds filled with different concrete mixtures, leaving 15mm protrusion for electrical connections. The molds were made from PVC pipe of diameter 70 mm and length 110 mm as shown in Fig. 4.

After 24 hours the samples were demolded, and air cured at room temperature for 7days. After air curing, samples were placed in sea water and conditioned for 28 days.

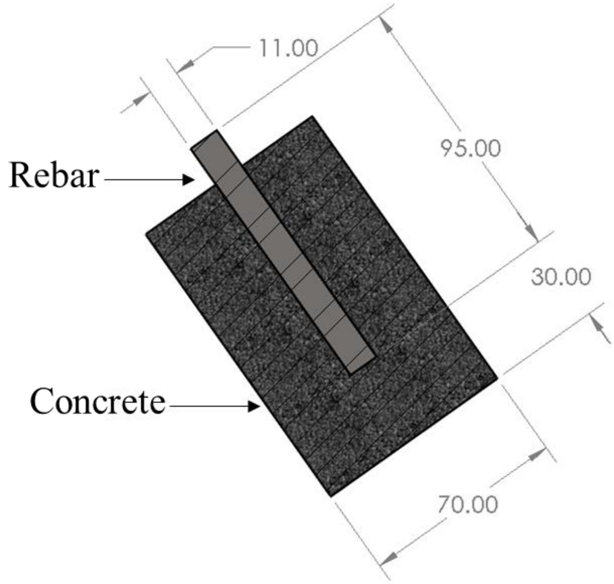

Fig. 4. Corrosion test sample

D. Corrosion Test

The experiment was conducted with each cast partially immersed in the seawater. Seawater was sourced from the Atlantic Ocean (Lagos, Nigeria). A distance was maintained between the exposed end of the steel rod and the medium. The exposed end was covered with paint to prevent environmental interaction, which might affect the accuracy of the readings. After 28 days of initial conditioning the impressed voltage set-up was used to accentuate the rate of corrosion, the embedded steel in concrete was made anodic with respect to an external electrode (Steel bar of similar dimension with the rebar) serving as cathode. A constant potential of 6V was applied to the system through a DC source (Rectifier) The test blocks were connected in parallel to the D.C rectifier. Testing was initiated by applying a voltage of 6 V through the rectifier between the steel bars embedded in samples (Anode) and 10cm long steel bars (Cathode) suspended in the sea water. The amount of current flowing between the bars was measured using Ammeter that was placed in each circuit. Potential readings were taken by firmly placing a Zinc rod electrode on the concrete block and the lead terminals of a digital voltmeter connected to the Zinc rod electrode and the exposed part of the embedded steel rod to make a complete electrical circuit as shown in Fig. 5.

After all readings were taken the switch on the rectifier was turned on and left at the on position for six hours daily until the following reading. Readings were taking at intervals of 2 days for period of 28 days.

The potential values obtained were converted to Saturated Calomel Electrode (SCE) using the formula: Electrode Potential mV (SCE) = $[E_{Zn} - 1030]$ mV [42]. Where E_{Zn} is the electrode potential obtained using zinc reference electrode.

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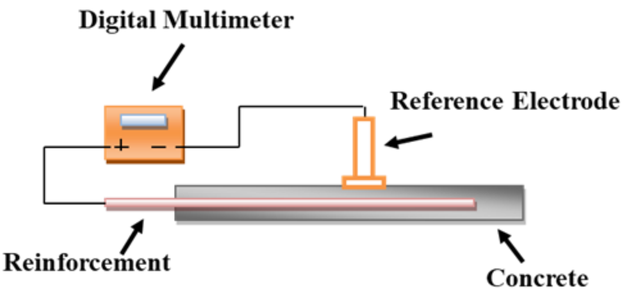

Fig. 5. Potential Measurement Set-up

III. RESULT AND DISCUSSION

A. Result

Fig. 6 compares the measured current values plotted against exposure time for all BSGA samples. As the test continues, the current deviated significantly from this stabilized value, indicating that corrosion has been initiated on the reinforcement, not long after cracking occurs. Once cracking occurs, the resistance of the concrete cover was reduced, increasing the current flow leading to current spike.

The time when this increase in current occurs is defined as the time-to-failure and the test is stopped soon after this occurs. The time-to-failure is more obvious in samples with 30% BSGA, 40% BSGA, and 50% BSGA. It can also be observed that the time to failure for 30% BSGA, 40%BSGA, 50%BSGA were 72, 24, 24 hours, respectively.

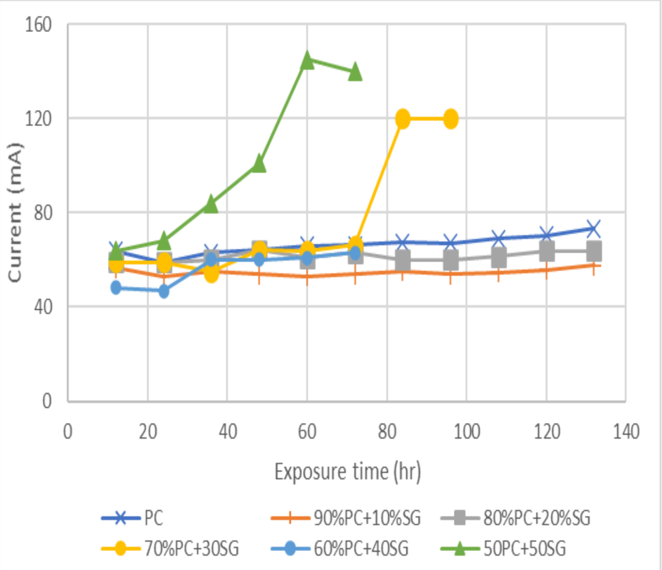

Fig. 6. Plots of Current and Exposure time comparing all BDGA Samples.

The potential against time plot is used to interpret the susceptibility of the rebar to corrosion. The porosity, defects, crevices determines the number of anodic and cathodic sites on the reinforcement. When the sites are few the surfaces are less reactive while larger number of sites indicate more reactive surface. A shift of potential in the negative direction generally indicates a more reactive surface. Fig. 7 compares the plot of potential reading against exposure time for the samples. Increase in potential was observed as the exposure time increases. The rate at which the value of negative potential reading increases in each of the samples differs from one to another.

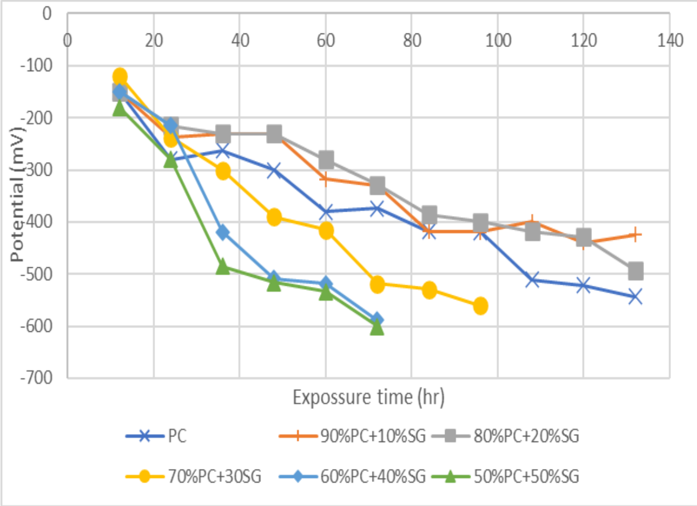

Fig. 7. Plot of Potential against Exposure time that compares all BSGA samples

10% BSGA substitution has the optimum corrosion resistance of the samples, 20 % BSGA exhibit a corrosion resistance better than that of the control sample, and the rate at which negative potential increases is highest in 50% BSGA as indicated on the plot this shows that corrosion resistance is lowest at 50% BSGA substitution.

B. Discussion

One major source of contamination of concrete in structures is fluid absorption which influences durability of the concrete. The more impermeable the concrete, the greater will be its resistance to deterioration. The incorporation of pozzolan reduces the average pore size and results in a less permeable paste. The radial expansion of Portland cement hydration products in pozzolanic particles would have a pore modification effect therefore reduces the interconnectedness among pores. This occurrence can be coupled with perfection on the interfacial transition zones among the cement matrix and aggregate. The presence of pozzolan leads to greater precipitation of cement gel products than occurs in Portland cement alone, which more effectively block the pores helping to reduce permeability.

Summarily, decrease in the permeability of concrete that accompany substitution of ordinary Portland cement by BSGA can be attributed to the reaction of calcium hydroxide produced by cement hydration process with silica contained in the ashes. On adding different amounts of BSGA as a partial replacement of Portland cement, they react with most of the Ca $(OH)_2$ formed during hydration and affects the pore-size distribution. The typical pozzolanic reaction shows that a regular decrease in the hydroxyl ion concentration of the solution and the pH value decreased towards relatively stable minima (depending on the silica content of the ash).

Optimum replacement amount in mixture will allow producing more C-S-H i.e Calcium Silicate Hydrate (more dense and durable concrete). Too large amount of pozzolan will increase required water to mix because the fineness of pozzolan, prevent water to reach the particles of cement and insufficient cement content therefore, weak and permeable concrete are obtained because insufficient amount of C-S-H are formed. This explains why increase in corrosion and reduction in time to failure was obtainable for 30% BSGA, 40%BSGA, 50% BSGA.

IV. CONCLUSSION

In this study, the suitability of Brewer's Spent Grain Ash (BSGA) as cementing replacement materials for ordinary Portland cement (OPC) in reinforced concrete was investigated. Based on the result of the study the following conclusions can be drawn:

i. There is high possibility of partial replacement of Ordinary Portland Cement (OPC) with Brewer's Spent Grain Ash (BSGA) in reinforced concrete.
ii. BDGA blend between 10% and 20% exhibit improved corrosion resistance compared to 100% Portland cement

The result encourages the use of BSGA, agro-waste ash as pozzolanic materials for partial cement replacement in making durable concrete, these will reduce the cost of concrete making, environmental pollution and landfill areas required for the disposal of agro-waste.

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