Research Article

Physicochemical Performance of Portland-Rice Husk Ash-Calcined Clay-Dried Acetylene Lime Sludge Cement in Sulphate and Chloride Media

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This paper reports leach and/or intake of SO_4^{2-}, Cl^-, Ca^{2+}, Na^+, and K^+ from and/or into cement mortar cubes made from a novel cementious material in naturally encountered environmental simulated media. The paper also reports changes in pH of the media over time of exposure to the cement mortar cubes. The compressive strength changes of the test cement in simulated media are also reported. The novel cement, labelled PCDC, made from intermixing ordinary Portland cement (OPC) with waste materials which included rice husks, waste bricks, acetylene lime sludge, and spent bleaching earth was previously tested and found to meet the Kenyan Standard requirements for Portland pozzolana cement (PPC). 100 mm mortar cubes were prepared, and their compressive strengths were determined after exposure to the sea water. The media included sea water, distilled water, and solutions of sulphates and chlorides separately for a period of six months. The tests were carried alongside commercial PPC and OPC. The results showed that the PCDC exhibited comparable selected ions intake and/or leach to PPC in sea water, sulphate solutions, and distilled water. In chloride solutions, the cement exhibited the highest leach in the selected ions except K^+ and Na^+ ions. The results further showed that PCDC exhibited lower pH in all the media compared to OPC and PPC. The tests showed that the novel cement can be used for general construction work in the tested media in a similar manner to PPC.

1. Introduction

Cement is a major building binder throughout the world. Ordinary Portland cement (OPC) has been used in vast construction activities in the past. However, OPC production requires significant amount of energy [1]. This makes the product unaffordable especially in low and middle economy counties. In addition, during the manufacturing process, enormous quantities of carbon dioxide (CO_2) are emitted to the atmosphere. CO_2 is one of the main greenhouse gases mainly responsible for global warming and climate change.

There is an increasing demand for greener construction materials with low carbon footprint globally [2]. Portland pozzolana cement (PPC) has recently emerged as a suitable alternative to OPC. PPC is mostly preferred to OPC due to the fact that it exhibits high ultimate strength and it is more durable than neat OPC. This is mainly attributed to the inclusion of pozzolanic materials in PPC. The pozzolanic materials are highly siliceous and aluminous, and in the presence of calcium hydroxide (CH), at ambient temperatures, they react with silica (SiO_2) and alumina (Al_2O_3) to form compounds processing cementitious properties [3].

Rice husk ash (RHA) and broken bricks (BBs) have been used as pozzolanic materials for many decades [4, 5]. Inclusion of these materials in cement production is considered an innovative solution to improve the performance of

cement-based materials and offer an environmentally friendly method of waste disposal. However, substitution of OPC with these pozzolanic materials above 35% has been reported to greatly lower the strength of the resulting cement-based materials [6]. This has largely been attributed to insufficient CH in PPC containing pozzolanic materials greater than 35 percent. Previous studies conducted using PPC made from blending 55 percent of OPC with dried acetylene lime cement and an incinerated mix of rice husks, reject bricks, and spent bleaching earth showed that a cementitious material is formed [7–11]. These showed that the cementitious material, labelled as PCDC in this work met the Kenyan standard [12] requirements for PPC in terms of compressive strength and setting times [8]. Further tests were therefore necessary to observe its resistivity in terms of main ions leach or intake in aggressive media commonly encountered in the natural environment during the construction activities.

2. Materials and Methods

2.1. Materials. Materials were sampled from their respective regions in Kenya. Pozzolana material preparation and incineration was done in accordance with the procedure outlined in [8] using a fixed bed kiln. Sea water as obtained from the sampling site was stored in clean plastic bottles. Table 1 gives the composition of various materials used in this study.

2.2. Methods. About 500 ml of it was sampled for analysis of Na^+, K^+, Ca^{2+}, Cl^-, and SO_4^{2-} using the usual methods in flame photometry (for Na^+ and K^+), atomic absorption spectrometry (Ca^{2+}), potentiometry (Cl^-), and turbidimetry (SO_4^{2-}).

100 mm mortar cubes were prepared using 1 : 3 cement to sand ratio and a w/c ratio of 0.46. Commercial OPC and PPC were also used alongside PCDC. A vibrating poker model B25DS was used for compaction purposes. The cubes were demoulded after 24 hours and then cured for additional 27 days in saturated calcium hydroxide solution under complete submersion. The cubes were then submerged into a 500 ml media in a 2 litre plastic container. The media used included sea water, distilled water, and separate solutions of magnesium chloride and sodium sulphate. Magnesium chloride, labelled Cl1, and sulphate solutions, labelled SO1, were prepared to have an equivalent of chloride and sulphate concentration in sea water, respectively. These were 20,000 and 2342 ppm, respectively. Similar solutions but with double the chloride and sulphate, Cl1 and SO2, were also used. An aliquot of the aggressive media was sampled each time for analysis of the selected ions (Ca^{2+}, Na^+, Cl^-, and SO_4^{-2}). An equal amount of the original solution of each category was replenished after sampling. The pH of the aggressive media was monitored by using the pH meter model number 3405. The analysis was done for a period of six months.

After about six months of monitoring of Ca^{2+}, Na^+, K^+, Cl^-, and SO_4^{2-} ions and pH changes in the corrosive media,

TABLE 1: Compositions of various materials used.

Material	Description
OPC	Commercial ordinary Portland cement (42.5 N/mm)
PPC	Commercial Portland pozzolana cement or blended cement (32.5 N/mm)
PCDC	A blend of 55% OPC and 45% test ash
Test ash	A blend of DALS and a calcined mix of RH, SBE, and ground BB
SO1	Sulphate-simulated solutions with sulphate concentration equal to the sea water
SO2	Sulphate-simulated solutions with sulphate concentration twice the sea water
Cl1	Chloride-simulated solutions with chloride concentration equal to the sea water
Cl2	Chloride-simulated solutions with chloride concentration twice the sea water
DALS	Dried acetylene lime sludge
Corrosive media	Sea water, 20,000 and 40,000 ppm Cl^- ($MgCl_2$) solution, distilled water, 2342 and 4684 ppm SO_4^{2-} (Na_2SO_4) solution

compressive strength of the three mortar cubes representative of each category was determined. The change in the compressive strength from the 28th day to the sixth month was calculated using the following equation:

$$\%C.S_{gain} = \frac{C.S\left(n^{th}\,day\right) - C.S_{DW}\left(n^{th}\,day\right)}{C.S_{DW}\left(n^{th}\,day\right)}, \qquad (1)$$

where $\%C.S_{gain}$ is the calculated percent gain in compressive strength; $C.S\left(n^{th}\,day\right)$ is the compressive strength at the nth day, which in this study was 180th day; and $C.S_{DW}\left(n^{th}\,day\right)$ is the compressive strength of the similar mortar cube in distilled water (which acquired a high pH within a short time of exposure) at the nth day.

3. Results and Discussion

3.1. Cl^- Analysis of Selected Ions from Chloride Solution. Figures 1 and 2 give the progressive intake and leaching of the chloride ions in magnesium chloride-simulated solutions against the monitoring period by mortar cubes of each category.

In chloride-simulated solution 1, the PCDC had the highest initial intake followed by an early subsequent leach in chloride ions. The high intake in PCDC could be associated with higher permeability due to the high levels of substitution coupled with the lower pozzolanic reaction.

OPC had a higher intake of the chlorides than the PPC from Cl1 solution. This could be attributed to the higher exchange capacity due to a higher OH^- ions [11]. Pozzolana reaction lowers the $Ca(OH)_2$ content and hence the buffer store of the OH^- ions. The additional cementious material from pozzolanic reaction, higher Al_2O_3 phase from the reactive constituents of pozzolana, and packaging of pozzolana grains between cements aggregates lower the diffusivity of chlorides into the bulk. This in turn lowers the intake of the ions in pozzolana-based cements.
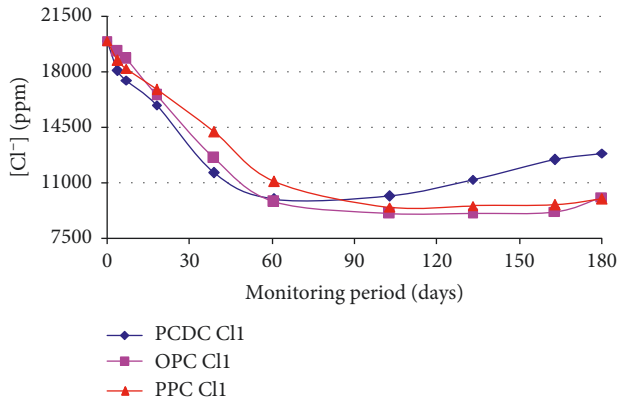
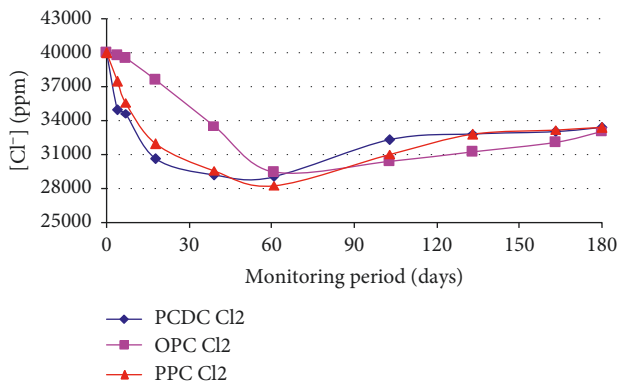Figure 1: Cl^- analyses in chloride-simulated solution 1.

Figure 2: Cl^- analyses in chloride-simulated solution 2.

Figure 3: SO_4^{2-} analyses in chloride-simulated solution 1.

Figure 4: SO_4^{2-} analyses in chloride-simulated solution 2.

As the concentration of the chloride is doubled in Cl2, OPC showed a decreased intake of chlorides than the PPC. Perhaps the beneficial effects above of denser mortar, reduced $Ca(OH)_2$ levels made PPC less resistant to the $MgCl_2$ attack. This was attributed to higher amount of $Ca(OH)_2$ in OPC than that in PPC. High content of $Ca(OH)_2$ in OPC made its CSH to be attacked more by chlorides than that in PPC. PPC being denser, from pozzolanic reaction may have left little space for expansive brucite from Mg attack [13, 14].

3.2. SO_4^{2-} Analyses in Chloride-Simulated Solutions.
Figures 3 and 4 show the sulphate leach and intake from the chloride-simulated solutions. Sulphates were observed to increase in the corrosive media rapidly up to about the 11th and 25th day in the simulated chloride solution 1 and 2, respectively. The ions then showed a fast decline to an almost constant amount.

The chloride solutions did not have sulphate ion in the first place, and therefore, the ions must have been leached from the cement mortars. The sulphates may have been leached as soluble salts of sodium and/or potassium or even the sparingly soluble calcium sulphates. These sulphates may have originated mainly from the interground gypsum.

The decrease in the sulphates from the corrosive solution could have been due to the precipitation of the sulphate ions as calcium sulphates. The reaction between Ca^{2+} and SO_4^{2-} is as shown in the following equation:
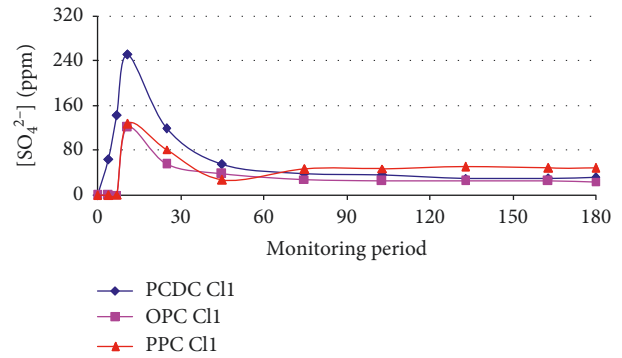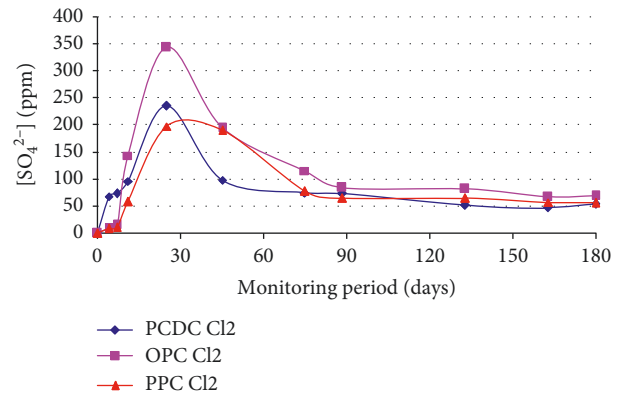
$$Ca^{2+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)} + 2H_2O_{(l)} \longrightarrow CaSO_4 \cdot 2H_2O_{(s)} \quad (2)$$
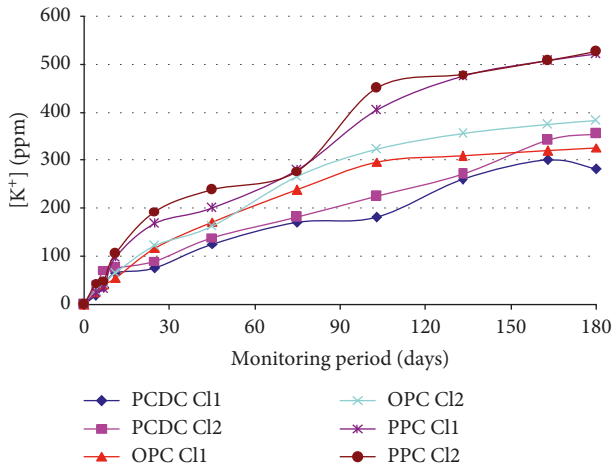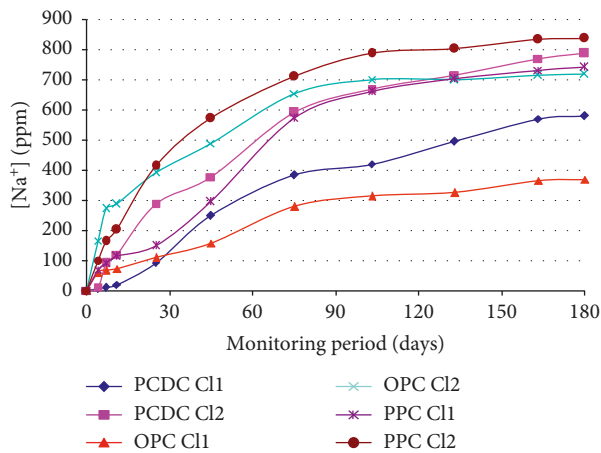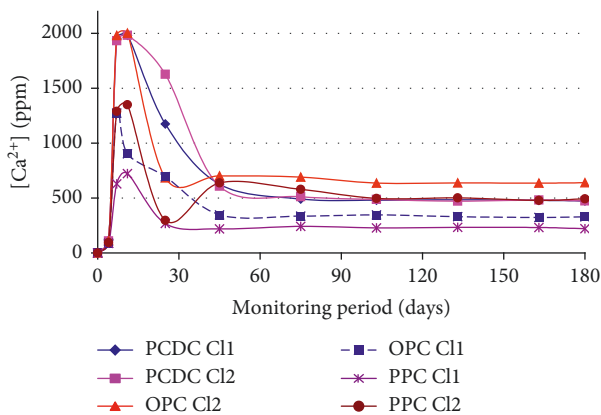
The sulphates could have also been precipitated due to the effect of the chlorides and hydroxides on the media. Sulphates, especially of alkalis and alkaline earth metals, have a diminishing solubility in the presence of chlorides and hydroxides [15].

As the concentration of the chloride solutions were doubled, the OPC showed the highest sulphate leach. This may have been attributed to a higher level of gypsum in OPC that became a vulnerable phase as the chloride concentration increased. The substitution of the OPC with pozzolana reduces the amount of available sulphate from cements. It was notable that, in both cases of chloride concentrations, the amount of leached sulphates from PCDC was about the same at the early days of subjection in the corrosion media.

As the monitoring period progressed, it was observed that the test-mortar cements exhibited a decline in SO_4^{2-} leach. The decline was most pronounced in PCDC especially with increased chloride concentration. With time, pozzolana-based cements become denser due to pozzolanic reactions. Thus, PCDC may have become less permeable and hence less vulnerable to the aggressive media.

3.3. K^+, Na^+, Ca^{2+}, and pH Analyses in Chloride-Simulated Solutions.
Figures 5–7 show the results of K^+, Na^+, and Ca^{2+}

FIGURE 5: K$^+$ analyses in chloride-simulated solution.

FIGURE 6: Na$^+$ analyses in simulated chloride solutions.

FIGURE 7: Ca^{2+} analyses in simulated chloride solutions.

FIGURE 8: pH measurements in simulated chloride solutions.

there was a decline in the Ca^{2+} leached. Ingress of chlorides could have improved the microstructure and hence permeability and strength of pozzolana-based cements. Pozzolanic reactions consume Ca(OH)$_2$. Thus blended mortars as observed were expected to show a decline in the amount of leached ions, for example, Ca^{2+} as permeability decreased because their resistivity to aggressive agents had increased.

There was a marked increase in pH of the chloride solution accompanied by leaching of the alkali metal ions from the test cement mortars. Generally, contact water with concrete is expected to attain a pH value above 9 or almost at equilibrium with the pore water. This corresponded with the leach of the alkali ions observed in all the test cements.

The ingress of Cl$^-$ is accompanied by leaching (in exchange) of OH$^-$ from the cement paste. This introduces OH$^-$ from the pore solution into the corrosive media which attains a pH equilibrium between the pore water and cement mortar environment. This could also be achieved through ionic transfer [16]. In all cements, the K$^+$ ion was highly leached from the mortar cubes, perhaps due to its higher concentration than Na$^+$ in the pore solution [17].

The leaching of the alkali ions continued up to a certain point where it almost attained a constant amount. This is a similar scenario observed by Herold [18], who analysed for Ca, Mg, Fe, Al, Si, Na, and K in solutions where hardened pastes of OPC with a w/c ratio of 0.5 were immersed. The author [18] observed that there was a marked reduction in leaching in stationary systems. And this was attributed to the growth of residual protective layer which changed the dissolution rate from reaction controlled to a diffusion controlled process. The worker also attributed the decline in leaching of the ions to the growth of temporary concentration buildup in the corrosive media which caused a depression of the dissolution behaviour of the paste.

It was observed that the alkali metal ions were leached most from PPC. The higher leaching of alkalis in PPC may be attributed to the observed higher pH in the chlorides solutions. Perhaps the microcracking associated with Mg attack was more severe in PPC. This may have made the cement more porous and hence highly leached.

The leaching of the alkali and alkali earth metal ions is deleterious as it may lead to disintegration of the CSH. The leach could also lead to loss in concrete strength, lowering of

analyses. Figure 8 shows the results of pH variation of chloride-simulated solutions over a period of six months.

In the test solutions, an increase in the amount of leached Ca^{2+} from the mortar cubes followed by a decline immediately around the 11th day was observed. Upon continued monitoring of the test cement mortars, it was observed that
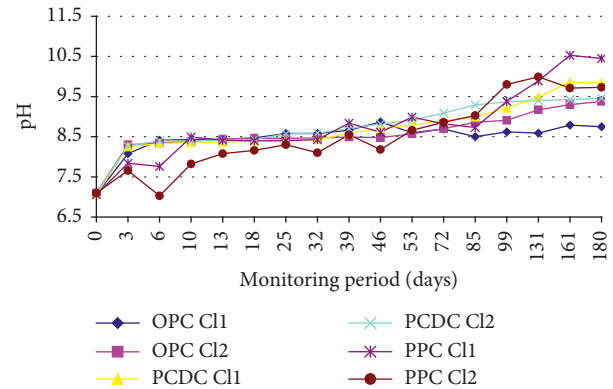
the pore pH and hence leading to breakdown in passivity of reinforcement. It would also lead to disruption of the media through which concrete phases and reactions are held. PPC exhibited the highest main ion loss for maintenance of the pore pH, for example, Na$^+$, an important aspect in the concrete system.

3.4. Sulphate Analyses in Sulphate-Simulated Solutions.

Figures 9 and 10 show the analyses of sulphate ions against the monitoring period from the sulphate-simulated solutions. PCDC showed a continuous intake of the ions up to about 103rd and 163rd day for the SO1 and SO2 solutions, respectively. After these days, a subsequent leach was observed. Similar observations were made for the PPC (intake was observed up to about the 163rd day followed by leaching). OPC exhibited an intake up to about 103rd and 45th day for simulated solution 1 and 2, respectively, after which leaching was observed. An increased intake of the sulphates was observed when the concentration of the sulphates was doubled.

OPC showed an initial reduced sulphate intake at the lower sulphate-simulated solution up to about the 11th day of monitoring. Ingress of sulphates results in formation of, for example, gypsum and ettringite (3CaO·Al$_2$O$_3$·3CaSO$_4$·32H$_2$O) [19]. These are expansive products which may have created microcracks at an early time in OPC that would have paved way for leaching of the sulphates after ingress.

PCDC and PPC showed a similar intake of the sulphates in both solutions. PCDC had a higher substitution level than PPC. The pozzolanic reaction and cement hydration were therefore expected to be slower in PCDC compared to PPC. Therefore, its resistivity to sulphates may not only have been due reduction in its permeability from secondary CSH from the pozzolanic reaction. This may also have been attributed to the packaging of the pozzolana particles in between the aggregates and cement grain which reduces permeability.

3.5. K$^+$, Na$^+$, and pH Analyses in Sulphate-Simulated Solutions.

Figures 11–13 show the changes in K$^+$, Na$^+$, and pH in the simulated sulphate solutions. There was progressive increase in K$^+$ ions in the solutions. The pH rose from the near neutral to higher than 9.

It was observed that Na$^+$ ions ingressed the cement mortar cubes initially. After sometime, the ions were subsequently leached. K$^+$ exhibited a continuous leach throughout the experimental period. The alkalis predominantly maintain the high pH of pore water. The leaching preferentially of K$^+$ ions helped maintain the pH equilibrium between the mortar matrix and the surrounding environment. The intake of the Na$^+$ ion was mainly due to the ion concentration gradient between the aggressive media (which was prepared from sodium sulphates salt) and the cement pore system.

All the aggressive media, except PCDC and OPC sulphate solution 1, showed an increase in pH to approximately 11 upon the immersion of the mortar cubes in the solutions. There was a decline in these solutions' pH after sometime, but PPC's solutions maintained a higher pH to the end of the
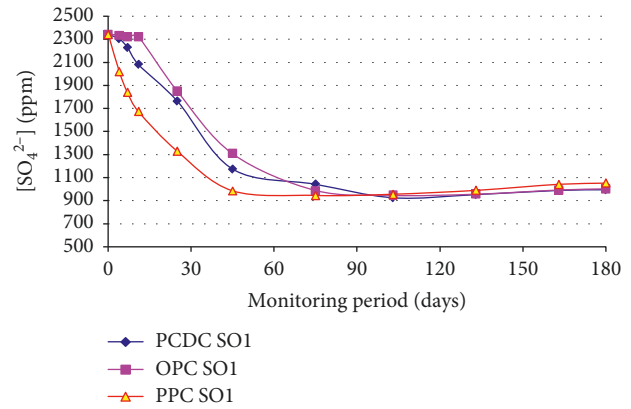

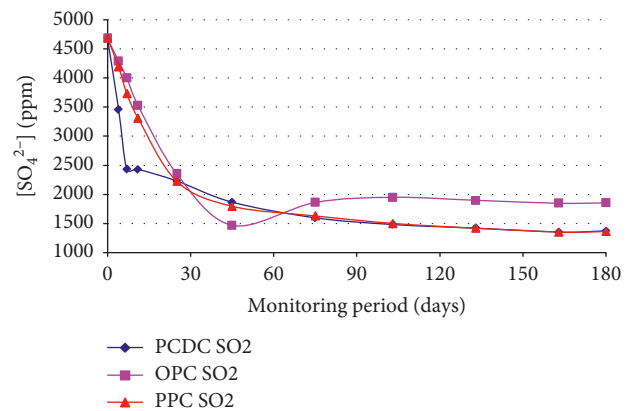FIGURE 9: SO$_4$$^{2-}$ analyses in sulphate-simulated solution 1.

FIGURE 10: SO$_4$$^{2-}$ analyses in sulphate-simulated solution 2.
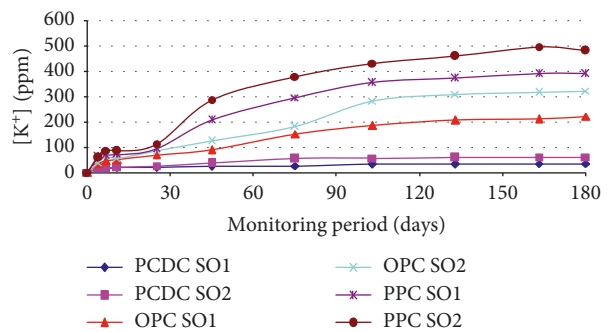

FIGURE 11: K$^+$ analyses in sulphate-simulated solution.

monitoring period. Some authors [20, 21] observed a steady rise in pH of the corrosive media in few days, to about 12, due to release of the OH$^-$ from the pore solution of the associated concrete. The interdependence of sulphate intake and OH$^-$ to be related as shown in the following equation:

$$\left[SO_4{}^{2-} \right]_t = \left[SO_4{}^{2-} \right]_o - \frac{1}{2} [OH^-]_t \tag{3}$$

The subscripts o and t denote concentrations (in the solution under investigation) of the bracketed ions at initial and after a given time, respectively. This shows that there is a rise in OH$^-$ and hence pH as the sulphates ingress into a cement mortar [20].
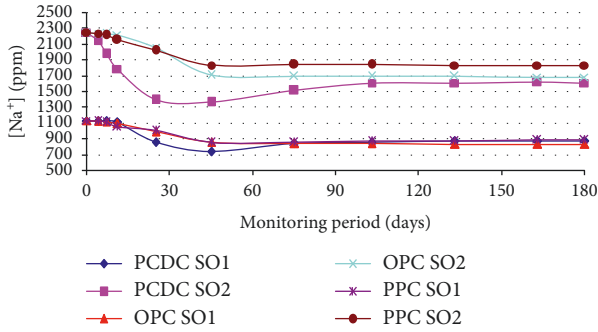
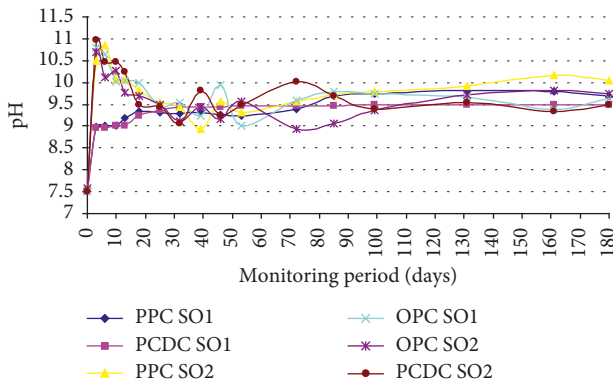FIGURE 12: Na^+ analyses from simulated sulphate solutions.

FIGURE 13: pH measurements in simulated sulphate solutions.

PCDC showed the lowest leach in K^+ than the PPC and OPC as shown in Figure 10. This corresponded to the observed least pH as can be seen from Figure 12. This could be attributed to the high replacement of the OPC by the test-ash hence lower leacheable alkalis from the cement pore solution. The lower leach of the K^+ ions maintains the PCDC pore solution pH from the fact that blended cements have lower alkali content, with K^+ taking the larger portion of the alkalis.

3.6. Sulphate Analyses in Distilled Water. Figure 14 shows the analyses of sulphate ions versus the monitoring period in distilled water.

Leaching of the sulphates was noted in all the test cements. With time, the amount of leached sulphates got to a constant level. This could be compared to a scenario where a protective layer development on cement mortar and a concentration buildup in the solution are observed [18].

PPC and PCDC exhibited a continued leaching with PPC showing a higher leach. PCDC had a higher substitution level than PPC. It was therefore expected, as observed, that PPC would exhibit a higher sulphate leach. This is because of its initial higher amount of sulphates, added as gypsum to control flash set.

3.7. Ca^{2+}, K^+, Na^+, and pH Analyses in Distilled Water. Figures 15–18 show the analyses of Ca^{2+}, K^+, Na^+, and pH from distilled water versus the monitoring period. The Ca^{2+} ions were only detectable for a few days in OPC
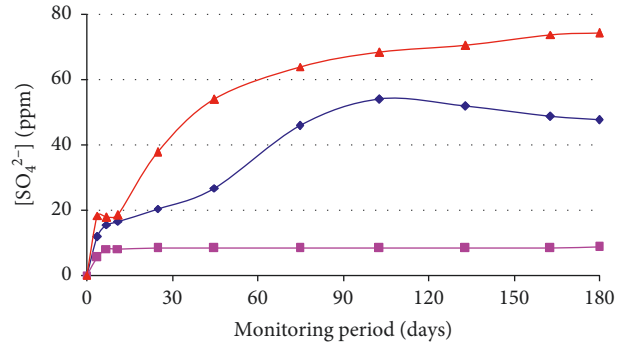

FIGURE 14: SO_4^{2-} analyses in distilled water.

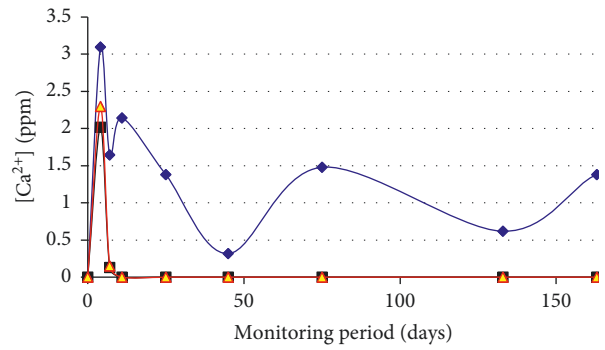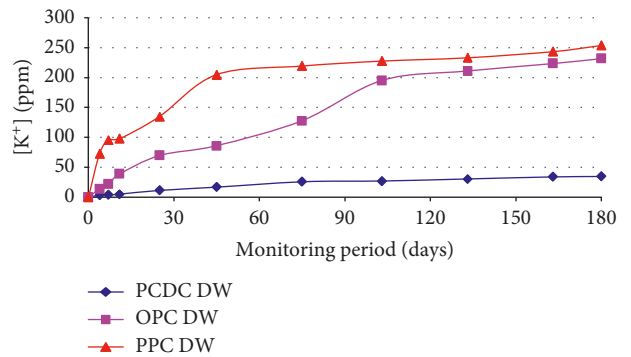FIGURE 15: Ca^{2+} analyses in simulated distilled water.

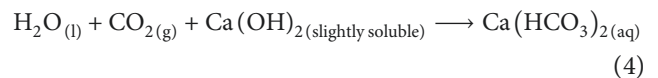FIGURE 16: K^+ analyses in simulated distilled water.

and PPC media. Ca^{2+} levels in PCDC varied from one testing day to the other.

Ca^{2+} either as CaO or $Ca(OH)_2$ leaching through water can be through its slight solubility or through attack via solubilization of atmospheric CO_2 [22] as shown in the following equation:
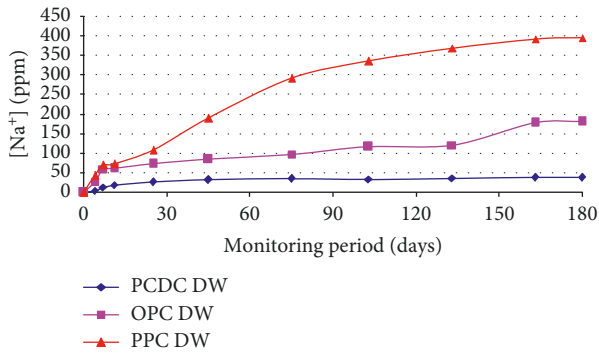
$$H_2O_{(l)} + CO_{2(g)} + Ca(OH)_{2\,(slightly\ soluble)} \longrightarrow Ca(HCO_3)_{2\,(aq)} \tag{4}$$

FIGURE 17: Na$^+$ analyses in simulated distilled water.
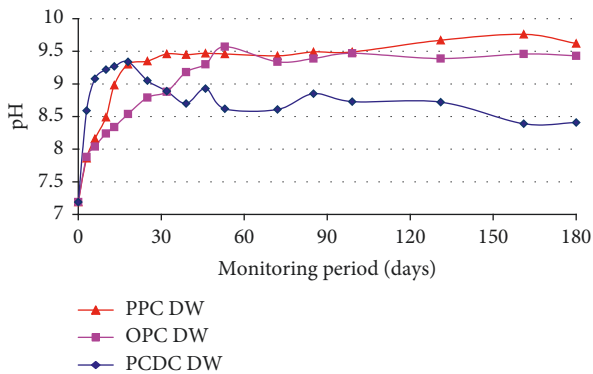
FIGURE 18: pH measurements in simulated distilled water.

FIGURE 19: Cl$^-$ analyses in sea water.

The leaching of Ca^{2+} from OPC and PPC declined immediately after the first few days. The lower Ca^{2+} leach could probably be explained from a pH point of view. As discussed earlier, the solubility of Ca^{2+} decreases with increase in pH; thus higher leach in K$^+$ and Na$^+$ from OPC and PPC would have inhibited the leach of Ca^{2+} from the pore solution of the hydrated cement matrix.

As observed in other experimental results above, Na$^+$ and K$^+$ were least leached from PCDC. The lower leach of these alkalis from the PCDC could explain the lower pH observed of the PCDC cement's aggressive media as compared to OPC and PPC. PPC exhibited the highest leach of the alkalis combined, and correspondingly, the highest pH in its aggressive media was observed.

Distilled water was not as deleterious as had been observed of the chlorides and sulphates especially in the leaching of the main cement constituents, for example, Ca^{2+}, Na$^+$, and K$^+$ among others. The leach of these constituents in distilled water could have mainly been due to concentration difference between the cement matrix and corrosive environment as opposed to chemical attack. More so, with time, hydration of the cement mortar progresses, thus making the mortar less permeable and hence less vulnerable to attack.

3.8. Chloride Analyses in Sea Water. Figure 19 shows the analyses of chlorides against monitoring period in sea water.

It was observed that the test cements showed an intake of Cl$^-$ that was continued up to the 103th day. After this, the test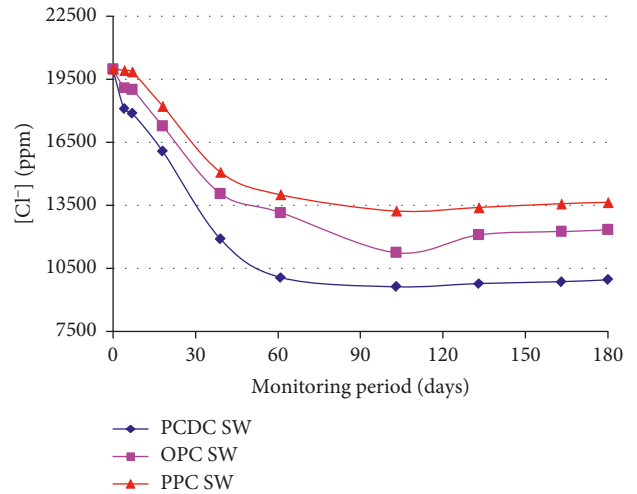 samples showed an increase in the chloride content in the corrosive media. The leaching could be attributed to the saturation of the chlorides in the mortar cubes. Some workers [23] attributed the decline in Ca(OH)$_2$, due to pozzolanic reaction, to increase in solubility of the chloroaluminate. This may lead to the formation of soluble salts of the chlorides of calcium, aluminium, and iron from decomposition of the same [24]. The salts may leach from the concrete mass. A similar trend of intake and subsequent leaching was observed in [25]. The author [25] attributed this to the saturation of the chlorides in the mortar.

PPC showed the lowest intake of Cl$^-$. PPC is known to cure over a long time compared to OPC. It is well documented that a majority of blended cements show a greater resistance to aggressive media [13, 26–29] such as sea water. It was therefore expected as observed that PPC would show greater resistance to ingress in the constituents of the sea water.

The high intake of chlorides by PCDC could be attributed to its high level of substitution. This could be attributed to a lower hydration rate of cement. Thus the cement showed a higher permeability than OPC and PPC.

3.9. Sulphates Analyses in Sea Water. Figure 20 shows the results of analyses of sulphates in sea water media against the monitoring period. OPC showed the highest intake of the sulphates after which the cement mortar showed leaching of the same evidenced by increase in the sulphates in its aggressive media.

All the cement mortars showed intake of sulphates. OPC showed an intake up to about the 45th day after which it showed subsequent leaching. OPC is known to be easily attacked by sulphates [30–33]. In sulphate-simulated solutions, OPC showed higher intake especially at higher concentrations of the sulphate solutions (Figure 10). It was observed that, at the higher sulphate concentration, the OPC exhibited leach after intake of the sulphates. In simulated chloride solution, OPC showed the highest leach in the sulphates especially at the higher chloride concentration (Figure 4). It would then appear that the combined effect of
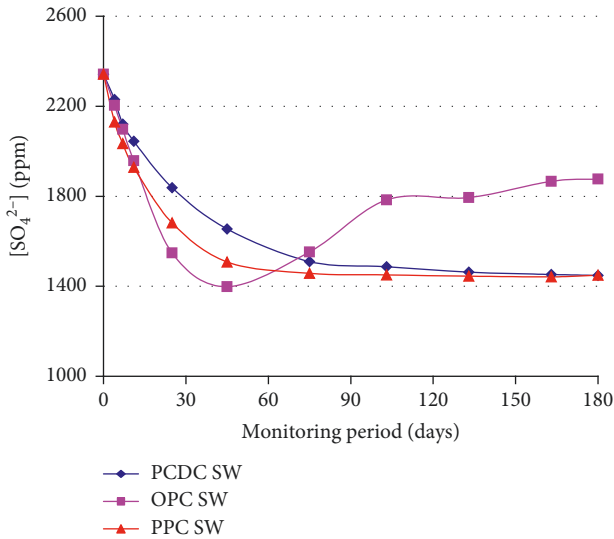
FIGURE 20: SO_4^{2-} analyses in sea water.

FIGURE 21: K^+ analyses in sea water.

FIGURE 22: Na^+ analyses in sea water.

FIGURE 23: Ca^{2+} analyses in sea water.

the two ions (sulphates and chlorides in sea water) exhibited the same trend where they were more aggressive to OPC than the blended cements. But the severity of attack in the separate aggressive solutions was noted to be higher compared to sea water.

There was no significant difference between PCDC and PPC in terms of sulphate intake in sea water. This was despite the high intake of chlorides by PCDC from the same solution. This could be accounted for the pozzolana included which makes them less permeable to aggressive agents or intake of chlorides suppressing the intake of the sulphates.

3.10. Ca^{2+}, K^+, Na^+, and pH Analyses in Sea Water. Figures 21–24 show the results for analyses of Ca^{2+}, K^+, Na^+, and pH in sea water against the monitoring period.

The cements were observed to leach K^+ with the highest leach observed from PPC. There was an initial intake of Na^+ and then a subsequent leach. This is a similar trend as observed in the above experimental results. The high leach of the K^+ ion corresponded to the observed pH in the aggressive media. PPC aggressive media exhibited the highest pH.

PPC had the highest intake of Na^+ followed by PCDC and least OPC especially toward the end of the monitoring period. The intake of Na^+ may have been to counter for the leached K^+ on an ion exchange point of view.

The corrosive media was shown to exhibit a decline in Ca^{2+} ions, a similar scenario to the chloride-simulated solutions. PCDC maintained a higher amount of the ions in its corrosion media. Ca^{2+} ion solubility decreases with the increase in pH. Thus the observed least pH in PCDC media favoured a higher concentration of the same as opposed to PPC which exhibited the highest pH with least Ca^{2+} concentrations in its aggressive solution.

The corrosion media was observed to have attained a pH greater than 9. A rise in pH from about 7.52 to 9.17 in sea water into which concrete was immersed in a month's time
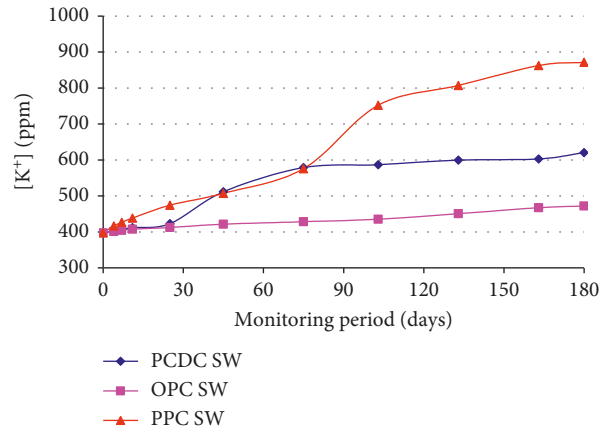
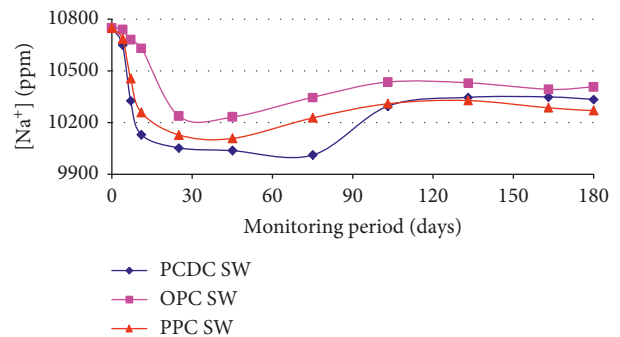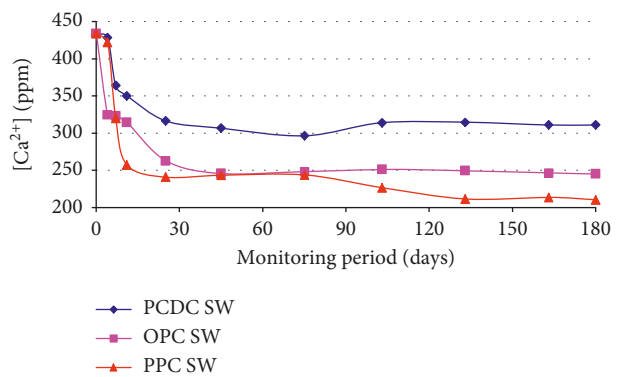had been observed elsewhere [34]. This has been attributed to $Ca(OH)_2$ leach from the concrete. Oxides of potassium and sodium have also been found to be leached from concrete immersed in sea water, simulated sea water, and tap water [27].

3.11. Compressive Strength Changes in Mortars

3.11.1. Compressive Strength Changes in Mortars Immersed in Chloride Solution. Figure 25 represents the percent gain and loss in compressive strength of cement in simulated magnesium chloride solutions.

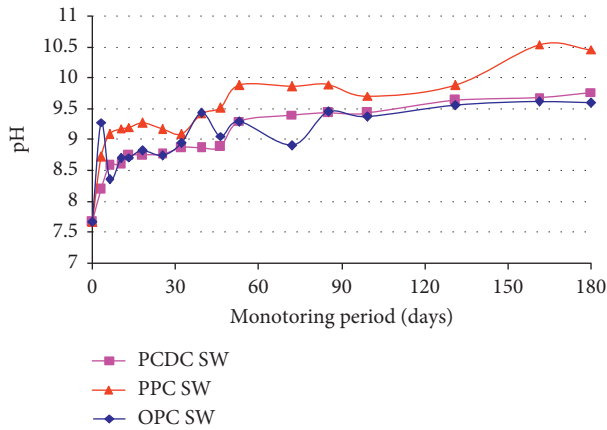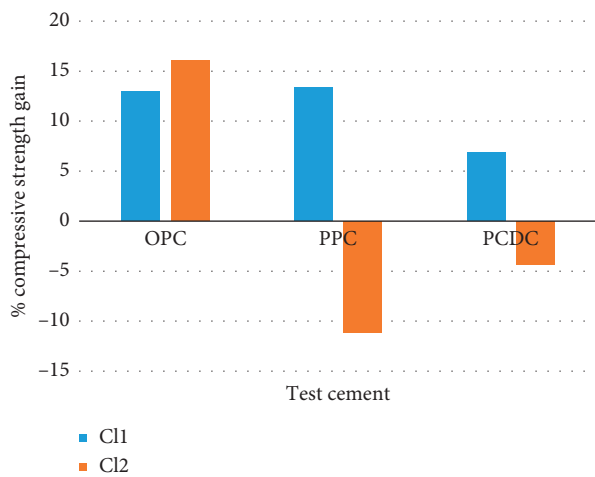FIGURE 24: pH measurements in sea water.

FIGURE 25: Percent gain in compressive strength versus test cement in chloride solutions.

There was an observed increase in strength for the test cements immersed in Cl$^-$-simulated solution, but it decreased when the Cl$^-$ concentration was doubled in PPC and PCDC ($T_{Cal} = -15.03$ and -7.50, respectively). PPC had the highest strength gain in simulated solution 1. This can be attributed this to ingress of the chloride ions. Chlorides are active in enhancing the strength gain because of both their small charge and ionic sizes which enhances its diffusivity. Chloride ions activate pozzolanic reactions and initiate residual cement hydration [6] thus increasing their strength.

There was a marked decrease in compressive strength when chloride concentration was doubled. This could be attributed to the formation of brucite [Mg(OH)$_2$] as a result of increased ingress of MgCl$_2$ on mortar which introduces both chlorides and Mg ions. Brucite [Mg(OH)$_2$] is formed via the magnesium ion attack as shown in the following equation:

$$Mg^{2+} + Ca(OH)_2 \longrightarrow Mg(OH)_2 + Ca^{2+} \qquad (5)$$

Brucite is an expansive product and can lead to cracking and hence lowering cement strength. Pozzolanic reaction makes blended cements denser. This leaves little space for the expansive brucite in case of Mg attack on the mortar.

This exaggerates the damage due to Mg-attack in the pozzolana-based cements. This may have explained why, although, at the lower chloride concentration, PPC had the highest strength gain, and it showed a decline in simulated chloride 2 solution. The results thus suggested that, at higher chloride concentration, the medium was more aggressive and hence an earlier Mg attack.

Pozzolanic reaction leaves limited Ca(OH)$_2$ for the Mg attack. The reduced Ca(OH)$_2$ leaves the CSH as the immediate culprits. The result is the formation of non-cementious MSH. The attack was not severe in PCDC compared to PPC. The less severity could be attributed to the level of substitution. Thus the pozzolanic-Ca(OH)$_2$ reaction was not expected to have consumed all Ca(OH)$_2$ or made the mortar as dense as PPC. More so, it would seem that the introduced Ca(OH)$_2$ as DALS may have offered a phase for Mg attack prior to silica.

3.11.2. Compressive Strength Changes in Mortars Immersed in Sulphate Solution. The percent gain in the compressive strength of mortar cubes immersed in sodium sulphate-simulated solutions was also determined after about six months of subjecting the mortar cubes to the corrosive agents. The results are presented in Figure 26.

PCDC and PPC mortar cubes under this corrosive media registered a significant gain in compressive strength. The gain was even more pronounced with increase in sulphate concentration ($T_{Cal} = 4.49$ for PCDC SO2 versus PCDC SO1. $T_{Cal} = 18.40$ for PPC SO2 versus PPC SO1 way above T_{Crit} value of 4.30). The strength gain in OPC was also notable in the sulphate solution, but there was a significant decline in gain when the solution concentration was doubled ($T_{Cal} = -5.59$ for OPC SO2 versus OPC SO1: the negative sign indicating a decline in strength gain). Sulphates have two effects on hydrated cements; first, they raise the pH of pore water in cement matrix owing to ion exchange as shown in the following ionic equation [7];

$$SO_4^{2-}{}_{(aq)} + Ca(OH)_{2(s)} + 2H_2O_{(l)}$$
$$\longrightarrow CaSO_4 \cdot 2H_2O_{(s)} + 2OH^- \qquad (6)$$
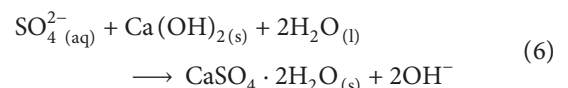
This increases the concentration of OH$^-$ in the pore water hence increasing the pH of cement mortar matrix. The high pH results in increased dissolution of pozzolanic materials in PPC and PCDC hence promoting the pozzolanic reaction. Enhanced pozzolanic reaction subsequently increases the early compressive strength of cement mortars due to increased formation of CSH that is responsible for strength [8, 9]. Secondly, sulphates react with aluminium oxide in the glass phase of pozzolanic materials to form ettrigite (AFt phase). Ettrigite formed at early ages of curing results in a significant densification hence forming a less porous structure and subsequently leads to higher strength [6]. Increase in compressive strength of OPC can be attributed to the presence of Na$^+$ which promotes the hydration residual cement phases. OPC is the most susceptible to the deleterious effects of sulphates. The two effects tend to give an increase and then a decline in physical properties such as strength in mortars or concrete.
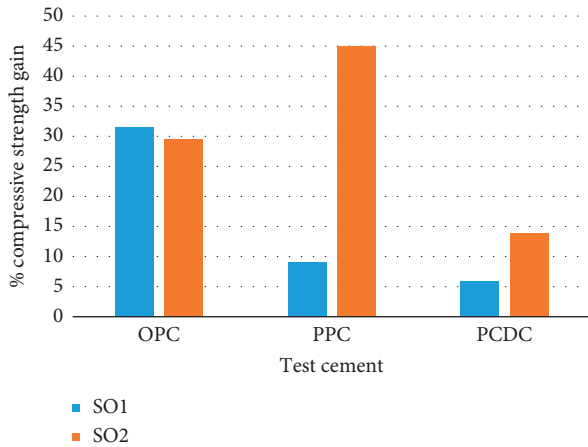
FIGURE 26: Percent gain in compressive strength versus test cement.

FIGURE 27: Percent gain in the compressive strength versus test cement in distilled water.

PCDC registered a lower strength gain than PPC. As observed from even the 28th day compressive strength in saturated calcium hydroxide solution, PCDC had the least compressive strength development. This perhaps could be due to the high substitution level coupled with slow development of strength from pozzolanic reaction. Although SO_4^{2-} and Na^+ may have activated pozzolanic reaction, the reaction is still slower compared to the PPC's. High levels of substitution of OPC have been observed elsewhere to have low-strength gain.

The lower strength in OPC as the sulphate concentration was doubled could be inferred from the three stages of sulphate attack classified as early attack, transition, and later stages. At the early stage, densification of mortar or concrete due to sulphate products increased strength, but in transition and later stages, the deleterious effects of the sulphates were observed. The deleterious effects brought about decline in physical properties such as the compressive strength. An increase in sulphate concentration, in this study, may have caused an earlier lapse of the early stages compared to the lower sulphate concentration. This may be attributed to the observed decline in strength gain as the sulphate concentration was increased.

In general, the PPC had the highest strength gain, followed by PCDC in the sulphate solutions. This is expected of blended cements compared to OPC. This is mainly attributed to low permeability from the resultant secondary CSH from pozzolanic reaction. The packaging of pozzolana grains between the cement grains and aggregates also reduce permeability. The reduction in $Ca(OH)_2$ content through pozzolanic reaction reduces a phase that is most vulnerable to sulphate attack. These factors make blended cements to be less vulnerable to the sulphate form of attack.

3.11.3. Compressive Strength Changes in Mortars Immersed in Distilled Water. The change in the compressive strength of the cement mortars subjected to distilled water for six months was compared to their respective strength of the 28 days of curing in saturated calcium hydroxide solution. Figure 27 shows these results.
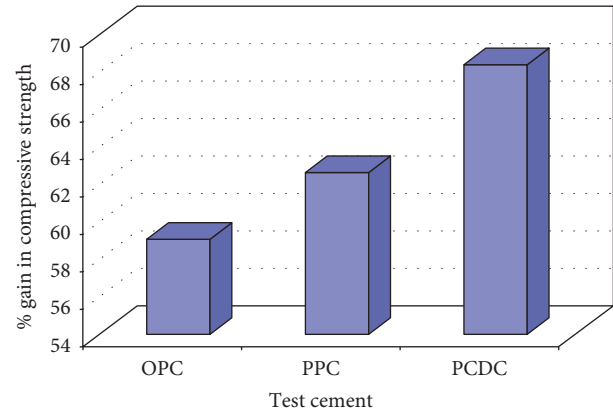
There was observed strength gain for all the test cements in water. The increase in the compressive strength in distilled water could mainly be attributed to a continued hydration of the cement without activators, for example, Na^+, Cl^-, and SO_4^{2-} as experienced in other aggressive solution. The water did not contain these activators that initiate residue cement hydration or pozzolanic reaction and thus strength development increase as observed was expected to be low.

PCDC had the highest strength gain which is significantly higher than OPC ($T_{Cal} = 5.17$ against $T_{Crit} = 4.30$). There was no significant difference in strength gain between PCDC and PPC ($T_{Cal} = 2.17$). Pozzolana-based cement has slow development in strength as compared to OPC if aggressive ions are not encountered. This is attributed to lower pozzolanic reaction. With time, due to continued pozzolanic reaction, blended cements are expected to exhibit higher gain in compressive strength than OPC as observed in this case.

3.11.4. Compressive Strength Changes in Mortars Immersed in Sea Water. Figure 28 shows the percent gain in compressive strength versus test cement in sea water.

PPC had significant higher strength gain than OPC and PCDC in sea water ($T_{Cal} = 7.14$ for PPC against OPC, 9.85 for PPC against PCDC, and 4.03 for OPC against PCDC [$T_{Crit} = 4.30$]). This could be attributed to the activation of pozzolanic reaction and rehydration of residual cements due to ingress of the sulphate, chloride, and sodium ions. This improves the compressive strength of the resultant mortar. In sea water, deleterious products, for example, magnesium silicate hydrates, calcium sulphates, and ettringite, are formed. Brucite [$Mg(OH)_2$], an expansive product, is formed via the magnesium ion attack as shown in the following equation:

$$Mg^{2+} + Ca(OH)_2 \longrightarrow Mg(OH)_2 + Ca^{2+} \qquad (7)$$
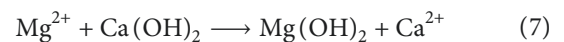
The buildup process of the magnesium and sodium salts, for example, sulphates, through hydration, dehydration, and finally rehydration is another expansive process that is deleterious and likely in sea water are shown in the following equations:
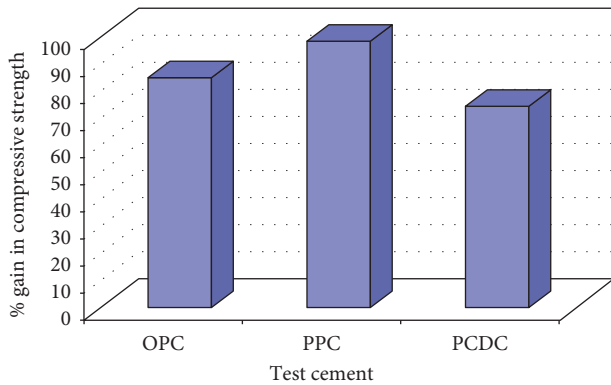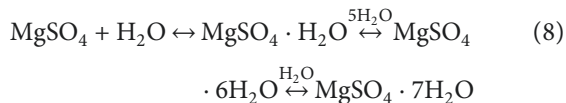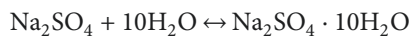
Figure 28: Percent gain in compressive strength versus test cement in sea water.

$$Na_2SO_4 + 10H_2O \leftrightarrow Na_2SO_4 \cdot 10H_2O$$

$$MgSO_4 + H_2O \leftrightarrow MgSO_4 \cdot H_2O \overset{5H_2O}{\leftrightarrow} MgSO_4 \qquad (8)$$

$$\cdot 6H_2O \overset{H_2O}{\leftrightarrow} MgSO_4 \cdot 7H_2O$$

A combination of the above products would be expected to exhibit higher deleterious effects by sea water compared to separate aggressive media of sulphates and chlorides. The comparatively low percent gain in strength for PCDC could be attributed to the high substitution level.

4. Conclusion

From this study, the following conclusions were made:

(i) Despite the leaching and/or intake of the selected ions analysed in this study, PPC and PCDC exhibited comparative results, suggesting that PCDC could be used in similar manner to PPC in general construction.

(ii) Increased concentration of sulphate ions in the presence of magnesium ions resulted in decreased compressive strength

Data Availability

The data used in the manuscript will be provided upon request.

Conflicts of Interest

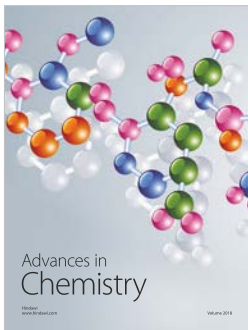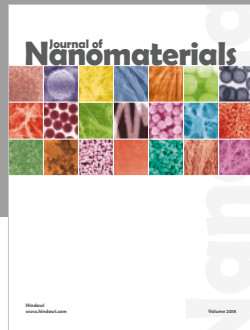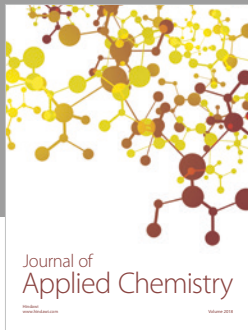The authors declare that there are no conflicts of interest in this paper.

Acknowledgments

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