Electrochemical study of the inhibition effect of cow bone ash on the corrosion resistance of mild steel in artificial concrete pore solution

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Abstract: Substitution of cement powder with sustainable waste products is the focus of research in concrete technology. Cow bone ash (CBA) was studied to determine its inhibition effect on Mild Steel corrosion in artificial concrete pore solution by potentiodynamic polarization technique (between potentials of −1 V and + 1.75 V and scan rate of 0.0015 V/s) and current–time displacement method. Results showed CBA significantly decreased the corrosion rate of the steel with peak inhibition efficiency of 80.18% at 20% CBA concentration and polarization resistance of 20,570 Ω. CBA exhibits anodic type inhibition. The cathodic branch of the polarization curve shows significant decrease in slope after 0% CBA. CBA decreases the pitting corrosion resistance of mild steel at lower concentrations while higher concentrations of CBA decrease the pitting current of the steel adding no additional public interest statements

The economic impact and problems resulting from corrosion has drawn strong attention from scientists and engineers worldwide. Corrosion of carbon steel in reinforced concrete is a problematic phenomenon worldwide. Research on concrete pore solution is important because of the mobility of trace elements which accounts for ion exchange of concrete in the hardened state. In the pursuit of cost-effective, sustainable and eco-friendly concrete, recent research in concrete technology now focus on partial replacement of cement using some sustainable admixtures and wastes such as cow bone ash. Million tons of these waste is generated daily and the re-use of this material is important in a bid to reduce solid waste in line with sustainable development goals.

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PUBLIC INTEREST STATEMENTS

The economic impact and problems resulting from corrosion has drawn strong attention from scientists and engineers worldwide. Corrosion of carbon steel in reinforced concrete is a problematic phenomenon worldwide. Research on concrete pore solution is important because of the mobility of trace elements which accounts for ion exchange of concrete in the hardened state. In the pursuit of cost-effective, sustainable and eco-friendly concrete, recent research in concrete technology now focus on partial replacement of cement using some sustainable admixtures and wastes such as cow bone ash. Million tons of these waste is generated daily and the re-use of this material is important in a bid to reduce solid waste in line with sustainable development goals.
advantage. Current time displacement shows CBA decreases the thermodynamic instability of the passive film on the steel with respect to concentration and the tendency of the steel to corrode.

Subjects: Chemistry; Composites; Metals & Alloys; Civil, Environmental and Geotechnical Engineering

Keywords: corrosion; cow bone ash; concrete pore solution; steel

1. Introduction
About 4,100 million metric tons of cement was produced in 2017 with negative consequence on the environment. Reinforced concrete is the most widely used building materials in construction due to its good durability and significantly lower cost. Cement production depletes huge amount of unsustainable resources adding to carbon emission. Reduction of carbon emission during cement production has become a major focal point for scientist and engineers due to greenhouse effect. According to Malhotra and Mehta (2002), 7% of the total greenhouse emission to the earth emanates from cement production. Cement is majorly applied in the construction of concrete infrastructures. Concrete is one of the most-utilized construction materials worldwide, second only to water most-utilized substance on the earth (Gambhir, 2004). Current research in concrete technology now adopts the use of sustainable cementitious material such as geo-materials and solid wastes as partial replacement for cements in concrete structures. Emphasis on the need to improve the recycling of solid waste management and the strength of concrete in infrastructures has driven the goal for reapplication of solid waste (Adebanji, Ayobami, & Emmanuel, 2018; Akinwumi, Awoyera, Olofinnade, Ayobami, & Okotie, 2016; Ayobami, Joseph, & Bamidele, 2018). Agro-industrial waste is one most common solid waste available for application in concrete. In Nigeria, production of cow bone runs into millions of tons each year. Disposal of cow bone by incineration results in the formation of cow bone ash. This is a serious environmental problem (Akhionbare, 2013; Chukwu, Adeoye, & Chidiebere, 2011; Falade, Ikponmwosa, & Fapohunda, 2012). A dearth of literature exists on the effect of this supplementary cementitious material effect on the corrosion of reinforcing steel in concrete. Corrosion of reinforcing steel encased in concrete is the result of breakdown of the passive film formed within the high alkaline condition of the concrete (Briz, Biezrm, & Bastidas, 2018). This results in durability deterioration of reinforced concrete structures, persistent structural failures and huge maintenance cost (Hussain & Ishida, 2010; Perez, 2004; Zhao, Zhang, & Jin, 2017). Partial replacement of cement in reinforced concrete causes chemical changes of the cement matrix in addition to changes in the pore solution and its pH value compared to ordinary Portland cement. This necessitates the need to further study their effect on the electrochemical behaviour of the reinforcing steels (Loto & Busari, 2019; Perez, 2004). This research aims to study the effect of cow bone ash corrosion resistance of mild steel in concrete pore solution.

2. Experimental methods

2.1. Materials
Mild Steel (MS) rods procured locally in Nigeria, was examined with PhenomWorld scanning electron microscope (Model No. MVE0224651193) at the Materials Characterization Laboratory, Covenant University in Nigeria. Nominal chemical (wt. %) content of the steel is shown in Table 1. MS is of a circular dimension with diameter of 1.2 cm. MS rods were machined to mean thickness of

| Table 1. Nominal chemical composition (wt. %) of mild steel |
|---------------------------------|-----------------|----------------|----------------|-----------------|----------------|
| Element Symbol | Manganese (Mn) | Phosphorus (P) | Sulphur (S) | Carbon (C) | Iron (Fe) |
| % Composition | 0.8 | 0.04 | 0.05 | 0.16 | 98.95 |
1 cm and mounted in acrylic resin. The exposed surface of the steel was smoothened with emery grinding papers (80, 320, 600, 800 and 1000 grits) and polished with 6 µm diamond polishing paste before cleaning with distilled water and acetone. Cow Bone Ash (CBA) used in this research was obtained from a local abattoir in Lagos, Nigeria, being relatively abundant. The CBA was cleaned to remove the ruminant meat, fat and tissue content due to its effect on the pozollanic and mineralogy of the CBA (Akinyele, Adekunle, & Ogundaini, 2016). It was thereafter burnt at a regulated temperature of 900°C and grinded to reduce the surface area (powdery form). Portland lime stone cement (NIS 444–1:2003 standard), fine aggregate sand (NIS 13:1974 standard) and the coarse aggregate (ASTM C33 and ASTM 125) obtained from Ota, Nigeria were used for the research. Portable H$_2$O was used in the batching of the concrete (Busari, Akinmusuru, & Dahunsi, 2018; Busari, Akinmusuru, Dahunsi, Ofuyatan, & Ngene, 2017; Mindess, Young, & Darwin, 2003).

### 2.2. Concrete mix design

CBA powder was used as a fractional substitute for cement in the design of a sustainable concrete mix. It was added in wt. % concentrations of 0%, 5%, 10%, 15% and 20% CBA per the weight of cement used. The H$_2$O/cement (W/C) ratio of 0.88 was applied based on the assertion of Kulakowski (2002). The concrete mix design is shown in Table 2.

### 2.3. Pore electrolyte extraction

The concrete pore electrolyte was extracted 4 hrs after initiation of the hydration of cement in the fresh concrete mix as shown in Figure 1. Further extraction was done manually. Additionally, load was applied on the specimen with the intention to promote confinement tension and expel the pore electrolyte (Ortolan, Mancio, & Tutikian, 2016).

![Figure 1. Schematic of concrete pore electrolyte extraction (Liu, Niu, Li, Lv, & Fu, 2018).](image)

| Cement Replacement (%) | Coarse Aggregate (Kg) | Fine Aggregate (Kg) | Total Aggregate Weight (Kg) | Cement (Kg) | CBA (Kg) | H$_2$O/Cement Ratio |
|------------------------|-----------------------|---------------------|-----------------------------|-------------|---------|-------------------|
| 0                      | 80                    | 40                  | 120                         | 20          | 0       | 0.88              |
| 95                     | 80                    | 40                  | 120                         | 19          | 1       | 0.88              |
| 90                     | 80                    | 40                  | 120                         | 18          | 2       | 0.88              |
| 85                     | 80                    | 40                  | 120                         | 17          | 3       | 0.88              |
| 80                     | 80                    | 40                  | 120                         | 16          | 4       | 0.88              |
2.4. Electrochemical analysis
Application of electrochemical methods through potentiodynamic polarization and current–time measurement was done at 30°C with a ternary multicomponent electrode system (acrylic mounted MS working electrodes with exposed surface area of 1.13 cm², Ag/AgCl reference electrode and platinum counter electrode) within a transparent glass cell containing 200 mL of the electrolyte solution at predetermined CBA concentrations interfaced with Digi-Ivy 2311 potentiostat and computer. Potentiodynamic polarization plots were produced at scan rate of 0.0015 V/s between potentials of −1 V and + 1.75 V. Corrosion current density $C_D$ (A/cm²) and corrosion potential $C_P$ (V) were determined from the Tafel extrapolation method.

Corrosion rate $C_R$ (mm/y) was calculated from the formula below:

$$C_R = \frac{0.00327 \times C_D \times E_{QV}}{D}$$

$E_{QV}$ is the equivalent weight (g) of MS, 0.00327 is a corrosion rate constant and $D$ is the density (g/cm³). Current–time measurement was performed for 5000 s with Digi-Ivy potentiostate 2311 to study the thermodynamic stability and extent of anodic reaction on MS surface interaction with the electrolyte at rest potentials.

3. Results and discussion

3.1. Potentiodynamic polarization studies
Figure 2 shows the potentiodynamic polarization plots of MS corrosion in 0%, 5%, 10%, 15% and 20% CBA/concrete pore electrolyte while Figure 3 shows the cathodic reduction curves for MS corrosion in concrete pore electrolyte. The results from the electrochemical tests are shown in Table 3. In the alkaline concrete pore electrolyte, a protective passive film forms on the surface of MS making it resistant to corrosion. In the presence of CBA compound, the corrosion rate of MS decreased significantly. At 0% CBA, MS has a corrosion rate of $7.31 \times 10^{-2}$ mm/y. During the corrosion reaction process (without CBA compound), Fe²⁺ (the initial product created by the anodic corrosion reaction) from MS goes into the concrete pore solution. Valence electrons from the anodic sites on MS transfer through the steel surface to the adjacent cathodic sites, where they combine with $O_2$ and $H_2O$ to form OH⁻ anions. These react with the Fe²⁺ from the anode to produce Fe(OH)$_2$, which is subsequently oxidized to produce Fe$_2$O$_3$·3H$_2$O (red rust). The reaction is shown below. Gradual oxidation of Fe²⁺ causes the steel to oxidize as colloidal iron, producing non-protective, porous layers

$$Fe + 3O_2 + 2H_2O \rightarrow 2Fe_2O_3 \cdot 3H_2O \text{[hydrated ferric oxide (rust)]}$$
The passivation process of MS in concrete pore electrolyte involves spontaneous electrochemical reduction mechanism through interaction with CBA influenced alkaline pore solution. The cathodic branch of the polarization curve in Figure 2 shows significant decrease in slope after 0% CBA due to decrease in adsorption of O₂ molecules from the bulk solution. This is due to decrease in O₂ reduction reactions, being the main reaction mechanism in alkaline concrete pore electrolyte solution. The decreased slope shows CBA with respect to its concentration increases the surface impedance MS surface through modification of the pore solution. It’s clearly evident that shift in corrosion potential to positive values increases the anodic reaction, corresponding to decrease in cathodic reaction, hence a decrease in rate of reduction of oxygen molecules and restricted diffusion of oxygen to the metal surface as shown in the equation below.

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \]

At 5% CBA, the corrosion rate of MS decreases to \(2.96 \times 10^{-2}\). This corresponds to inhibition efficiency value of 59.52%. Further increase in CBA concentration decreased the corrosion rate of MS to \(1.45 \times 10^{-2}\) mm/y (inhibition efficiency of 80.18%) at 20% CBA concentration. Increase in polarization resistance with respect to CBA concentration confirms this assertion. The electrochemical performance of CBA is noted to be highly effective considering that the pore electrolyte solution is neutral and the general rate of corrosion is minimal without CBA. Nevertheless the lifespan of reinforcing MS in concrete is extended. Observation of the corrosion potential shows the significant anodic shift after 0% CBA, signifying anodic type inhibition. This property is related to surface coverage effect of CBA on the exposed steel surface in the pore electrolyte. No significant variation in the anodic-cathodic Tafel constants from 0% CBA to 10% CBA concentration occurred. This confirms the electrochemical effect of CBA in the concrete pore electrolyte is not under activation control. Visible changes occurred from 15% CBA due to the lower anodic exchange current density.

### 3.2. Pitting corrosion inhibition

The concrete pore electrolyte reacts with steel and forms a thin passive layer of iron and calcium hydroxides, respectively \([\text{Fe(OH)}_2]\) and \([\text{Ca(OH)}_2]\) resulting in comparatively low corrosion rate for MS with and without CBA addition. Observation of the polarization curves in Figure 2 shows passivation behaviour due to the reasons earlier given, following anodic polarization. The transpassive and stable pitting region of the polarization curves are shown in Figure 4. It is evident that MS at specific CBA concentration undergoes pitting at certain pitting potentials. However, CBA despite improving the general corrosion resistance of MS in the concrete pore electrolyte, it decreases the pitting corrosion resistance of MS at lower concentration as shown in Figure. 5(a) and (b). At 0% CBA, the potential at which metastable pitting events initiates is 0.80V, corresponding to a pitting current of \(1.78 \times 10^{-5}\) A. Addition of CBA at 5% and 10% CBA decrease the potential at which metastable pitting occurs to 0.75 V at pitting current of \(1.33 \times 10^{-5}\) A and \(1.98 \times 10^{-5}\) A respectively. This shows CBA at low
| Sample | CBA Conc. (%) | MS Corrosion Rate, $C_r$ (mm/y) | Inhibition Efficiency, $E$ (%) | Corrosion Current, $C_i$ (A) | Corrosion Current Density, $C_d$ (A/cm²) | Corrosion Potential, $C_p$ (V) | Polarization Resistance, $R_p$ (Ω) | Cathodic Tafel Slope, $B_c$ (V/dec) | Anodic Tafel Slope, $B_a$ (V/dec) |
|--------|--------------|---------------------------------|-------------------------------|-----------------------------|----------------------------------------|--------------------------------|--------------------------------|--------------------------------|-------------------------------|
| A      | 0            | 7.31E-02                        | 0                             | 7.12E-06                    | 6.30E-06                               | -0.652                        | 3609.00                         | -5.414                         | 5.412                          |
| B      | 5            | 2.96E-02                        | 59.52                         | 2.88E-06                    | 2.55E-06                               | -0.618                        | 8935.00                         | -5.500                         | 6.970                          |
| C      | 10           | 2.91E-02                        | 60.19                         | 2.84E-06                    | 2.51E-06                               | -0.572                        | 9107.00                         | -5.510                         | 5.349                          |
| D      | 15           | 2.50E-02                        | 65.83                         | 2.43E-06                    | 2.15E-06                               | -0.592                        | 10560.00                        | -6.012                         | 7.951                          |
| E      | 20           | 1.45E-02                        | 80.18                         | 2.91E-05                    | 1.25E-06                               | -0.501                        | 20570.00                        | -2.070                         | 7.023                          |
concentration interferes with the mechanism of formation of the protective passive film in the alkaline media. Increase in CBA concentration to 15% and 20% CBA improves the pitting resistance of MS in the concrete pore electrolyte to 0.80 V. However, the corresponding pitting current value shows the protective film offered by CBA is thermodynamically unstable and any change in concentration of CBA can result in the onset of metastable pitting activity.

3.3. Current–time measurement
The current–time relationship for MS in the concrete pore electrolyte at specific CBA concentration is shown in Figure 6. The transient current displacements visible at 0% CBA are the product of anodic oxidation of the MS surface. At this concentration, MS has a relatively higher current with time due to the occurrence of anodic reaction under free corrosion condition. The current flows for MS at 5%–20% CBA are significantly less anodic, signifying the prevalence of low magnitude oxidation reactions on MS surface (Singh, Singh, & Das, 2015). This is a direct consequence of the electrochemical action of CBA compound on the composition of the passive film formed on MS in the concrete pore electrolyte. As earlier stated, the pore solution obtained during cement hydration is highly alkaline. The thermodynamically unstable metallic compounds formed on the steel surface at 0% CBA complexes with the anions in the concrete pore electrolyte (Collepardi, Coppola, Troli, & Collepardi, 1999). The rapid increase and decrease in corrosion current at this concentration indicates repetitive re-passivation and breakdown in the passive film. The current initiated at
\[ -8.80 \times 10^{-4} \text{ A (0 s)}, \text{ peaking at } -4.22 \times 10^{-4} (4400 \text{ s}) \text{ before reaching a final value of } -4.79 \times 10^{-4} \text{ at 5000 s after progressive decrease.}\]

Magnified view of current–time relationship for MS in concrete pore electrolyte at 5%–20% CBA shown in Figure 7. At 5% CBA, the current time plot of MS is still thermodynamically unstable, though to a lesser degree compared to the plot at 0% CBA. The lesser thermodynamic instability is due insufficient CBA compound to effectively counteract the electrochemical action of corrosion anions in the concrete pore solution. Further increase in CBA concentration improved the stability of the current potential plot indicating the formation of effective passive film on MS.

4. Conclusion

Addition of cow bone to reinforcing concrete as partial substitute for cement content significantly influenced the corrosion resistance of mild steel in the concrete pore solution. Increase in cow bone ash weight content decreases the corrosion rate of the steel with respect to concentration of the composite. Studies showed the composite displays anodic type inhibition with significant positive displacement in corrosion potential. The influence of the composite on the pitting corrosion resistance of the steel is limited. Current–time displacement shows cow bone ash stabilizes the passive film formed on the steel within the pore electrolyte compared to visible breakdown and re-passivation of the steel.
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References
Adebanji, O., Ayobami, B., & Emmanuel, A. (2018). Pavement interlayer material improvement using industrial waste: Review of literatures. International Journal of Civil Engineering and Technology, 3(6), 1114–1122.
Akhiobare, W. N. (2013). A comparative evaluation of the application of agro waste as construction material. International Journal of Science and Nature, 4(1), 141–144.
Akinwumi, I. S., Awoyera, P. O., Ololfinnade, O. M., Ayobami, B., & Okotie, M. (2016). Rice husk as a concrete constituent: Workability, water absorption and strength of the concrete. Asian Journal of Civil Engineering, 17(7), 887–898.
Akinyle, J. O., Adekunle, A. A., & Ogundaini, O. (2016). The effect of partial replacement of cement with bone ash and wood ash in concrete. ANNALS of Faculty Engineering Hunedoara, International Journal of Engineering Tome, XIV(4). Retrieved from http://annals.fh.upt.ro/pdf-full/2016-ANNALS-2016-4-31.pdf
Ayobami, B., Joseph, A., & Bamidele, D. (2018). Mechanical properties of de-hydroxylated kaolinic clay in self-compacting concrete for pavement construction. Silicon, 2018, 1–9.
Brett, E., Bizim, M. V., & Bostidas, D. M. (2018). Stress corrosion cracking of new 2001 lean-Duplex stainless steel reinforcements in chloride contained concrete pore solution: An electrochemical study. Construction and Building Materials, 192, 1–8. doi:10.1016/j.conbuildmat.2018.10.108
Busari, A. A., Akinmusuru, J. O., & Dahunsi, B. I. (2018). Review of sustainability in self compacting concrete: The use of waste and mineral additives as supplementary cemenitious material and aggregate. Portuguese Electrochimica Acta, 36(3). doi:10.4152/pea.201803147
Busari, A. A., Akinmusuru, J. O., Dahunsi, B. I., Ofuyatan, T., & Njene, B. (2017). Pavement construction using self-compacting concrete: Mechanical properties. International Journal of Advanced and Applied Sciences, 4(8), 50–55. doi:10.21833/ijas.2017.08.008
Chukwu, O., Adeoye, P. A., & Chidiebere, I. (2011). Abattoir wastes generation, management and the environment: A case of Minna, North Central Nigeria. International Journal of Biosciences, 1(6), 100–109.
Collepardi, S., Coppola, L., Troli, R., & Collepardi, M. (1999). A critical review of the durability in the new European standard (ENV 206). Proceedings of international conference on infrastructure regeneration and rehabilitation, 28 June - 2nd July. Improving the quality of life through better construction. A vision for the next millennium, pp. 1007–1017. Sheffield.
Falade, F., Ikponmososa, E., & Fapohunda, C. (2012). Potential of pulverized bone as a pozzolanic material. International Journal of Scientific & Engineering Research, 3(7), 1–6.
Gambhir, M. L. (2004). Concrete technology (3rd ed.) New Delhi: Tata Mc Grow Hill Company.
Hussain, R. R., & Ishida, T. (2010). Influence of connectivity of concrete pores and associated diffusion of oxygen on corrosion of steel under high humidity. Construction and Building Materials, 24(6), 1014–1019. doi:10.1016/j.conbuildmat.2009.11.017
Kulokowski, M. P. (2002). Contribution to the study of carbonation in concretes and composite mortars with active silica addition. (Doctoral Thesis). Federal University of Rio Grande do Sul, Porto Alegre.
Liu, X., Niu, D., Li, X., Lv, Y., & Fu, Q. (2018). Pore solution pH for the corrosion initiation of rebars embedded in concrete under a long-term natural carbonation reaction. Applied Sciences MDPI, 8(1), 128–143. doi:10.3390/app8010128
Loto, R. T., & Busari, A. A. (2019). Influence of white aluminum dross on the corrosion resistance of reinforcement carbon steel in simulated concrete pore solution. Journal of Bio and Tribio Corrosion, 5(19). doi:10.1007/s40735-018-0211-7
Malhotra, V. M., & Mehta, P. K. (2002). High-performance, high-volume fly ash concrete (pp. 101). Ottawa: Supplementary Cementing Materials for Sustainable Development.
Mindess, S., Young, J. F., & Darwin, D. (2003). Concrete (2nd ed.). Upper Saddle River, NJ: Pearson Education.
Ortolan, V. K., Mancio, M., & Tutkian, B. F. (2018). Evaluation of the influence of the pH of concrete pore solution on the corrosion resistance of steel reinforcement. Journal of Building Pathology and Rehabilitation, 1(10). doi:10.1007/s41024-016-0011-8
Perez, N. (2004). Electrochemistry and corrosion science. Boston: Kluwer Academic Publishers.
Singh, I. B., Singh, M., & Das, S. (2015). A comparative corrosion behavior of Mg, AZ31 and AZ91 alloys in 3.5% NaCl solution. Journal of Magnesium and Alloys, 3(2), 142–148. doi:10.1016/j.jma.2015.02.004
Zhao, Y. X., Zhang, X. W., & Jin, W. L. (2017). Influence of environment on the development of corrosion product-filled paste and a corrosion layer at the steel/concrete interface. Corrosion Science, 124, 1–9. doi:10.1016/j.corsci.2017.03.026
