Research Article

Physicochemical Properties of Hydrated Portland Cement Blended with Rice Husk Ash

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In the presence of significant quantities of carbon dioxide (CO_2) and elevated temperatures in the atmosphere due to climate change, cement-based materials are susceptible to carbonation. Blended cements are more prone to carbonation attack than Portland cement. There is a need to evaluate the carbonation resistance of blended cements in a carbonation-prone environment. This paper presents experimental findings obtained from an evaluation of carbonation resistance tests on Rice Husk Ash- (RHA-) blended cement. The blended cement was made by intergrinding of Portland Cement (PC) and RHA to make the test cement (PC-RHA). The RHA dosage in the PC-RHA was varied from 0 to 30% by mass of PC. Pozzolanicity, standard consistency, and setting time tests were conducted on PC-RHA. Mortar prisms measuring 160 mm × 40 mm *x* 40 mm were separately cast at a water/cement ratio (w/c) of 0.50 and 0.60 and cured in water for 2, 7, 14, 28, and 90 days. Compressive strength tests were conducted on the mortar prisms at each of the testing ages. The prepared mortars were also subjected to accelerated carbonation tests in two Relative Humidity (RH) curing regimes, one maintained at an RH greater than 90% and the other between 50–60%. Carbonation resistance of the mixtures was evaluated in terms of the changes in carbonation depth using a phenolphthalein test at the age of 7, 14, 28, and 56 days of curing in a continuous flow of CO_2. Compressive strength measurements were also taken during each of the carbonation testing ages. For comparison, similar tests were conducted using commercial PC. The results showed that PC-RHA was pozzolanic while PC was nonpozzolanic. Higher water demand and longer setting times were observed in PC-RHA than in PC. Moreover, there was increased strength development in water-cured samples with increased curing duration. Carbonation results indicated that there was a marked increase in carbonation depth with increased dosage of RHA in PC-RHA binders, increased duration of exposure to CO_2, and decreased RH (RH between 50–60%). PC-RHA binders exhibited lower carbonation resistance than PC. In conclusion, for mortars at any w/c ratio, carbonation resistance decreased with increase in RHA dosage and increased w/c ratio.

1. Introduction

Presently, there is an increase in greenhouse gas emissions, mainly anthropogenic CO_2, hence adversely affecting the earth's climate [1–3]. Recently, the global average surface air temperature has been reported to have increased [4, 5]. Rising sea levels, decreased snowpacks, and increased glacial melting increased heat waves and drought occurrences and increased extreme precipitation events, leading to increased flood risks in Africa and the rest of the world [6, 7]. As a consequence, the risks of decreased global food production potential for extinction of biodiversity are some of the potential effects of climate change in the world. However, limited attention has been paid to the effect of climate change on cement-based structures [8, 9].

Cement-based structures represent the major components of the built environment [10]. There is a growing need to evaluate the impact of climate change on our cement-based infrastructure. Reinforced concrete structures form an essential part of our world. Climate change has the potential to impact negatively on the durability of a cement-based infrastructure [8, 11]. There is need to recognize the effects that global climate change may have on a cement-based infrastructure in order to develop resilient construction

materials [12]. Due to climate change, there is a prevalence of significant quantities of carbon dioxide (CO_2) and elevated temperatures in the atmosphere, and under these conditions, cement-based materials are susceptible to carbonation [13, 14]. Carbonation of cementitious materials occurs due to a reaction between atmospheric CO_2 and the hydrated phases of cement, leading to a drop in its pH [15]. In reinforced concrete, a drop in pH of pore water leads to the depassivation of embedded rebar. Increased carbonation rates of reinforced concrete structures are expected as a result of increased temperatures and CO_2 concentrations, with the enhanced risk of carbonation-induced corrosion likely affecting the service life of cement-based structures. Therefore climate change may alter the ambient construction environment, especially in the longer-term, causing acceleration of carbonation-induced corrosion that leads to cracking and spalling, which result in more costly and disruptive repairs and maintenance activities, as well as strength loss of concrete structures [16].

Portland Cement (PC) is the main binder used in building and construction worldwide [17]. However, the manufacture of PC is an intensive process both in terms of raw material acquisition and energy. In the process, about 5% of carbon dioxide (CO_2) is emitted into the atmosphere. CO_2 is the main greenhouse gas mainly responsible for global warming and climate change [2]. In addition, due to the high energy demand associated with the production of PC, the resultant cement is expensive, especially to low-income earners. Blending of PC with pozzolanic materials has been found to be an innovative strategy to lower the cost of cement and reduce the amount clinker and, hence, lower CO_2 emission [18–20]. However, blended cements have been found to be susceptible to carbonation than PC due to lower amounts of calcium hydroxide (CH) in their hydrated phases [13, 21, 22]. Therefore, the performance of blended cements must be properly investigated to validate their application in carbonation-prone areas such as coastal and offshore regions and in present atmospheric conditions marked with increased CO_2 emission.

Increased demand for low-cost and environment-friendly cement has increased the demand for supplementary cementitious materials [23]. Rice is an agricultural crop produced in vast quantities globally [24]. Large amount of Rice Husks (RH) generated in the world is mostly burnt in open fields leading to environmental pollution, and the resultant Rice Husk Ash (RHA) is not beneficial to the soil. This is because the silica in RHA is in an unreactive and nonabsorbable form. This results in the use of RHA in land filling as a method of disposal. However, RHA has the potential to meet the growing need for production and use of sustainable construction materials in the world if used as a pozzolana in the manufacture of blended cements [25–30]. The durability of cement-based structures is a global pervasive problem. In view of changing environmental conditions due to climate change, there is a need to evaluate the performance of blended cements in aggressive media such as carbonation-prone environments [31, 32]. The carbonation-induced corrosion is the major cause of degradation and subsequent reduction in the service life of cement-based

materials and increased maintenance-related costs more so in structures located in coastal and offshore regions [33, 34]. Replacement of clinker with RHA is recently gaining the world attention as a viable option to lower the cost of cement and promote environmental conservation. However, increased substitution of clinker in cement with RHA has the potential to increase the susceptibility of the resulting cement-based structure to carbonation attack mostly due to prevalence of high quantities of CO_2 and elevated temperatures in the atmosphere due to climate change. It is, therefore, important to evaluate the robustness of PC-RHA cement blend under carbonation conditions to validate its applicability in such aggressive media. In this study, carbonation resistance of blended cement by intergrinding of Ordinary Portland Cement (PC) and Rice Husk Ash to make the test cement (PC-RHA) was investigated. The study aimed to evaluate the performance of a rice husk ash-based cement under ambient and severe carbonation conditions.

2. Materials and Methods

2.1. Materials.
Rice Husk (RH) was obtained from a rice processing plant located at Mwea town, Kirinyaga County, Kenya. The RH was incinerated at 600°C for 3 hours using a Muffle furnace model number OSK 9540-MK-SP 38351 to obtain RHA which was used as a pozzolana in the preparation of blended cement. Requisite amounts of RHA and PC were mechanically mixed in an automatic mixer to make PC-RHAs at 0, 10, 15, 25, and 30 percent substitution of PC by mass. Commercial 42.5 N Portland Cement (PC) was supplied by East Africa Portland Cement, located in Athi River, Machakos County, Kenya.

Brunauer–Emmett–Teller (BET) testing was used to evaluate the surface area of RHA. In this test, Nitrogen adsorption-desorption measurements were conducted at 77 K on a Micromeretics Tristar 3000 apparatus to determine the Brunauer–Emmett–Teller (BET) surface area. Prior to measurements being taken, samples were dried at 105°C and kept in a desiccator until testing. In addition, the samples were cooled with liquid nitrogen and analyzed by measuring the volume of gas (N_2) adsorbed at specific pressures. The BET adsorption theory was used for the determination of surface area, using the corresponding values of the relative pressure between 5-35% of the adsorption curve assuming that there was complete pore saturation.

The composition of RHA- and PC-RHA-blended cements used in this study is given in Table 1.

2.2. Methods

2.2.1. Pozzolanicity Test.
A saturated lime test was used to assess the pozzolanic activities of the test cements [35]. The testing reagents were prepared by separately dissolving requisite amounts of ethylenediaminetetraacetic acid disodium salt dehydrate (EDTA), concentrated HCl, and NaOH in water to make 0.025M EDTA, 0.1M HCl, and 5M NaOH solutions, respectively. The 0.025M EDTA solution was standardized against dried calcium carbonate while 0.1M HCl was standardized against dried sodium carbonate. Murexide indicator

Table 1: Composition and physical properties of RHA and PC.

Composition	RHA	PC
SiO_2	82.43	20.28
Al_2O_3	1.35	4.98
Fe_2O_3	1.28	3.42
CaO	1.22	62.97
MgO	1.97	2.65
SO_3	0.18	2.75
K_2O	2.51	0.28
Na_2O	0.15	0.36
LOI	2.95	1.38
BET (m^2/g)	51.4	
Blaine surface area (m^2/g)	2.31	
Specific gravity	2.12	2.95

was prepared by intergrinding 0.5 g of murexide and 100 g of dried potassium chloride using a pestle and mortar.

Curing of the test sample for the test was performed by pipetting 100 ml of freshly boiled water into a 0.5 litre plastic container and the sealed container placed in a thermostatic enclosure at $40 \pm 0.2°C$ until equilibrium was reached in about an hour. The container was removed from the thermostatic enclosure, and 20.00 g of test cement was poured into it using a wide funnel. The container was then immediately sealed and shaken vigorously for about 20 seconds. A horizontal rotary motion was adopted, thus preventing any sample or liquid from being thrown up and remaining separated from the rest of the solution. The container was then placed back in the thermostatic enclosure. After a period of testing (3, 8, 21, or 28 days), the container was removed from the enclosure and filtered immediately under vacuum. A Butchner funnel, a vacuum flask, and dry Whatmann filter paper were used for the filtration. The flask was then sealed immediately to avoid carbonation. The filtrate was allowed to cool to room temperature in about ten minutes.

To determine the concentration of the OH^- ions, 50 ml of the filtrate were pipetted into a 250 ml conical flask, and about five drops methyl orange indicator was added. The resulting solution was titrated against 0.1 M HCl. The OH^- concentration in millimoles per litre was calculated using the following equation:

$$[OH^-] = \frac{1000 \times 0.1 \times V}{50}, \tag{1}$$

where V is the volume of the 0.1 M HCl used for the titration.

To determine the concentration of CaO, about 5 ml of 5 M NaOH and 50 mg of the murexide indicator were added to a measured solution that remained after completion of OH^- determination. The resulting solution was titrated against the 0.025 M EDTA solution. During titration, the pH of the solution was maintained at 13 by the addition of the NaOH solution. The pH was monitored using a pH meter. The concentration of $Ca(OH)_2$ was calculated using the following equation:

$$[CaO] = \frac{1000 \times .025 \times V}{50}, \tag{2}$$

where, in this case, V is the volume of the EDTA solution used for the titration.

2.2.2. Standard Consistency. Standard consistency was determined in accordance with the KS EAS 148-3:2000. In this test, about 500 g of test cement was weighed and a known quantity of water was added and mixed thoroughly for about 5 minutes on a nonporous surface using two trowels to avoid loss of water or cement. The paste was transferred to the Vicat apparatus, was placed on a lightly greased plane glass base plate, and was filled to excess without compacting or vibrating. The excess paste was removed by a gentle sawing motion with a straight edge. The Vicat apparatus was then calibrated with a plunger by lowering the plunger to rest on the base plate which was used to adjust the pointer to read zero on the scale. The plunger was later raised to the standby position. The mould and the base plate were transferred to the Vicat apparatus immediately after levelling the paste and were positioned centrally under the plunger. The plunger was then lowered gently until it came in contact with the paste.

The plunger was allowed to pause in that position for about two seconds so as to avoid initial velocity. The moving parts were released quickly, and the plunger was allowed to penetrate vertically into the centre of the paste. The scale was read when penetration ceased. The recorded scale reading indicated the distance between the bottom face of the plunger and the base plate. The water content of the paste was expressed as a percentage by mass of the various cement categories. The plunger was cleaned, and the process was repeated with pastes containing different water contents determining to find the one that would produce a distance between plunger and base plate of 6 ± 2 mm; the water content of this paste was calculated as a percentage by mass and was recorded as water that was required for standard consistency.

2.2.3. Setting Time. The setting time of test cement was determined in accordance with the KS EAS 148-3:2000. In this method, the Vicat apparatus were used for the determination of both initial and final setting times of the samples. For the determination of initial setting time, the calibrated Vicat apparatus were used. The needle with a diameter 1 mm (0.04 inch) was lowered to rest on the base plate used, and the pointer was adjusted to read zero from the scale. The needle was raised to a standby position which was followed by filling the Vicat mould with the paste under a prescribed standard consistency. The filled mould and paste were placed in the curing room, and after 45 minutes, they were transferred and positioned under the needle. The point at which the needle penetrated to a point of 5 mm (0.2 inch) from the bottom of the mould after adding water to the cement signalled that the initial set had occurred and was taken as the initial setting time. KS EAS 18 : 2001 prescribes a minimum initial setting time of 75 minutes for Portland pozzolana cements.

Final setting time was determined using the replacement needle with a hollow circular metal attachment of diameter 5 mm and was set 0.5 mm behind the tip of the needle. The

filled mould and the base plate were placed in the room after determination of the initial setting time. After 30 minutes, it was transferred and positioned under the needle. The final set occurred when the needle circular ring would fail to make a mark on the paste, and the time was recorded from the zero scale of the Vicat apparatus. KS EAS 18 : 2001 prescribes 600 minutes as the maximum final setting time for Portland pozzolanic cement.

2.2.4. Compressive Strength. Compressive strength for the mortars was determined in accordance to KS EAS 148-1: 2000. From each cement category, three mortar prisms measuring 160 mm × 40 mm *x* 40 mm were separately cast at a water/cement ratio (*w/c*) of 0.50 and 0.60 and cured in water for 2, 7, 14, and 28 days. Compressive strength tests were conducted on the mortar prisms at each of the testing ages using the compressive machine. The prisms were tested for compressive strength using a compressive strength machine model number SSC-546 following the instructions on the instrument manual. Average of triplicate measurements was taken as the final compressive strength.

2.2.5. Carbonation Test. Accelerated carbonation tests were performed on cement mortars prepared from each test cement. For each type of cement, at a particular *w/c* ratio, six mortar prisms measuring 40 mm × 40 mm × 160 mm were cast. The prisms were placed in a curing chamber maintained at $23 \pm 1°C$ and a relative humidity greater than 90% for 24 hours. After 24 hours $\pm$ 30 minutes, the specimens were demoulded and marked accordingly for identification purposes. Half of the specimens were placed in the humidity chamber maintained at $23 \pm 1°C$ and 50–60% relative humidity in a closet for 14 days. Another half of the specimens was placed in the humidity chamber maintained at $23 \pm 1°C$ and relative humidity greater than 90% for 14 days as well.

After 14 days of curing, all specimens were introduced into the closed box which had a continuous flow of CO_2. At the age of 7, 14, 28, and 56 days, the specimens were taken out from the box and each specimen was broken longitudinally into half. The weight and compressive strength measurements were taken on each specimen. The depth of carbonation was measured by taking measurements over multiple points perpendicular to the edges of the split face after application of a phenolphthalein indicator solution on each half of the broken prism.

3. Results and Discussions

3.1. Pozzolanic Activity. The pozzolanic activity was used to measure the degree of reaction between an RHA and $Ca(OH)_2$ in the presence of water at ambient temperature. The quantity of $Ca(OH)_2$ in the test cement solution was evaluated in terms of the concentration of CaO and OH^- at different curing durations, as shown in Figures 1 and 2, respectively. Generally, the lower the resulting quantity of CaO and OH^-, the higher the pozzolanicity, and vice versa.

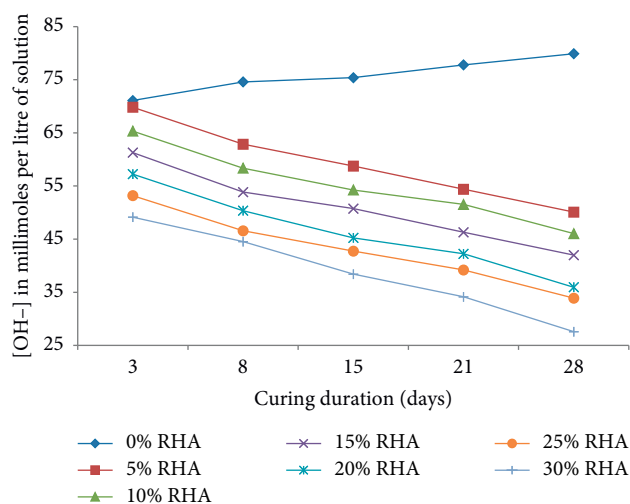In both Figures 1 and 2, a progressive decrease in the concentration of CaO and OH^- was observed in all the
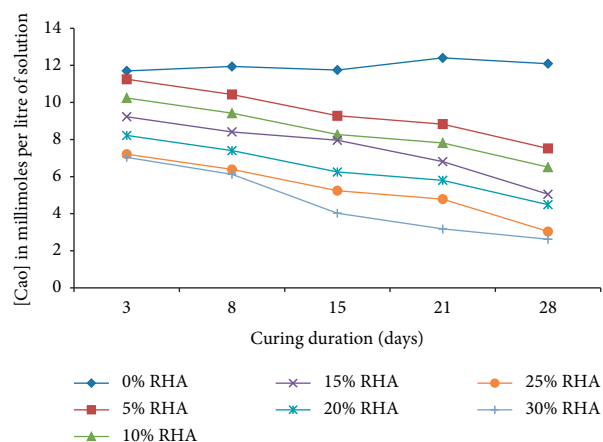

FIGURE 1: Concentration of OH^- in RHA-PC-blended cements.

FIGURE 2: Concentration of CaO in RHA-PC-blended cements.

RHA-PC-blended cements and decreased in PC with increased curing duration. This can be attributed to the differences in their cement hydration processes. During the hydration process in PC, C_3S and C_2S undergo hydration reactions to produce CH as shown in the following equations:

$$2C_3S + 6H \longrightarrow 3CSH + 3CH \qquad (3)$$

$$2C_2S + 4H \longrightarrow 2CSH + 2CH \qquad (4)$$
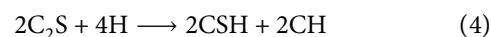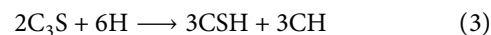
The CSH formed in equations (3) and (4) is mainly responsible for strength development in the cement-based structures. The increase in concentration of CaO and OH- in PC can be attributed to the production of CH with continued curing.

Conversely, the decrease in concentration of OH^- and CaO can be attributed to the consumption of CH during the pozzolanic reaction in RHA-blended cements. RHA contains amorphous silica and alumina and, therefore, exhibits pozzolanic properties. During the pozzolanic reaction, the hydration of PC produces CH which reacts with silica and

alumina present in RHA as shown in the following equations:

$$3CH + S + H \longrightarrow CSH \tag{5}$$

$$A + H + CH \longrightarrow CAH \tag{6}$$

Increased curing period results in higher consumption of CH in pozzolanic reactions and results in progressive decrease in the amount of CH in the hydrated RHA-blended cement matrix.

It was observed that the concentration of OH^- and CaO decreased with increase in the amount of RHA added. This could be possibly due to the fact that increased amount of RHA introduced more amorphous silica and alumina in RHA-blended cement mixtures. Increased availability of amorphous silica and alumina results in greater pozzolanic activity. In conclusion, RHA was found to exhibit pozzolanic properties.

3.2. Standard Consistency.

The standard consistency as a function of percentage replacement of RHA of the test cements is presented in Figure 3.

It was observed that the standard consistency of RHA-blended cements increases from 25.10 to 35.52 percent as RHA replacement increased from 0 to 30 percent. Increase in standard consistency with increase in RHA addition can be attributed to the high fineness and surface area of RHA. According to Raheem and Kareem [36], RHA is considered hygroscopic; hence, more water is required for wetting the particles as the total specific surface of the particle increases.

3.3. Setting Time.

The initial and final setting time of RHA-blended cements are presented in Figure 4.

PC (0% RHA) exhibited shorter initial and final setting time than RHA-blended cements. This could be attributed to higher content of clinker phases (C_3S and C_3A) in PC (0%RHA) than in the other blended cements. C_3S hardens rapidly in the presence of water; hence, it is responsible for the early setting of cement paste. Hydration of C_3A produces significant amount of heat that increase the prevailing setting temperature resulting to faster setting behaviour of PC (0%RHA) compared with blended cements. The setting time of cement decreases with a rise in temperature. Moreover, the slow pozzolana reactions that take place in RHA-blended cements result in slow cement hydration and, hence, increased setting times [37].

It was observed that both initial and final setting time of RHA-blended cements were observed to increase with increase in addition of RHA in the order% 0 RHA< 5% RHA< 10% RHA <20% < 25 RHA< 30% RHA. This is could be attributed to the increased quantity of RHA added at 0, 5, 10, 15, 20, 25, and 30 percent, respectively. Increase in the content of RHA incorporated in the RHA-blended cements resulted to longer initial and final setting times, perhaps due to the fact that the increased addition of RHA in RHA-blended cements progressively
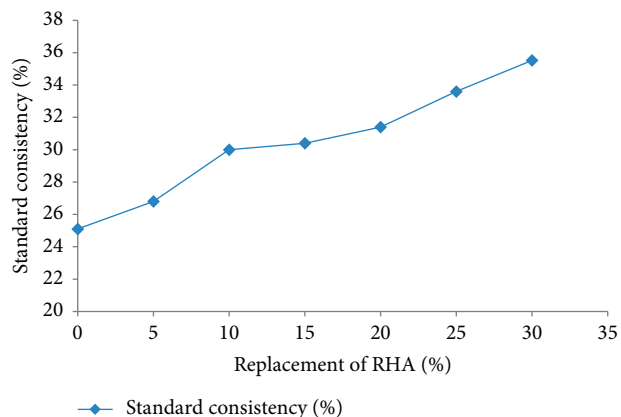

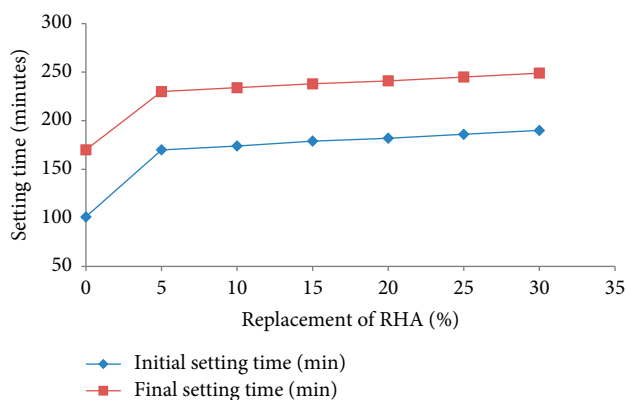FIGURE 3: Standard consistency as a function of percentage replacement of RHA.

FIGURE 4: Setting time of RHA-blended cements at different replacements of RHA.

reduced the amounts of C_3S and C_3A components resulting in the slow setting of these cements.

In conclusion, the EAS 148-3:2000 prescribes that blended cements should have setting times of between 180 ± 10 minutes and 240 ± 10 minutes while PC should be between 100 ± 10 minutes and 170 ± 10 minutes for initial and final setting times, respectively. All the test cements conformed to this specification. Generally, for each cement category, nonblended cement exhibited shorter setting time than RHA-blended cements.

3.4. Compressive Strength.

The compressive strength results for various RHA-blended cements at different curing duration and w/c are shown in Figure 5.

Compressive strength increased with increased duration of curing for all the RHA-blended cements. This can be attributed to the hydration reactions occurring in the hydrated cement matrix resulting in the formation of CSH, as shown in equations (3) and (4). The reference nonblended binder (0% RHA) exhibited higher compressive strength than the other RHA-blended cements at all the w/c ratios. This can be attributed to the fact that the 0% RHA contained the highest proportion of PC; hence, the clinker phases (C_3S and C_2S) which are mainly responsible for strength are
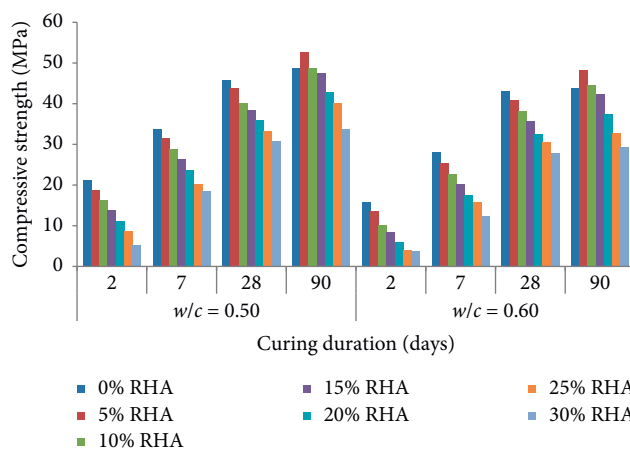
Figure 5: Compressive strength verses curing duration for RHA-blended cement.

relatively high in proportion compared to the RHA-blended cements mixtures [23, 38]. Similarly, there was a progressive decrease in compressive strength with increased substitution of PC with RHA due to the progressive decrease in the amount of PC in RHA-blended cements at all the w/c ratios. This implied that the added RHA did not contribute to strength development but was mainly a filler material in mortar.

At each curing age, an increase in w/c ratio resulted in decrease in compressive strength of all cements considered. The strength decreased in the order $w/c = 0.50 > w/c = 0.60$. w/c ratio is considered as the most important factor affecting mortars/concrete strength. This is because it affects the porosity of the hardened paste. Increased quantity as a result of use of high w/c ratio also affects the flow or rheology of the mixture, as well as cohesion between paste and aggregate. High w/c increases the voids and reduces the cohesion in the mortar matrix, and as a result, it reduces the overall strength of the mortar [39].

In conclusion, the KS EAS 18:1-2001 requires that blended cements should have a minimum compressive strength of 32.5 MPa at 28 days of curing. The RHA-blended cements satisfied this requirement up to 20 percent of replacement with RHA.

3.5. Carbonation

3.5.1. Depth of Carbonation. The carbonation depth obtained from the phenolphthalein test profiles for various RHA-blended cement mixtures at different humidity regimes is given in Figure 6.

It was observed that carbonation depths in mortars cured at 50–60 percent relative humidity was greater than that found in mortars cured at 90 percent relative humidity. The differences in relative humidity during curing explain the difference in carbonation depths observed. In the presence low relative humidity (50–60 percent), mortars were relatively dry; hence, the penetration of carbon dioxide in the mortar matrix is high resulting in greater depths of carbonation than at high relative humidity (90 percent). At low humidity, the hydration of cement is poor due to

insufficient moisture; hence, limited hydration of cement occurs resulting in the formation of low amounts of CSH and calcium hydroxide (CH) [13, 14, 40, 41]. CH binds the ingressed carbon dioxide, preventing further penetration into the mortar. Low quantities of CSH result in a very porous hydrated mortar matrix which increases the permeability of hardened cement and allows greater depth of CO_2 penetration. On the other hand, at high RH, the mortars were relatively wet; hence, greater amount of CSH is formed, thus reducing the porosity of the hydrated mortars. Low porosity leads to low permeability of the hydrated mortars and, hence, low CO_2 penetration [13, 42].

It was observed that the depth of carbonation also increased with increase in the curing period for all the cement categories considered. Increase in curing duration has been found to effectively increase the extent of carbon dioxide penetration in the mortars [43]. Similar observations were made by Balayssac et al. [44] while studying the effects of curing upon carbonation of concrete.

RHA-blended cement (5% RHA and 20% RHA) mortars exhibited higher depth of carbonation than OPC mortars (0% RHA-blends). This can be attributed to the fact that blended cements contain lower quantities of $Ca(OH)_2$ than 0%RHA mortars. The SiO_2 and Al_2O_3 in the calcined clays react with $Ca(OH)_2$ resulting from the hydration of Portland cement. As a consequence, the blended cement leads to a lower $Ca(OH)_2$ content in the hardened cement paste so that a smaller amount of CO_2 is required to remove all the $Ca(OH)_2$ by producing $CaCO_3$ during carbonation [45–47]. Therefore, the depth of carbonation was observed to be greater in blended cements since the amount of $Ca(OH)_2$ present was lower. It follows that the presence of RHA resulted in a more rapid carbonation. In a related study [48], it was observed that PC showed shorter depth of carbonation than blended cements. The workers attributed this to the differences in the content of $Ca(OH)_2$ present in both PC and blended cements.

There was a slight increase in the depth of carbonation with increase in w/c. The depth of CO_2 penetration increased in the order $w/c = 0.50 < w/c = 0.60$. This can be attributed to the fact that increased w/c results in increased permeability
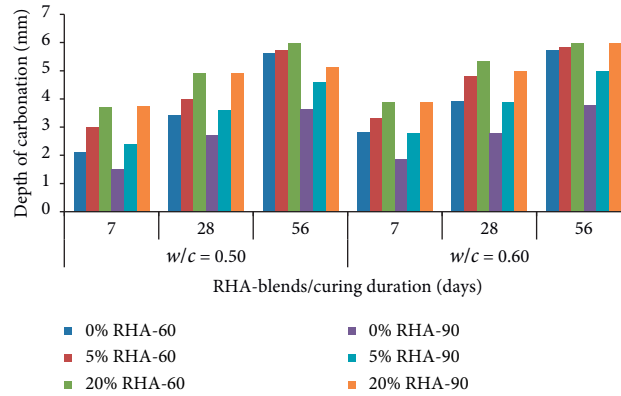
FIGURE 6: Depth of carbonation at different curing periods verses RHA-blends.

of the hydrated mortar matrix and, thus, higher penetration of CO_2 [11, 41, 49–51].

3.5.2. Effects of Carbonation on Compressive Strength.
The compressive strength development for various RHA-blended cement mortars exposed to different curing humidity is shown in Figure 7.

Higher compressive strengths were observed in mortars cured at 90 percent than their corresponding mortars cured at 60 percent relative humidity. This can be attributed to the different curing humidity conditions that the mortars were subjected to. Low humidity (60 percent) allows more ingress of CO_2 than mortars cured at high humidity (90 percent) [41]. CH which is one of the products formed during hydration of cement readily reacts with CO_2 resulting in precipitation of sparingly soluble calcium carbonate ($CaCO_3$) as shown in the following equations [52–55]:

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O \qquad (7)$$

$$CSH + CO_2 \longrightarrow SiO_2 + 2CaCO_3 + H_2O \qquad (8)$$
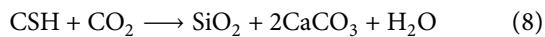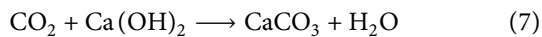
Equation (7) represents the moderate carbonation process that occurs on the surface layer of cement-based materials leading to the formation of $CaCO_3$. The $CaCO_3$ formed is deposited on the pore network in the hydrated cement matrix resulting in pore refinement of the carbonated layer [56–60]. This is beneficial since pore refinement subsequently results in increased strength, reduced porosity, and improved durability of hydrated cement. This explains why there was an increase in compressive strength of mortars with continued curing when exposed to a CO_2-laden environment [60]. Conversely, equation (8) shows that continued ingress of CO_2 attacks CSH resulting in its disintegration, and subsequent loss of strength in cement-based structures mostly occurs if there is low RH. This explains why mortars cured at 60% RH exhibited lower compressive strength than those cured at 90% RH [13, 61].

During carbonation, OH^- present in CH is consumed resulting in the decrease of pore solution pH. In case of reinforced concrete, reduction in the pH value leads to the destruction of the protective passive surface layer around steel
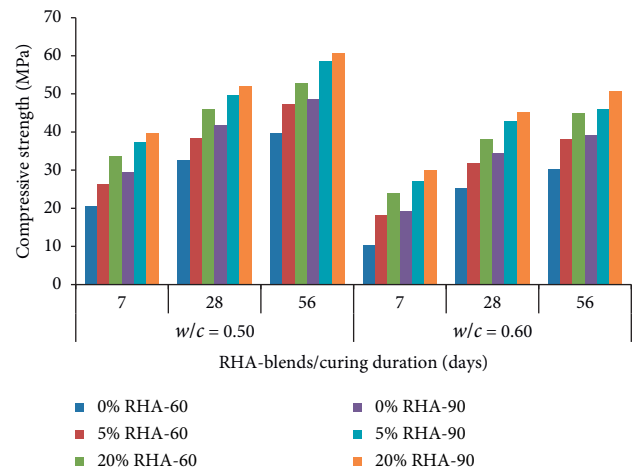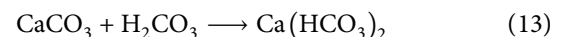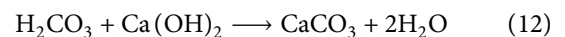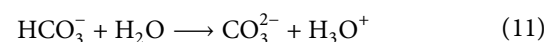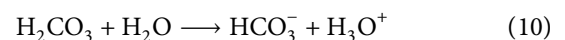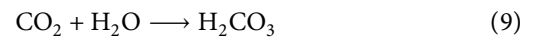

FIGURE 7: Compressive strength development at different curing durations verses RHA-blends type.

reinforcement resulting in rebar corrosion [15, 61, 62]. In areas with high concentration of dissolved CO_2, for example, in estuaries, the effects of carbonation are more deleterious since carbonic water is more acidic in seawater than in fresh water [63]. This can be worsened by the decaying organic matter releasing CO_2 [63]. The carbonation-related chemical reactions that result in the degradation of cement-based materials due to dissolved CO_2 are presented as follows [13, 13]:

$$CO_2 + H_2O \longrightarrow H_2CO_3 \qquad (9)$$

$$H_2CO_3 + H_2O \longrightarrow HCO_3^- + H_3O^+ \qquad (10)$$

$$HCO_3^- + H_2O \longrightarrow CO_3^{2-} + H_3O^+ \qquad (11)$$

$$H_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2H_2O \qquad (12)$$

$$CaCO_3 + H_2CO_3 \longrightarrow Ca(HCO_3)_2 \qquad (13)$$

Equation (9) represents the formation of carbonic acid (H_2CO_3) from dissolved CO_2 present in the pore solution or

due to decaying organic matter or polluted water bodies. Based on equations (10) and (11), H_3O^+ produced results in significant reduction in the pH of the pore solution in the hydrated cement matrix [63]. Reduction in the alkalinity of the pore solution is deleterious since it results in carbonation-induced corrosion of rebars through dissolution of its passive surface layer. In addition, equations (12) and (13) show that significant penetration of CO_2 results in the conversion of insoluble $CaCO_3$ to soluble $Ca(HCO_3)_2$ which is easily leached out, thus decreasing porosity and subsequent strength of hydrated cements [13]. This explains why continued exposure of mortar prisms results in progressive loss of strength.

4. Conclusions

The following conclusions can be drawn from the study:

(1) The RHA-blended cement was pozzolanic while PC used was nonpozzolanic. This shows that the blended RHA was reactive.

(2) RHA-blended cement satisfied the EAS 18:1-2001 standards for blended cements up to 20 percent substitution with RHA. This implied that the RHA was a potential pozzolanic material for the production of blended cement.

(3) Nonblended cements (0% RHA) exhibited greater resistance to carbonation at all the w/c ratios used than RHA-blended cement. Therefore, one needs to be cautious if the RHA-blended cements are considered for application in CO_2-rich areas such as estuaries or marine construction activities.

(4) all the mortars at any w/c ratio, carbonation resistance decreased with increase in RHA dosage and increased w/c ratio. This is mainly due to the decreased amount of calcium hydroxide in hydrated mortars as a result of pozzolana reaction. Low amount of calcium hydroxide effectively reduces the buffering capacity of hydrated cements against carbonation attack.

Data Availability

The data used to support the findings of this study can be obtained from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

Acknowledgments

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