Properties of activated blended cement containing high content of calcined clay

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Abstract

This paper presents findings of an experimental investigation on sodium sulphate (Na2SO4) activated calcined clay — Portland cement blends in sulphuric acid media. Calcined clays were blended with Ordinary Portland Cement (OPC) at replacement levels of 40%, 45% and 50% by mass of OPC to make blended cement labelled PCC40, PCC45 and PCC50 respectively. Initially, pozzolanicity and setting time tests were conducted. Mortar prisms measuring 40 mm × 40 mm × 160 mm were cast using 0.5M Na2SO4 solution and their compressive strengths determined on the 2nd, 7th, 28th and 90th day of curing. The 28th day cured mortar prisms were subjected to porosity test. Moreover, 5 × 5 × 5 cm mortar cubes were also prepared and their weight and strength loss was taken as a measure of their acid resistivity. After an immersion time of 7, 14, 28, 56, 84 and 120 days in 3% of sulphuric acid at 23 ± 1 °C. OPC, commercial Portland Pozzolana Cement (PPC) and PCC40, PCC45 and PCC50 cement were cast using water and similarly investigated for comparison purposes. The results obtained showed that chemically activated cements exhibited higher pozzolanic activity, lower porosity, shorter setting times and higher resistance to acid attack compared to non-activated cements. However, OPC was found to be non-pozzolanic.

Keywords: Civil engineering, Industrial engineering, Materials science
1. Introduction

Calcined clays are considered as a pozzolanic material due to their siliceous and/or siliceous alumininous nature and ability to chemically react with calcium hydroxide (CH) in presence of moisture at ordinary temperatures to form compounds possessing cementious properties [1]. The desire to improve the performance of cement-based materials has led to an increased use of pozzolanic materials [2, 3, 4, 5, 6]. Calcined clays, as a pozzolanic material, have been successfully used in partial substitution of Ordinary Portland Cement (OPC) in blended cements [7]. Blending OPC with pozzolanic materials makes it less permeable, thus reducing the ingress of aggressive media. CH released during the hydration of OPC is prone to degradation especially if the cement based structures are exposed to aggressive environment such as chlorides, sulphates and acidic media [8, 9, 10]. The additional cementious material formed during the pozzolanic reaction makes hydrated blended cements gain overall higher strength but after a longer period as compared to neat OPC [11, 12, 13]. Consumption of CH during pozzolana reaction improves the durability of hydrated cement by reducing the CH content, the most susceptible component to attack by corrosive media [4, 14, 15, 16, 17]. Due to the incorporation of pozzolanic materials, blended cements have been reported to exhibit high resistance to thermal cracking due to lower heat of hydration, improved ultimate strength and low permeability as a result of pore refinement, enhanced resistance to chemical attack as a result of corrosive media, mitigation of alkali-aggregate reaction and resistance to carbonation attack [10, 18, 19, 20, 21, 22, 23].

There is an increasing demand for production and use of blended cements since apart from the aforementioned benefits; they are arguably affordable and sustainable [24]. Production of OPC is an energy intensive process and results in emission of carbon dioxide (CO₂) into the environment. CO₂ is the chief greenhouse gas mainly responsible for global warming and climate change [24]. Presently, calcined clays are enjoying a renaissance as pozzolanic materials for partial substitution of OPC in blended cements in order to enhance the performance of the hydrated cements [6, 7, 25, 26, 27, 28]. Increasing the content of calcined clays in blended cements has a potential advantage to lower the cost of cement by reducing the amount of OPC in blended cement and emission of CO₂ into the atmosphere thus promoting sustainable development [29, 30, 31, 32, 33].

Apparently, little research has been conducted using calcined clays at substitution level above 35% OPC in blended cement. Several authors have reported some undesirable properties of blended cements such as decline in compressive strength and longer setting times in hydrated blended cements containing calcined clays beyond 35 % substitution of OPC [7, 34, 35, 36, 37, 38, 39, 40]. According to [34], these undesirable properties of blended cements mostly arise from the slow reaction rate.
of pozzolana reaction involving the active pozzolana constituents with the liberated CH from the hydration of OPC. It is estimated that the extent of pozzolana reaction is only about 20 percent at 90 days, compared with 80 percent for OPC [41]. It is generally agreed that the extent of pozzolana reaction therefore determines the mechanical and durability performance of the resulting cement based structures [34, 41]. Various techniques have been employed by different researchers to accelerate the pozzolana reaction and allow for inclusion of high content of pozzolanic materials in blended cements. These methods include thermal activation, chemical activation and mechanical activation. Thermal activation where high temperatures are involved; chemical activation entails use of chemicals such as sodium hydroxide (NaOH), sodium carbonate (Na$_2$CO$_3$), sodium silicate (Na$_2$SiO$_3$), sodium sulphate (Na$_2$SO$_4$), calcium chloride (CaCl$_2$) among others and mechanical methods that involve the use of prolonged grinding of pozzolana to fine sizes [34, 42, 43, 44]. Among the three methods of enhancing reactivity, chemical activation has been reported as the most economically viable method [45].

Cement based materials are not chemically stable in acidic environments containing sulphuric acid, nitric acid, hydrochloric acid and carbonic acid among other aggressive solutions [46, 47, 48, 49, 50, 51, 52]. Sulphuric acid solution is the most common acidic media mostly originating from acid rain as a result of atmospheric pollution, effluents in car garage, wastewater treatment plants, industrial effluent and sewage [46, 47, 48, 49, 50, 51, 52]. Hydrated cements mortars are prone to degradation when they are exposed to sulphuric acid media [53]. Sulphuric acid, besides attacking Ca(OH)$_2$, it also causes degradation on calcium silicate hydrate (CSH) and the aluminate phases resulting increased porosity and strength loss [50, 53, 54]. It is reported that in acidic media, the attack on CH takes place in a series of reactions given by Equations (1), (2) and (3) [47, 52, 53, 55];

$$\text{Ca(OH)}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \quad (1)$$

$$3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{Si(OH)}_4 \quad (2)$$

$$3\text{CaSO}_4 + 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O} + 25\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O} \quad (3)$$

The ettringite (calcium aluminate trisulfate hydrate, CaO·Al$_2$O$_3$·3CaSO$_4$·31H$_2$O) and gypsum (calcium sulfate dihydrate, CaSO$_4$·2H$_2$O) formed are deleterious in hardened cement structures. The formation of ettringite can result in a significant increase in solid volume within the hydrated hardened cement matrix leading to expansion and subsequent cracking. On the other hand, the formation of gypsum can lead to softening and loss of strength. Additionally, it has been reported that sulphuric acid attack can damage hardened cement structures without expansion. This occurs since the acid attack result in softening of the hardened cement structures and
subsequently increases the overall porosity, either of which diminishes durability ultimately reduces their service life.

The present work aimed at evaluating the performance of blended cement containing a high content of calcined clay (40–50%) as pozzolanic material through its activation by chemical method using sodium sulphate (Na₂SO₄) solution as an activator. The research was engineered at assessing the robustness of PCC40, PCC45 and PCC50 vis a vis commercial PPC and OPC when immersed in sulphuric acid solution.

2. Materials and methods

2.1. Materials

The materials used in this research comprised of PPC (32.5N), OPC (42.5N) and standard sand and analytical grade chemicals. Sampling, composition and calcination of clays used in this work is given our earlier publication [2]. The preparation of calcined clay based cements (PCC's) involved addition of requisite amounts of calcined clay and OPC at 40%, 45% and 50% by mass. They were labelled PCC40, PCC45 and PCC50 respectively with respect to the percentage of calcined clay in the blended cement. The chemical, mineralogical and physical composition of cements used in this work is given in Table 1.

The chemical composition of calcined clays is given in Table 2.

The various binder formulations used in this work are presented in Table 3.

Preliminary trial tests were conducted to assess the optimum Na₂SO₄ dosage for chemical activation. Concentrations of 0.1–2.5 M Na₂SO₄ were chosen. It was observed that 0.5M was the optimum concentration.

2.2. Methods

2.2.1. Determination of setting time

The Vicat method was used to determine the initial and final setting times of the test cements as specified by the EAS 148-3:2000 standard. The change in initial and final setting time as a result of chemical activation was calculated using Equations (4) and (5) respectively;

$$I_0 = \left(\frac{IST_{H_2O}^n - IST_{H_2O}^{act}}{IST_{H_2O}^{act}}\right) \times 100$$

where $I_0$ is the % change in initial setting time, $IST_{H_2O}^{act}$ is the initial setting time of chemically activated pastes, $IST_{H_2O}^n$ is the initial setting time for non-activated paste and $n$ is the cement type PCC40, PCC45 and PCC50.
where $F_0$ is the % change in final setting time, $F_{\text{H}_2\text{O}}^{n}$ is the final setting time of chemically activated pastes, $F_{\text{H}_2\text{O}}^{n}$ is the final setting time for non-activated pastes and $n$ is the binder type PCC40, PCC45 and PCC50.

### 2.2.2. Pozzolanicity

Pozzolanicity test was conducted using modified Frattini test [56]. In this method, 20 g of PCC40 was mixed with 100 ml of freshly boiled distilled water. The mixture was placed in a 500 ml plastic container and sealed. The sealed container, was placed in a thermostat enclosure set at 40 ± 0.2 °C maintained at 40 °C. The samples were left to cure for 3, 8, 15, 21 and 28 days. At each test period, samples were vacuum filtered through 8 μm nominal pore size filter paper and allowed to cool to ambient temperature in sealed Buchner funnels. The concentration of OH⁻ present in the
filtrate was analyzed by titration against dilute HCl with methyl orange indicator. Prior to the determination of the concentration of calcium ions in the filtrate, pH adjustment to 13 of the filtrate was done, followed by titration with 0.025 MEDTA solution using Murexide indicator. This procedure was repeated using PCC45 and PCC50 instead of PCC40 and also 100 ml of 0.5M Na₂SO₄ solution instead of boiled distilled water.

### 2.2.3. Compressive strength determination

Mortar prisms measuring 40 mm × 40 mm × 160 mm were cast and cured using the test cements in accordance to EAS 148-1:2000 standard. However, w/c of 0.55 was used. Compressive strength was determined on the 2\textsuperscript{nd}, 7\textsuperscript{th}, 28\textsuperscript{th} and 90\textsuperscript{th} days of curing.

The change in compressive strength at different curing periods as a result of chemical activation was calculated using Equation (6):

\[
\Delta C \cdot S^n = \frac{C \cdot S^n_{\text{act}} - C \cdot S^n_{\text{H}_2\text{O}}}{C \cdot S^n_{\text{H}_2\text{O}}} \times 100
\]  

where $\Delta C \cdot S^n$ is the % change compressive strength, $C \cdot S^n_{\text{act}}$ is the compressive strength of chemically activated mortars, $C \cdot S^n_{\text{H}_2\text{O}}$ is the compressive strength for non-activated paste and $n$ is the testing age for each cement type PCC40, PCC45 and PCC50.

| Oxide | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | K₂O | Na₂O | TiO₂ | Others | LOI |
|-------|------|-------|-------|-----|-----|-----|------|------|--------|-----|
| % Composition | 55.26 | 15.35 | 11.43 | 0.54 | 2.13 | 4.70 | 3.19 | 4.40 | 4.40 | 3.00 |

### Table 2. Chemical composition of calcined clays (Adapted from [2]).

| Cement | % Composition by weight | Mixture | Formulations |
|--------|-------------------------|---------|--------------|
| OPC | Calcined clay | PCC40-H₂O | PCC40-0.5M Na₂SO₄ |
| PCC40 | 60 | 40 | PCC40 | Water |
| | | | PCC40 | 0.5M Na₂SO₄ |
| PCC45 | 55 | 45 | PCC45-H₂O | PCC45-0.5M Na₂SO₄ |
| | | | PCC45 | Water |
| | | | PCC45 | 0.5M Na₂SO₄ |
| PCC50 | 50 | 50 | PCC50-H₂O | PCC50-0.5M Na₂SO₄ |
| | | | PCC50 | Water |
| | | | PCC50 | 0.5M Na₂SO₄ |
| PPC | Commercial | PPC-H₂O | PPC | Water |
| OPC | Commercial | OPC-H₂O | OPC | Water |

### Table 3. Characteristics of the binder mixtures.
2.2.4. Porosity

The 28-day cured mortar prisms were subjected to porosity test in accordance with the ASTM C642-97 standard. In this regard, the porosity of the mortar prisms was calculated using Equation (7):

\[
P = \frac{W_a - W_b}{W_a - W_c} \times 100
\]  

(7)

where \( P \) is the porosity (100%), \( W_a \) is the specimen weight in the saturated surface-dry condition, \( W_d \) is the specimen dry weight until reaching constant weight in oven and \( W_c \) is the weight of saturated specimen.

2.2.5. Resistance to sulphuric acid attack

The sulphuric acid resistance test was conducted in accordance with ASTM C 267 (2003) standard. Mortar cubes measuring 5 × 5 × 5 cm were prepared and cured in for 28 days thereafter half of the mortar cubes were completely immersed in 3% sulfuric acid solution maintained at 23 ± 1 °C while the rest were cured in a temperature and humidity controlled room maintained at a temperature of 22 ± 2 °C and relative humidity above 90 percent respectively. Residual weight and compressive strength of each specimen was taken at every immersion time conducted after 7, 14, 28, 56, 84, and 120 days. At each testing age, the specimens were carefully removed from solutions and gently rinsed with tap water and then air dried for about 3 h in the laboratory. Subsequently, residual weight and residual compressive strength were calculated using Equations (8) and (9) respectively. Three identical specimens were used for each test. Sulphuric acid solution was replaced with fresh solution after each immersion time to maintain its pH.

\[
R_w = \frac{w_a - w_s}{w_a} \times 100
\]  

(8)

where \( R_w \) is Residual weight, \( w_i \) is the weight of the air cured specimens, \( w_s \) is the weight of the specimen after immersion in sulphuric acid media while \( t \) is the immersion time, \( t = 7, 14, 28, 56, 84 \) and 120 days

\[
R_s = \frac{c_i - c_t}{c_i} \times 100
\]  

(9)

where \( R_s \) is Residual compressive strength, \( c_i \) is the compressive strength of the air cured specimens, \( c_t \) is the specimen after immersion in sulphuric acid media while \( t \) is the immersion time, \( t = 7, 14, 28, 56, 84 \) and 120 days.
3. Results and discussion

3.1. Setting time

According to EAS 148-3:2000 standard, PPC should have setting time of between $180 \pm 10$ minutes and $240 \pm 10$ minutes while OPC should be between $100 \pm 10$ minutes and $170 \pm 10$ minutes for initial and final setting times respectively. **Fig. 1** represents the initial and final setting times for the test cements. **Fig. 2** gives the percentage decrease in setting time when activators were used.

It was observed that OPC exhibited shorter setting time than blended cements (PCC40, PCC45, PCC50 and PPC). This could be attributed to higher content of C$_3$S and C$_3$A phases in OPC than blended cements as shown in **Table 1**. C$_3$S hardens rapidly in presence of water hence it is responsible for the early setting of cement paste [57, 58, 59]. Hydration of C$_3$A produces significant amount of heat that increase the prevailing setting temperature resulting to faster setting behaviour of OPC compared with blended cements. The setting time of cement decreases with a rise in temperature [60, 61, 62, 63]. The longer setting times of blended cements could also be attributed to the fact that blended cements contain pozzolanic materials that raises their water demand/standard consistency. High standard consistency of cements has also been found to retard the setting behaviour of cement pastes. High standard consistency lowers the cohesiveness/rheology of the pastes and subsequently prolongs the setting time [64, 65].

**Fig. 1.** Initial setting/final setting times for different cements.
It was observed that both initial and final setting time of blended calcined clay based cements was observed to increase with increase in addition of calcined clay in the order PCC40 < PCC45 < PCC50. This is could be attributed to the increased addition of calcined clays in PCC40 and PCC45, PCC50 cements at 40, 45 and 50 % respectively. Increase in the content of calcined clays incorporated in the blended cements resulted to longer initial and final setting times. Increased incorporation of calcined clays in blended cements progressively reduces the amounts of C₃S and C₃A components resulting in the slow setting of these cements. Moreover, the prolonged setting of blended cements could be attributed to the slow nature of the pozzolana reactions. In blended cements, the pozzolanic reaction will only take place when CH is released during hydration of Portland cement [25, 33, 66]. The released CH reacts with pozzolanic materials such as calcined clays in presence of water to form calcium silicate hydrate (CSH) and calcium aluminate hydrate (CAH) as shown in Equations (10) and (11) [66, 67];

\[
3\text{CH} + 2\text{S} + 3\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_3 \tag{10}
\]

\[
\text{A} + \text{H} + \text{CH} \rightarrow \text{CAH} \tag{11}
\]

Calcium silicate hydrate (CSH) and calcium aluminate hydrate (CAH) are the secondary cementious materials [68]. In non-activated blended cements, the pozzolanic reaction is slow, so the setting behaviour associated with this reaction is low. This is attributed to the fact that the reaction between the resultant CH from Portland cement hydration and the pozzolana to give rise to additional CSH is slow due to the delay in the start of pozzolanic reactions as hydration of OPC must first occur to produce CH. The slow pozzolanic reaction leads to retarded setting times in blended cements.
Based on Fig. 1, chemically activated pastes (Na₂SO₄ activated PCC40, PCC45, PCC50 pastes) exhibited shorter setting times compared to non-activated (PCC40, PCC45, PCC50 pastes). This could be attributed to the use of Na₂SO₄ activator solution. Na₂SO₄ activator solution accelerates pozzolanic reaction resulting in faster setting.

Both initial and final setting time of blended calcined clay based cements increased as the amount of insoluble residue in blended cements increased. This is perhaps due to the fact that progressive addition of calcined clay (in PCC40 < PCC45 < PCC50) resulted to increased quantity of insoluble materials as shown in Table 1. The insoluble residues represents the unreactive hence did not participate in the hydration reactions as well as pozzolana reaction of the blended cement [69]. The insoluble material could have acted as a filler material in the hydrated cement and subsequently slowed down the pozzolanic reaction. In conclusion, the presence of Na₂SO₄ reduced both the initial and final setting times of the blended cement.

3.2. Pozzolanicity

Pozzolanic activity was used to measure the degree of reaction between a calcined clays and Ca⁺⁺ or Ca(OH)₂ in the presence of water and sodium sulphate solution. Pozzolanic materials such as calcined clays contain active amorphous silica and alumina which react with Ca(OH)₂ at ambient temperature. The quantity of Ca(OH)₂ in the cement solution in terms of the concentration of CaO and OH⁻ was determined. In practice, the lower the resulting quantity of Ca(OH)₂ or CaO and OH⁻, the higher the pozzolanicity. In this study, a comparison on the quantity of CaO and OH⁻ in different cement blends in water and sulphate solution over time was made and the findings are presented in Figs. 3 and 4 respectively.

From Figs. 3 and 4, it was observed that in all the blended cement categories considered the concentration of CaO and OH⁻ decreased as curing continued while OPC exhibited a slight increase in the concentration of CaO and OH⁻ with continued curing. This is perhaps due the differences in the nature of hydration reactions occurring in both cement types. The hydration reactions of OPC are given by Equations (12) and (13) [68];

\[
2\text{C}_3\text{S} + 6\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_3 + 3\text{CH} \quad (12)
\]

\[
2\text{C}_2\text{S} + 4\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_3 + \text{CH} \quad (13)
\]

The CH produced in reactions (12) and (13) increase the concentration of OH and CaO with continued curing of OPC. On the contrary, in blended cements, The CH produced during the hydration of OPC is consumed during pozzolanic reaction resulting to the formation of calcium silicate hydrate (CSH) and calcium aluminate hydrate (CAH) as shown in Equations (14) and (15) [68];

\[
10\text{C}_3\text{S} + 10\text{OH}^{-} + 2\text{Ca}^{2+} + 3\text{H}_2\text{O} \rightarrow 10\text{CSH} + 2\text{CAH}_2
\]
The progressive consumption of CH in blended cement effectively reduces the concentration of OH and CaO in the cement matrix [7, 11, 70]. Indeed, blended cements

\[
3\text{CH} + 2\text{S} + 3\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_3
\]

\[
\text{A} + \text{H} + \text{CH} \rightarrow \text{CAH}
\]
are known to continuously consume and hence reduce CH in hydrated cement pastes as opposed to OPC.

The extent of pozzolanic reaction can be deduced from decrease in the concentration of CaO and OH\(^{-}\) at all the testing ages [56, 70, 71, 72, 73]. It was observed that for non-activated blended cements, the concentration of CaO and OH\(^{-}\) at all the testing ages was in the order PCC40 < PCC45 < PCC50. This may be attributed to the fact that whereas the pozzolana reaction leads to consumption of CH from the pore water in the cement mix, increased content of calcined clays due to high substitution levels could have resulted in increased unreacted CH from calcined clays.

Chemically activated blended cements exhibited greater decrease in concentration of CaO and OH\(^{-}\) compared to non-activated blended cements. This is probably due to the presence of Na\(_2\)SO\(_4\) activator solution. Na\(_2\)SO\(_4\) has been reported to activate pozzolana reaction by raising the pH and forming pore filling AFt phases [3, 45, 74, 75, 76]. The raised pH of cement matrix enhances dissolution of silica and alumina in pozzolana materials and hence promoting their reactivity with CH produced from the hydration of OPC forming more hydration products such as CSH and CASH among others.

### 3.3. Compressive strength

The compressive strength development for the test cements at different curing ages is presented in Fig. 5. The improvement in strength as a result of chemical activation at different curing durations is given in Fig. 6;

![Compressive strength (Mpa) as a function of curing period (Days).](image-url)
It was observed that all the non-activated blended cements exhibited lower compressive strength than OPC. This can be attributed to the hydration process occurring in OPC as well as blended cements. In OPC, the hydration reactions of the main components of Portland cement as a result of curing are given by Equations (16), (17), (18) and (19) [68]:

\[
2\text{C}_3\text{S} + 6\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_3 + 3\text{CH}
\]

\[\text{(16)}\]

\[
2\text{C}_2\text{S} + 4\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_3 + \text{CH}
\]

\[\text{(17)}\]

\[
\text{C}_3\text{A} + 6\text{H} \rightarrow \text{C}_3\text{AH}_6
\]

\[\text{(18)}\]

\[
\text{C}_4\text{AF} + 4\text{CH} + 22\text{H} \rightarrow \text{C}_4\text{AH}_{13} + \text{C}_2\text{F}_{13}
\]

\[\text{(19)}\]

According to [68] hydration of C$_3$S and C$_2$S mainly produces calcium silicate hydrates (C$_3$S$_2$H$_3$) or simply CSH and calcium hydroxide (CH). The calcium silicate hydrates (C$_3$S$_2$H$_3$) is a cementious material primarily responsible for strength of hydrated cement based materials. The hydration products of C$_3$A and C$_4$AF are of not of significance to the strength of cement hydrate pastes. Most of the early strength development (first four weeks) is mostly attributed to hydration of C$_3$S while C$_2$S influences the later gain in strength. In blended cements, the pozzolanic reaction takes place when CH is released during hydration of Portland cement. The released CH reacts with pozzolanic materials in presence of water to form calcium silicate
hydration (CSH) and calcium aluminate hydrate (CAH) as shown in Equations (20) and (21) [45, 68, 77, 78, 79, 80];

\[
3\text{CH} + 2\text{S} + 3\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_3 \tag{20}
\]

\[
\text{A} + \text{H} + \text{CH} \rightarrow \text{CAH} \tag{21}
\]

Calcium silicate hydrate (CSH) and calcium aluminate hydrate (CAH) are the secondary cementitious materials [11, 43, 81, 82, 83]. The pozzolanic reaction can be compared to the hydration of Portland cement since both reactions lead to the formation of calcium silicate hydrate (CSH). Both CSH and CAH from pozzolanic reaction contribute to the compressive strength of the blended cement mortars [40, 84, 85, 86, 87]. The higher compressive strength in OPC samples could be attributed to the fact that OPC contained a higher proportion of C₃S and C₂S that are mainly responsible for the strength development. This explains why blended cements exhibit lower compressive strength than OPC.

It was observed that chemically activated blended cements exhibited higher compressive strength compared to non-activated blended cements. This can be attributed to the presence of Na₂SO₄ activator solution in the cement mortars matrix. Firstly, Na₂SO₄ activator solution raises the pH of pore water in cement matrix due ion exchange as shown in ionic Equation (22) [44];

\[
\text{SO}_{4}^{2-} + \text{Ca(OH)}_{2(s)} + 2\text{H}_2\text{O}_{(l)} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}_{(s)} + 2\text{OH}^- \tag{22}
\]

The concentration of OH⁻ in the pore water is raised hence increasing the pH of cement matrix. High pH consequently increases the dissolution of calcined clays hence accelerating pozzolanic reaction. Enhanced pozzolanic reaction subsequently increases the early compressive strength of cement mortars due to increased formation CSH that is responsible for strength [88, 89]. Secondly, Na₂SO₄ solution contains sulphates that react with aluminium oxide in the glass phase of calcined clays to form ettringite. Ettringite formed at early ages of curing results in a significant solid volume increase hence forming a less porous structure and subsequently leads to higher early strength. East Africa cement standard (EAS 18:1-2001) requires that Portland Pozzolana Cements (PPC) should have a minimum compressive strength of 32.5 MPa at 28 days of curing. All the activated blended cements achieved 32.5 MPa at 28 days of curing.

Based on Fig. 5, the extent to which compressive strengths were enhanced as a result of the use of activators declined beyond 7 days although the strength gains relative the control samples still existed at 28 and 90 days. This could be attributed to accelerated pozzolana reaction. Between 2 and 7 days, it is likely that there is availability of large proportion of alumina and silica from the added pozzolana. Presence of the activators, increase the pH of the pore water in the cement matrix causing the
alumina and silica phases to readily dissolve react to form CSH leading to high early compressive strengths. However, progressive consumption of the CH, alumina and silica during pozzolana reaction with curing age results in minimal improvement in compressive strength on 28 and 90 days of curing. Low compressive strength was observed in the control samples in the early days of curing. This is probably due to the slow nature of the pozzolanic reaction; hence the rate of the strength development associated with this reaction is low. The reaction between the resultant CH from Portland cement hydration and the pozzolana to give rise to additional CSH is slow.

The differences in compressive strengths observed in this study could also be attributed to the setting characteristics of different cement categories. High early strength of OPC and chemically activated cement pastes as compared to non activated cement pastes can also be attributed to the shorter setting times of OPC and chemically activated cement pastes. Fast setting results in rapid hardening thus increasing the early compressive strength of the resultant mortars. In conclusion, the chemical activators used were very effective in improvement of 2 and 7 day compressive strength but minimal improvement in compressive strength was noted beyond 7 days of curing.

### 3.4. Porosity

Porosities of different mortars considered are given in Fig. 7.

All blended cements exhibited lower porosity compared with OPC mortars. This is perhaps due to the incorporation of calcined clays that increase the nucleation sites for precipitation of hydration products such as CAH, CSH and AFt phases that result in pore refinement thus lowering the porosity [90]. Additional secondary cementitious material formed during the pozzolanic reaction results in densification of mortars thus lowering their porosity [91].

Porosity was observed to increase with increase in addition of calcined clay in the order PCC40 < PCC45 < PCC50. This is could be attributed to the increased addition of calcined clays in PCC40 and PCC45, PCC50 cements at 40, 45 and 50 % respectively. Although increased content of calcined clays in blended cements increases the pore refinement, high content of calcined clays in blended cement mortars could have only served as a filler material and did not improve their compressive strengths.

Chemically activated blended cements exhibited the lower porosity compared to non-activated blended cements mortars. As earlier pointed out, presence of Na$_2$SO$_4$ solution results in the release of OH$^-$ through ion exchange process in the pore water hence its pH is raised [44, 45, 92, 93]. High pH could have accelerated pozzolanic reaction by increasing the dissolution of calcined clays and subsequently increased the early compressive strength of cement mortars due to increased
formation of more CSH that is responsible for strength. In addition, presence of Na₂SO₄ solution reacts with aluminium oxide contained in calcined clays to form ettringite. The ettringite formed at early ages results in significant pore filling of mortar matrix, subsequently leading to higher early strength and reduced porosity [94].

### 3.5. Acid attack resistance

Figs. 8 and 9 presents the weight and strength loss respectively for different binders subjected to varying immersion durations.

There was loss in both weight and strength of mortars after immersion in 3% sulphuric acid in all cement categories. Exposure of mortar specimens to acidic media generally leads to their degradation. In an acidic environment, a neutralization reaction between hydrogen ion and Ca(OH)₂ in the cementitious materials occurs. This decreases the alkalinity of mortar and causes dissolutions of the hydration products leading to the deterioration of mortar reflected in losses in weight and compressive strength [46, 48, 53]. Notably, there was progressive loss in both weight and strength with increased immersion period due to prolonged exposure in deleterious in acidic media.

OPC mortars exhibited greater loss in both weight and strength than blended cement mortars. This could be attributed to the fact that hydrated OPC contains higher
content of CH at 28 days of curing than blended cements. CH is the main phase in hydrate cement that is easily attacked by acid leading to degradation of cement based materials.

For each cement category, chemically activated mortars exhibited lower loss in both weight and strength than non activated blended cement mortars. This could be due to the higher strength developed by chemically activated mortars as a result of Na₂SO₄ activation. Additionally, chemically activated mortars exhibited lower porosity than the non activated blended cement mortars. Low porosity decreases the penetration of
corrosive sulphuric acid solution into the mortar bulk. In this study, it was noted that chemically activated mortars offer higher resistance to acid attack compared to non-activated mortars regardless of the immersion period.

4. Conclusion

The research evaluated the performance of blended cement containing a high content of calcined clay (40–50%) as pozzolanic material through its activation by chemical method using sodium sulphate (0.5 M Na$_2$SO$_4$) solution as an activator. From the study, the following conclusions were made;

1. Chemical activation of calcined clay—Portland cement blends with 0.5M Na$_2$SO$_4$ enabled substitution of OPC in blended cement from 40–50 percent of calcined clays.
2. Chemically activated blended cement samples exhibited greater pozzolanic activity than non-activated blended cement samples. OPC was however found to be non-pozzolanic.
3. Shorter initial and final setting times were noted in chemically blended activated pastes than non-activated blended pastes.
4. Chemically activated mortars exhibited lower porosity than non-activated mortars.
5. The minimum standard requirements of compressive strength for cement mortar prisms by EAS 148-1(2000), specifies a 28-day compressive strength of 32.5 MPa for Portland pozzolana cements. With 0.5M Na$_2$SO$_4$ blended cements containing high content of calcined clays (>35 %) exhibited compressive strengths above 32.5 Mpa.
6. Higher resistance to acid attack was observed in blended cements compared to neat OPC cement. Additionally, chemically activated blended cement exhibited greater resistance to acid attack than non-activated blended cement.
7. Resistance to acid attack increased with decrease in porosity and increase in compressive strength.

Declarations

Author contribution statement

Marangu J. Mwiti: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Joseph K. Thiong’o, Jackson W. Muthengia: Conceived and designed the experiments; Wrote the paper.
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The authors declare no conflict of interest.

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