

Received:
28 March 2018
Revised:
27 May 2018
Accepted:
13 August 2018

Cite as: Marangu J. Mwiti,
Thiong'o J. Karanja,
Wachira J. Muthengia.
Properties of activated
blended cement containing
high content of calcined clay.
Heliyon 4 (2018) e00742.
doi: [10.1016/j.heliyon.2018.e00742](https://doi.org/10.1016/j.heliyon.2018.e00742)



Properties of activated blended cement containing high content of calcined clay

Marangu J. Mwiti^{a,*}, Thiong'o J. Karanja^a, Wachira J. Muthengia^b

^a Department of Chemistry, Kenyatta University, Nairobi, Kenya

^b Department of Physical Sciences, University of Embu, Embu, Kenya

* Corresponding author.

E-mail address: jmarangu2011@gmail.com (M.J. Mwiti).

Abstract

This paper presents findings of an experimental investigation on sodium sulphate (Na_2SO_4) 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 Na_2SO_4 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

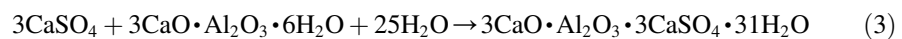
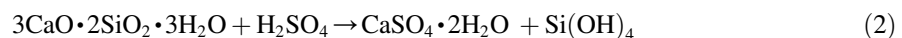
Calcined clays are considered as a pozzolanic material due to their siliceous and/or siliceous aluminous nature and ability to chemically react with calcium hydroxide (CH) in presence of moisture at ordinary temperatures to form compounds possessing cementitious properties [1]. The desire to improve 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 cementitious 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 (Na₂CO₃), sodium silicate (Na₂SiO₃), sodium sulphate (Na₂SO₄) calcium chloride (CaCl₂) 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];



The ettringite (calcium aluminate trisulfate hydrate, CaO·Al₂O₃·3CaSO₄·31H₂O) and gypsum (calcium sulfate dihydrate, CaSO₄·2H₂O) 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 (Na_2SO_4) 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 Na_2SO_4 dosage for chemical activation. Concentrations of 0.1–2.5 M Na_2SO_4 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;

$$I_0 = \frac{\text{IST}_{\text{H}_2\text{O}}^n - \text{IST}_{\text{act}}^n}{\text{IST}_{\text{H}_2\text{O}}^n} \times 100 \quad (4)$$

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

Table 1. Chemical, mineralogical and physical composition of cement.

Materials	Reference cements		Test cements		
	OPC	PPC	PCC40	PCC45	PCC50
Chemical composition					
SiO ₂	21.76	30.35	31.61	33.28	35.34
Al ₂ O ₃	5.55	6.33	14.22	15.67	15.69
Fe ₂ O ₃	3.40	3.36	6.75	7.27	7.31
CaO	61.57	44.83	38.57	35.57	33.02
MgO	1.16	2.26	0.85	0.82	0.71
SO ₃	2.03	1.76	1.63	1.58	1.18
K ₂ O	0.70	0.59	0.63	0.62	0.54
Na ₂ O	0.12	0.74	0.06	0.05	0.03
P ₂ O ₅	0.12	0.17	0.16	0.17	0.16
TiO ₂	0.34	0.29	1.82	2.06	2.03
Mn ₂ O ₃	0.07	0.2	0.09	0.09	0.08
Cl	0.01	0.058	0.007	0.006	0.006
Bogue formula					
C ₃ S	45.3	29.5	27.2	24.9	22.7
C ₂ S	28.2	18.3	16.9	15.5	14.1
C ₃ A	8.9	5.8	5.4	4.9	4.5
C ₄ AF	10.4	6.7	6.2	5.7	5.2
Physical composition					
Insoluble Residual (IR)	1.67	26.34	27.59	29.31	31.44
Loss on Ignition (LOI)	2.91	3.11	3.32	3.25	3.24
Specific Surface Area (SSA) (cm ² /g)	4402.4	4699.8	4892.9	4965.2	5078.7

$$F_0 = \frac{FST_{H_2O}^n - FST_{act}^n}{FST_{H_2O}^n} \times 100 \quad (5)$$

where F_0 is the % change in final setting time, FST_{act}^n is the final setting time of chemically activated pastes, $FST_{H_2O}^n$ 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 μ m nominal pore size filter paper and allowed to cool to ambient temperature in sealed Buchner funnels. The concentration of OH^- present in the

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

Oxide	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	Others	LOI
% Composition	55.26	15.35	11.43	0.54	2.13	4.70	3.19	4.40	4.40	3.00

Table 3. Characteristics of the binder mixtures.

Cement	% Composition by weight		Mixture	Formulations	
	OPC	Calcined clay		Cement	Liquid
PCC40	60	40	PCC40-H ₂ O	PCC40	Water
			PCC40-0.5M Na ₂ SO ₄	PCC40	0.5M Na ₂ SO ₄
PCC45	55	45	PCC45-H ₂ O	PCC45	Water
			PCC45-0.5M Na ₂ SO ₄	PCC45	0.5M Na ₂ SO ₄
PCC50	50	50	PCC50-H ₂ O	PCC50	Water
			PCC50-0.5M Na ₂ SO ₄	PCC50	0.5M Na ₂ SO ₄
PPC		Commercial	PPC-H ₂ O	PPC	Water
OPC		Commercial	OPC-H ₂ O	OPC	Water

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 2nd, 7th, 28th and 90th days of curing.

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

$$\Delta C \cdot S^n = \frac{C \cdot S_{act}^n - C \cdot S_{H_2O}^n}{C \cdot S_{H_2O}^n} \times 100 \quad (6)$$

where $\Delta C \cdot S^n$ is the % change compressive strength, $C \cdot S_{act}^n$ is the compressive strength of chemically activated mortars, $C \cdot S_{H_2O}^n$ is the compressive strength for non-activated paste and n is the testing age for each cement type PCC40, PCC45 and PCC50.

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);

$$P = \frac{W_a - W_b}{W_a - W_c} \times 100 \quad (7)$$

where P is the porosity (100%), W_a is the specimen weight in the saturated surface-dry condition, W_b 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 $5 \times 5 \times 5$ 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.

$$R_w = \frac{w_a - w_s}{w_a} \times 100 \quad (8)$$

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

$$R_s = \frac{c_i - c_t}{c_i} \times 100 \quad (9)$$

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 ± 10 minutes and 240 ± 10 minutes while OPC should be between 100 ± 10 minutes and 170 ± 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_3S and C_3A phases in OPC than blended cements as shown in Table 1. C_3S hardens rapidly in presence of water hence it is responsible for the early setting of cement paste [57, 58, 59]. Hydration of C_3A 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].

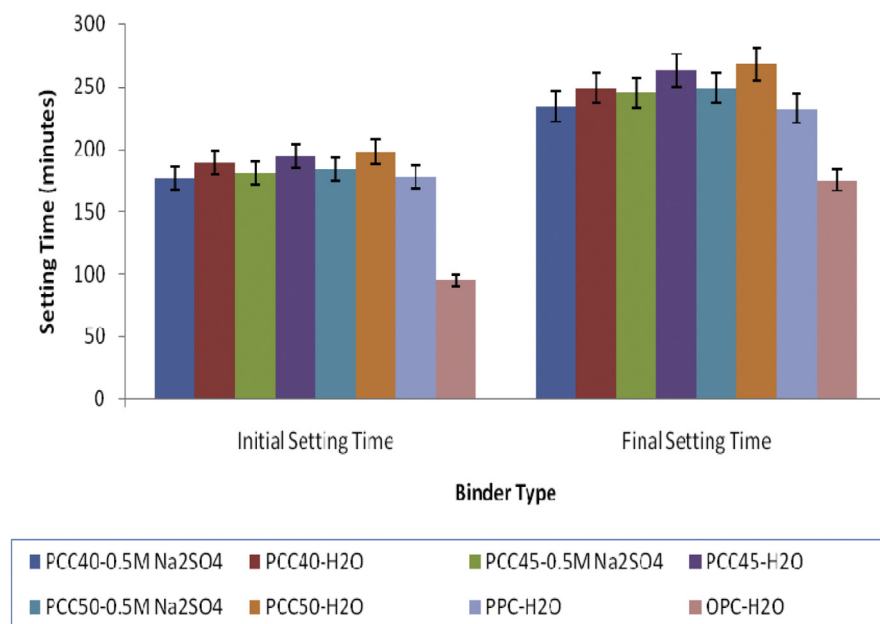


Fig. 1. Initial setting/final setting times for different cements.

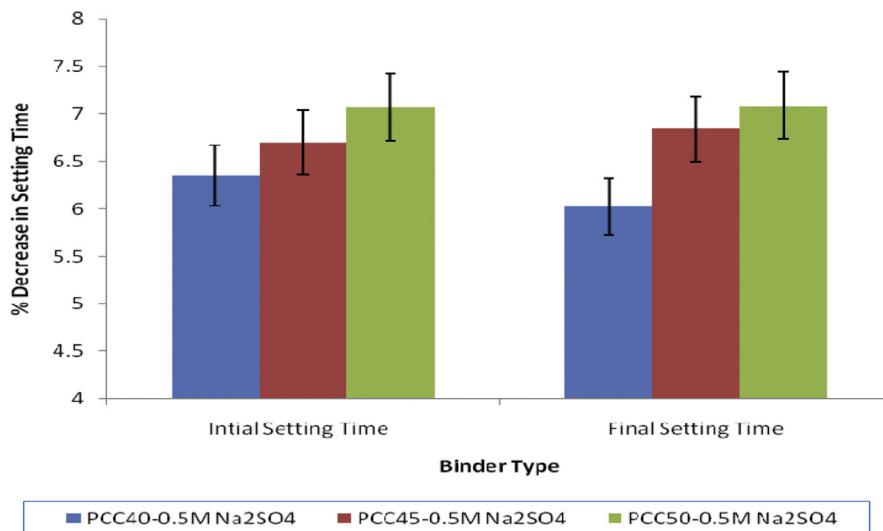


Fig. 2. Decrease in initial and final setting times of chemically activated cements.

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 C_3S and C_3A 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];



Calcium silicate hydrate (CSH) and calcium aluminate hydrate (CAH) are the secondary cementitious 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 (Na_2SO_4 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 Na_2SO_4 activator solution. Na_2SO_4 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 $\text{PCC40} < \text{PCC45} < \text{PCC50}$) 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 Na_2SO_4 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^{2+} or $\text{Ca}(\text{OH})_2$ in the presence of water and sodium sulphate solution. Pozzolanic materials such as calcined clays contain active amorphous silica and alumina which react with $\text{Ca}(\text{OH})_2$ at ambient temperature. The quantity of $\text{Ca}(\text{OH})_2$ in the cement solution in terms of the concentration of CaO and OH^- was determined. In practice, the lower the resulting quantity of $\text{Ca}(\text{OH})_2$ 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];



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];

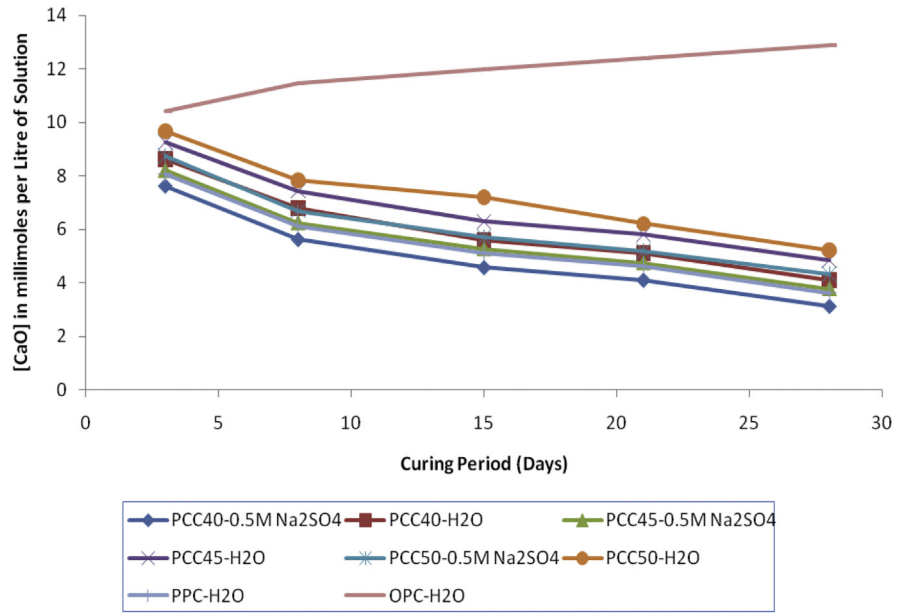


Fig. 3. Concentration of CaO as a function of curing period.

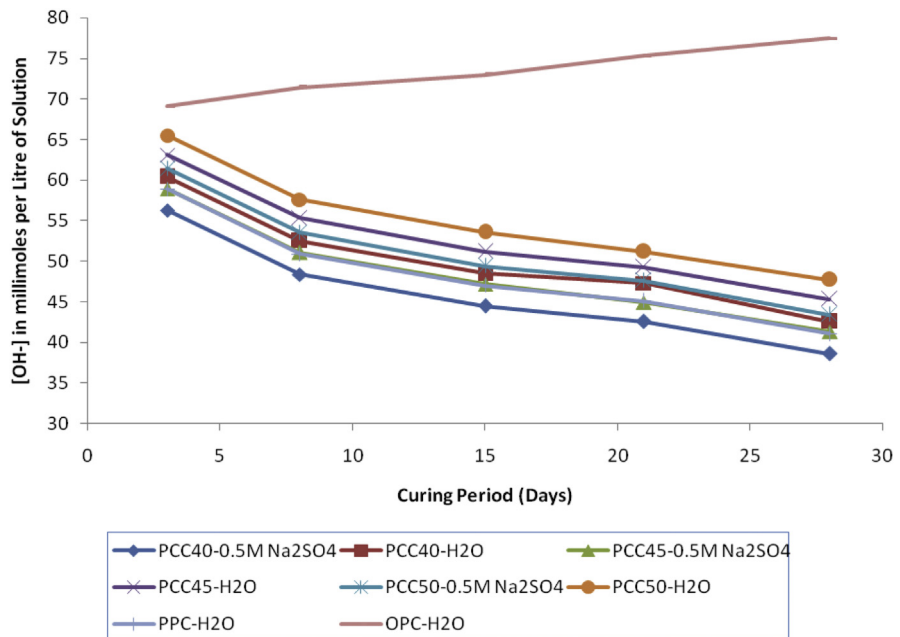
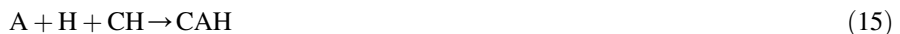


Fig. 4. Concentration of OH⁻ as a function of curing period.



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

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 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 $\text{PCC40} < \text{PCC45} < \text{PCC50}$. 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_2SO_4 activator solution. Na_2SO_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;

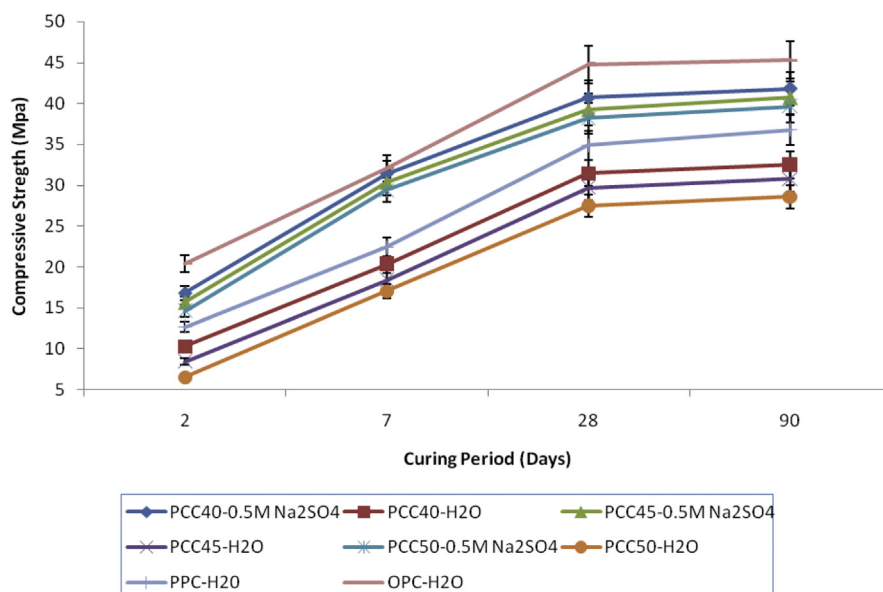


Fig. 5. Compressive strength (Mpa) as a function of curing period (Days).

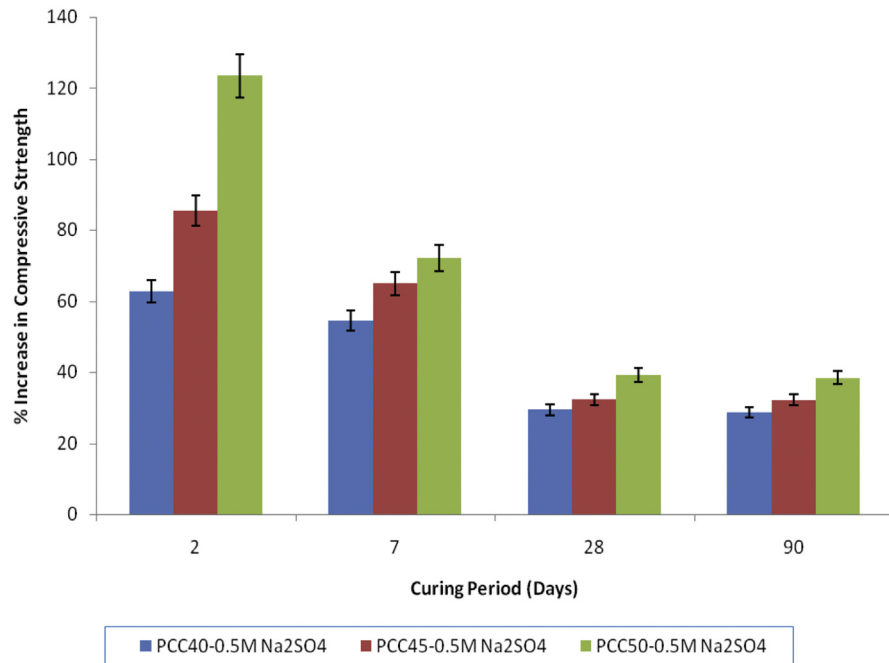
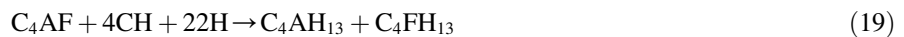


Fig. 6. Increase in compressive strength (%) as a function of curing period (Days).

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];



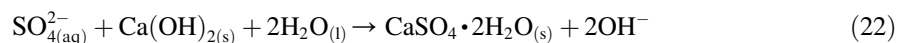
According to [68] hydration of C_3S and C_2S mainly produces calcium silicate hydrates ($C_3S_2H_3$) or simply CSH and calcium hydroxide (CH). The calcium silicate hydrates ($C_3S_2H_3$) is a cementitious material primarily responsible for strength of hydrated cement based materials. The hydration products of C_3A and C_4AF 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_3S while C_2S 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

hydrate (CSH) and calcium aluminate hydrate (CAH) as shown in Equations (20) and (21) [45, 68, 77, 78, 79, 80];



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 C_3S and C_2S 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 Na_2SO_4 activator solution in the cement mortars matrix. Firstly, Na_2SO_4 activator solution raises the pH of pore water in cement matrix due ion exchange as shown in ionic Equation (22) [44];



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, Na_2SO_4 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_2SO_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

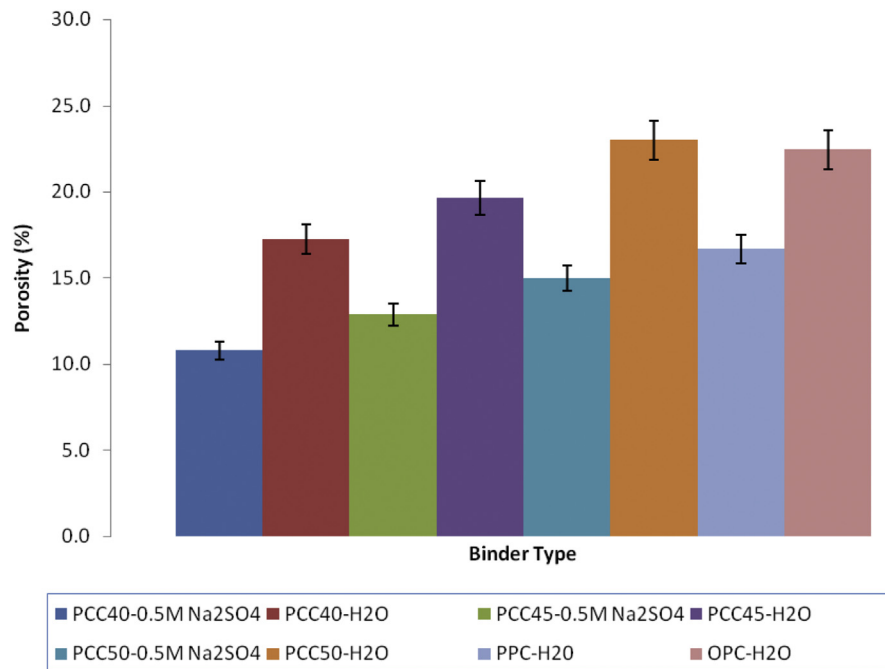


Fig. 7. Porosity (%) of different mortars.

formation of more CSH that is responsible for strength. In addition, presence of Na_2SO_4 solution reacts with aluminium oxide contained in calcined clays to form ettringite. The ettringite formed at early ages results in significant the 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 $\text{Ca}(\text{OH})_2$ 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

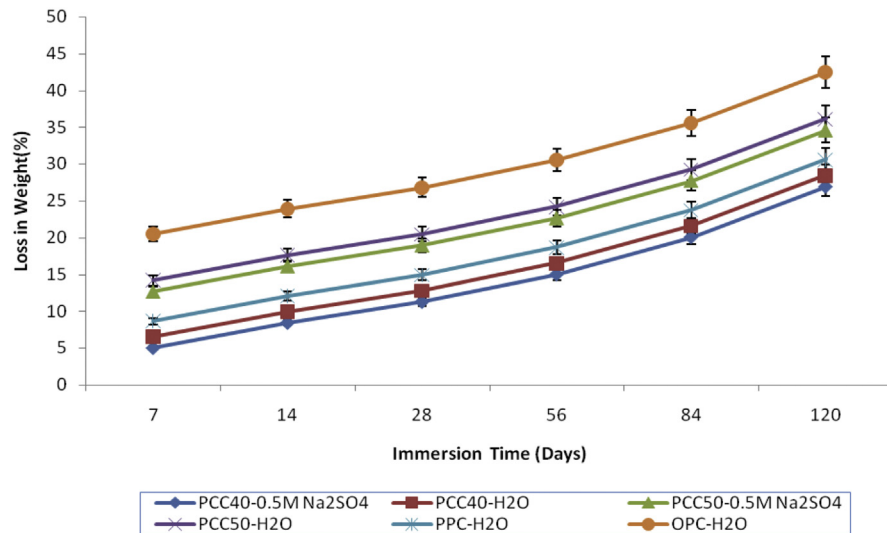


Fig. 8. Weight loss (%) at different immersion durations (Days).

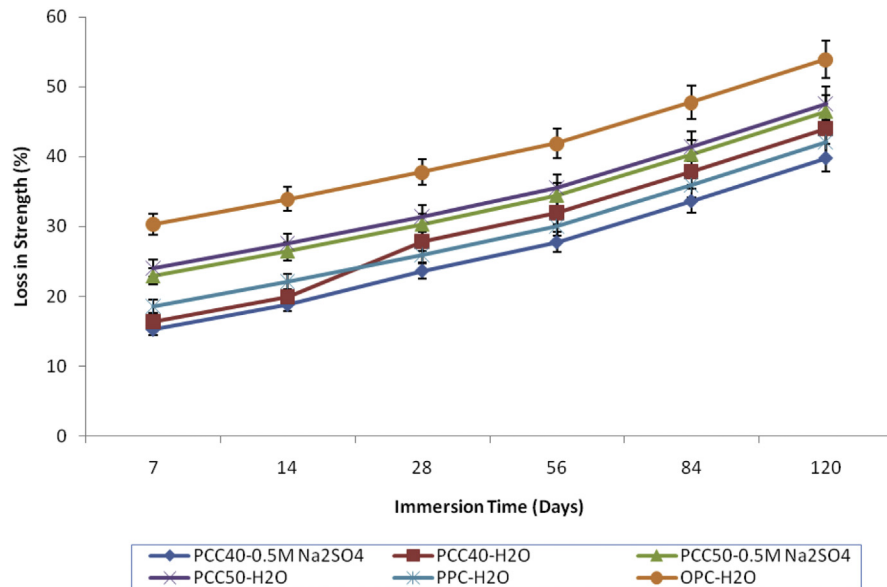


Fig. 9. Strength loss (%) at different immersion durations (Days).

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 Na₂SO₄) solution as an activator. From the study, the following conclusions were made;

1. Chemical activation of calcined clay –Portland cement blends with 0.5M Na₂SO₄ 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 Na₂SO₄ 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.

Funding statement

This work was supported by a National Research Fund grant.

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

Acknowledgements

The authors wish to sincerely thank the African Development Bank in Collaboration with the Ministry of Education, Science and Technology, Kenya for the PhD Scholarship award. The East Africa Portland Cement Company Limited – Athi River, Kenya is duly acknowledged for allowing us to use their Cement Laboratory facilities for this research work.

References

- [1] A.M. Neville, *Properties of Concrete*, fifth ed., Pearson, Harlow, England; New York, 2011.
- [2] M.J. Mwiti, T.J. Karanja, W.J. Muthengia, Thermal resistivity of chemically activated calcined clays-based cements, in: F. Martirena, A. Favier, K. Scrivener (Eds.), *Calcined Clays for Sustainable Concrete*, vol. 16, Springer Netherlands, Dordrecht, 2018, pp. 327–333.
- [3] J.L. Provis, Alkali-activation of calcined clays – past, present and future, in: F. Martirena, A. Favier, K. Scrivener (Eds.), *Calcined Clays for Sustainable Concrete*, vol. 16, Springer Netherlands, Dordrecht, 2018, pp. 372–376.
- [4] J. Sarfo-Ansah, E. Atiemo, K.A. Boakye, D. Adjei, A.A. Adjaottor, Calcined clay Pozzolan as an admixture to mitigate the alkali-silica reaction in concrete, *J. Mater. Sci. Chem. Eng.* 02 (2014) 20–26.
- [5] O.A. Adekitan, G.M. Ayininuola, Calcined clay-cement stabilisation – physicochemical attributes and stabilized strengths of A-1-A and A-2-6 soils, in: F. Martirena, A. Favier, K. Scrivener (Eds.), *Calcined Clays for Sustainable Concrete*, vol. 16, Springer Netherlands, Dordrecht, 2018, pp. 1–7.
- [6] S. Ng, B.P. Jelle, T. Staehli, Calcined clays as binder for thermal insulating and structural Aerogel incorporated mortar, *Cement Concr. Compos.* 72 (2016) 213–221.

- [7] J.M. Marangu, J. Muthengia, J. Wa-Thiong'o, Performance of potential pozzolanic cement in chloride media, *IOSR J. Appl. Chem.* 7 (2014) 36–44.
- [8] J. Bai, S. Wild, B.B. Sabir, Chloride ingress and strength loss in concrete with different PC–PFA–MK binder compositions exposed to synthetic seawater, *Cement Concr. Res.* 33 (2003) 353–362.
- [9] J.H. Potgieter, S.S. Potgieter-Vermaak, D.J. Delport, S. Verryn, Chloride-binding effect of blast furnace slag in cement pastes containing added chlorides, *South Afr. J. Chem.* 64 (2011) 108–114.
- [10] M.U. Khan, S. Ahmad, H.J. Al-Gahtani, Chloride-induced corrosion of steel in concrete: an overview on chloride diffusion and prediction of corrosion initiation time, *Int. J. Corros.* 2017 (2017) 1–9.
- [11] D.K. Mutitu, J.K. Karanja, J.M. Wachira, Diffusivity of Chloride Ion in Mortar Cubes Made Using Ordinary Portland and Portland Pozzolana Cements, 2014.
- [12] A. Tironi, C.C. Castellano, V. Bonavetti, M.A. Trezza, A.N. Scian, E.F. Irassar, Blended cements elaborated with kaolinitic calcined clays, *Proc. Mater. Sci.* 8 (2015) 211–217.
- [13] S. Krishnan, A.C. Emmanuel, S.K. Kanaujia, S. Bishnoi, Hydration and mechanical properties of limestone calcined clay cement produced with marble dust, in: F. Martirena, A. Favier, K. Scrivener (Eds.), *Calcined Clays for Sustainable Concrete*, vol. 16, Springer Netherlands, Dordrecht, 2018, pp. 249–253.
- [14] R. Pierkes, S.E. Schulze, J. Rickert, Durability of concretes made with calcined clay composite cements, in: F. Martirena, A. Favier, K. Scrivener (Eds.), *Calcined Clays for Sustainable Concrete*, vol. 16, Springer Netherlands, Dordrecht, 2018, pp. 366–371.
- [15] K.E. Barış, L. Tanaçan, Durability of steam cured pozzolanic mortars at atmospheric pressure, in: F. Martirena, A. Favier, K. Scrivener (Eds.), *Calcined Clays for Sustainable Concrete*, vol. 16, Springer Netherlands, Dordrecht, 2018, pp. 46–53.
- [16] E. Díaz, R. González, D. Rocha, A. Alujas, F. Martirena, Carbonation of concrete with low carbon cement LC3 exposed to different environmental conditions, in: F. Martirena, A. Favier, K. Scrivener (Eds.), *Calcined Clays for Sustainable Concrete*, vol. 16, Springer Netherlands, Dordrecht, 2018, pp. 141–146.
- [17] H. Maraghechi, F. Avet, K. Scrivener, Chloride transport behavior of LC3 binders, in: F. Martirena, A. Favier, K. Scrivener (Eds.), *Calcined Clays for*

- Sustainable Concrete, vol. 16, Springer Netherlands, Dordrecht, 2018, pp. 306–309.
- [18] C.G. Berrocal, K. Lundgren, I. Lafgren, Corrosion of steel bars embedded in fibre reinforced concrete under chloride attack: state of the art, *Cement Concr. Res.* 80 (2016) 69–85.
- [19] N. Chousidis, I. Ioannou, E. Rakanta, C. Koutsodontis, G. Batis, Effect of fly ash chemical composition on the reinforcement corrosion, thermal diffusion and strength of blended cement concretes, *Constr. Build. Mater.* 126 (2016) 86–97.
- [20] P. Chindapasirt, W. Chalee, Effect of sodium hydroxide concentration on chloride penetration and steel corrosion of fly ash-based geopolymer concrete under marine site, *Constr. Build. Mater.* 63 (2014) 303–310.
- [21] N. Amin, S. Alam, S. Gul, Effect of thermally activated clay on corrosion and chloride resistivity of cement mortar, *J. Clean. Prod.* 111 (2016) 155–160.
- [22] P. Chindapasirt, S. Rukzon, Strength, porosity and corrosion resistance of ternary blend Portland cement, rice husk ash and fly ash mortar, *Constr. Build. Mater.* 22 (2008) 1601–1606.
- [23] M. Balonis, *The Influence of Inorganic Chemical Accelerators and Corrosion Inhibitors on the Mineralogy of Hydrated Portland Cement Systems*, Aberdeen University, 2010.
- [24] Noor-ul-Amin, Use of clay as a cement replacement in mortar and its chemical activation to reduce the cost and emission of greenhouse gases, *Constr. Build. Mater.* 34 (2012) 381–384.
- [25] A. Tironi, M.A. Trezza, A.N. Scian, E.F. Irassar, Assessment of pozzolanic activity of different calcined clays, *Cement Concr. Compos.* 37 (2013) 319–327.
- [26] F. Avet, R. Snellings, A. Alujas Diaz, M. Ben Haha, K. Scrivener, Development of a new rapid, relevant and reliable (R3) test method to evaluate the pozzolanic reactivity of calcined kaolinitic clays, *Cement Concr. Res.* 85 (2016) 1–11.
- [27] A. Tironi, M.A. Trezza, A.N. Scian, E.F. Irassar, Incorporation of calcined clays in mortars: porous structure and compressive strength, *Proc. Mater. Sci.* 1 (2012) 366–373.
- [28] P.S.L. Souza, D.C.C. Dal Molin, Viability of using calcined clays, from industrial by-products, as pozzolans of high reactivity, *Cement Concr. Res.* 35 (2005) 1993–1998.

- [29] P. Sandberg, S. Bishnoi, Sulphate optimization of binders with calcined clay using isothermal calorimetry, in: F. Martirena, A. Favier, K. Scrivener (Eds.), *Calcined Clays for Sustainable Concrete*, vol. 16, Springer Netherlands, Dordrecht, 2018, pp. 422–426.
- [30] M. Schneider, M. Romer, M. Tschudin, H. Bolio, Sustainable cement production? Present and future, *Cement Concr. Res.* 41 (2011) 642–650.
- [31] P.M. Velasco, M.P.M. Ortiz, M.A.M. Giró, D.M. Melia, J.H. Rehbein, Development of sustainable fired clay bricks by adding kindling from vine shoot: study of thermal and mechanical properties, *Appl. Clay Sci.* 107 (2015) 156–164.
- [32] A.S.A. Rashid, M.I. Shahrin, S. Horpibulsuk, M.A. Hezmi, N.Z.M. Yunus, S. Borhamdin, Development of sustainable masonry units from flood mud soil: strength and morphology investigations, *Constr. Build. Mater.* 131 (2017) 682–689.
- [33] C. Kalb, Calcined clays – performance as composite material, in: F. Martirena, A. Favier, K. Scrivener (Eds.), *Calcined Clays for Sustainable Concrete*, vol. 16, Springer Netherlands, Dordrecht, 2018, pp. 226–231.
- [34] K.A. Boakye, E. Atiemo, J. Sarfo-Ansah, A. Osei-Frimpong, A.A. Adjaottor, Improvement of setting times and early strength development of clay pozzolana cement through chemical activation, *J. Chem. Eng. Chem. Res.* 1 (2014) 77–83.
- [35] K.W. Beckemeier, *Effects of High Volumes of Fly Ash on Cement Paste*, Missouri University of Science and Technology, 2012.
- [36] P. Chindapasirt, U. Rattanasak, Improvement of durability of cement pipe with high calcium fly ash geopolymer covering, *Constr. Build. Mater.* 112 (2016) 956–961.
- [37] P. Dinakar, P.K. Sahoo, G. Sriram, Effect of metakaolin content on the properties of high strength concrete, *Int. J. Concr. Struct. Mater.* 7 (2013) 215–223.
- [38] S. Donatello, C. Kuenzel, A. Palomo, A. Fernandez-Jimenez, High temperature resistance of a very high volume fly ash cement paste, *Cement Concr. Compos.* 45 (2014) 234–242.
- [39] M. Heikal, K.M. Zohdy, M. Abdelkreem, Mechanical, microstructure and rheological characteristics of high performance self-compacting cement pastes and concrete containing ground clay bricks, *Constr. Build. Mater.* 38 (2013) 101–109.

- [40] W. Huang, H. Kazemi-Kamyab, W. Sun, K. Scrivener, Effect of cement substitution by limestone on the hydration and microstructural development of ultra-high performance concrete (UHPC), *Cement Concr. Compos.* 77 (2017) 86–101.
- [41] C. Shi, An overview on the activation of reactivity of natural pozzolans, *Can. J. Civil Eng.* 28 (2001) 778–786.
- [42] A. Allahverdi, J. Ghorbani, Chemical activation and set acceleration of lime-natural pozzolan cement, *Ceram. Silik.* 50 (2006) 193.
- [43] C. Shi, R.L. Day, Acceleration of strength gain of lime-pozzolan cements by thermal activation, *Cement Concr. Res.* 23 (1993) 824–832.
- [44] C. Shi, R.L. Day, Chemical activation of blended cements made with lime and natural pozzolans, *Cement Concr. Res.* 23 (1993) 1389–1396.
- [45] C. Shi, R.L. Day, Comparison of different methods for enhancing reactivity of pozzolans, *Cement Concr. Res.* 31 (2001) 813–818.
- [46] P. Chindapasirt, P. Paisitsrisawat, U. Rattanasak, Strength and resistance to sulfate and sulfuric acid of ground fluidized bed combustion fly ash–silica fume alkali-activated composite, *Adv. Powder Technol.* 25 (2014) 1087–1093.
- [47] E. Dan, I. Janotka, Chemical resistance of Portland cement, blast-furnace slag Portland cement and sulphoaluminate-belite cement in acid, chloride and sulphate solution: some preliminary results, *Ceram. Silik.* 47 (2003) 141–148.
- [48] S. Izquierdo, E. Rodríguez, R.M. de Gutiérrez, Resistance to acid corrosion of blended cements mortars with Spent Fluid Catalytic Cracking (SFCC) catalyst Resistencia a la corrosión ácida de morteros de cementos adicionados con catalizador de craqueo catalítico gastado (SFCC), *Rev. Ing. Constr.* 30 (3) (2015). www.ricuc.cl.
- [49] A.M. Izzat, A.M.M. Al Bakri, H. Kamarudin, L.M. Moga, G.C.M. Ruzaidi, M.T.M. Faheem, A.V. Sandu, Microstructural analysis of geopolymer and ordinary Portland cement mortar exposed to sulfuric acid, *Mater. Plast.* 50 (2013) 171–174.
- [50] B.W. Jo, M.A. Sikandar, S. Chakraborty, Z. Baloch, Investigation of the acid and sulfate resistance performances of hydrogen-rich water based mortars, *Constr. Build. Mater.* 137 (2017) 1–11.
- [51] A. Koenig, A. Herrmann, S. Overmann, F. Dehn, Resistance of alkali-activated binders to organic acid attack: assessment of evaluation criteria and damage mechanisms, *Constr. Build. Mater.* 151 (2017) 405–413.

- [52] A. Mellado, M.I. Pérez-Ramos, J. Monzó, M.V. Borrachero, J. Payá, Resistance to acid attack of alkali-activated binders: simple new techniques to measure susceptibility, *Constr. Build. Mater.* 150 (2017) 355–366.
- [53] K. Kawai, S. Yamaji, T. Shinmi, Concrete deterioration caused by sulfuric acid attack, in: *International Conference on Durability of Building Materials and Components*, 2005, pp. 17–20. LYON [France].
- [54] H. Gay, T. Meynet, J. Colombani, Local study of the corrosion kinetics of hardened Portland cement under acid attack, *Cement Concr. Res.* 90 (2016) 36–42.
- [55] Z. Makhloufi, T. Bouziani, M. Hadjoudja, M. Bederina, Durability of limestone mortars based on quaternary binders subjected to sulfuric acid using drying–immersion cycles, *Constr. Build. Mater.* 71 (2014) 579–588.
- [56] S. Donatello, M. Tyrer, C.R. Cheeseman, Comparison of test methods to assess pozzolanic activity, *Cement Concr. Compos.* 32 (2010) 121–127.
- [57] N. Chikh, M. Cheikh-Zouaoui, S. Aggoun, R. Duval, Effects of calcium nitrate and triisopropanolamine on the setting and strength evolution of Portland cement pastes, *Mater. Struct.* 41 (2007) 31–36.
- [58] H.M. Setbon, J. Devaux, A. Iserentant, G. Leloup, J.G. Leprince, Influence of composition on setting kinetics of new injectable and/or fast setting tricalcium silicate cements, *Dental Mater.* 30 (2014) 1291–1303.
- [59] J. Liu, J. Li, J. Ye, F. He, Setting behavior, mechanical property and biocompatibility of anti-washout wollastonite/calcium phosphate composite cement, *Ceram. Int.* 42 (2016) 13670–13681.
- [60] T.K. Erdem, L. Turanli, T.Y. Erdogan, Setting time: an important criterion to determine the length of the delay period before steam curing of concrete, *Cement Concr. Res.* 33 (2003) 741–745.
- [61] S.U. Khan, M.F. Nuruddin, T. Ayub, N. Shafiq, Effects of Different Mineral Admixtures on the Properties of Fresh Concrete, 2014. Available online, <https://www.hindawi.com/journals/tswj/2014/986567/>. (Accessed 13 July 2017).
- [62] Y.L. Yaphary, Z. Yu, R.H.W. Lam, D. Lau, Effect of triethanolamine on cement hydration toward initial setting time, *Constr. Build. Mater.* 141 (2017) 94–103.
- [63] J. Zheng, J. Zhang, G.W. Scherer, Prediction of the degree of hydration at initial setting time of cement paste with particle agglomeration, *Cement Concr. Res.* 42 (2012) 1280–1285.

- [64] N. Dave, A.K. Misra, A. Srivastava, S.K. Kaushik, Setting time and standard consistency of quaternary binders: the influence of cementitious material addition and mixing, *Int. J. Sustain. Built Environ.* 6 (2017) 30–36.
- [65] J. Aparicio, J. Barbero, M. Kapelko, J.T. Pastor, J.L. Zofio, Testing the consistency and feasibility of the standard Malmquist-Luenberger index: environmental productivity in world air emissions, *J. Environ. Manag.* 196 (2017) 148–160.
- [66] S. Hollanders, R. Adriaens, J. Skibsted, Ö. Cizer, J. Elsen, Pozzolanic reactivity of pure calcined clays, *Appl. Clay Sci.* 132–133 (2016) 552–560.
- [67] E. Cabrera, R. Almenares, A. Alujas, Assessment of the pozzolanic reactivity of calcined kaolinitic clays by a rapid alkaline solubility test, in: F. Martirena, A. Favier, K. Scrivener (Eds.), *Calcined Clays for Sustainable Concrete*, vol. 16, Springer Netherlands, Dordrecht, 2018, pp. 98–104.
- [68] A.M. Neville, *Properties of Concrete*, fourth and final ed., Longman, Harlow, Essex, 1997 reprint.
- [69] K. Kiattikomol, C. Jaturapitakkul, J. Tangpagasit, Effect of insoluble residue on properties of Portland cement, *Cement Concr. Res.* 30 (2000) 1209–1214.
- [70] O.M. Munyao, *Effects of Surface and Subsurface Mixing Water of Nairobi, Machakos and Kajiado Counties on Cement Mortar Performance*, Kenyatta University, 2015.
- [71] M.P. Luxán, F. Madruga, J. Saavedra, Rapid evaluation of pozzolanic activity of natural products by conductivity measurement, *Cement Concr. Res.* 19 (1989) 63–68.
- [72] J.S. Uchima, O.J. Restrepo, J.I. Tobón, Pozzolanicity of the material obtained in the simultaneous calcination of biomass and kaolinitic clay, *Constr. Build. Mater.* 95 (2015) 414–420.
- [73] S. Mohammed, G. Elhem, B. Mekki, Valorization of pozzolanicity of Algerian clay: optimization of the heat treatment and mechanical characteristics of the involved cement mortars, *Appl. Clay Sci.* 132–133 (2016) 711–721.
- [74] F. Sajedi, H.A. Razak, Comparison of different methods for activation of ordinary Portland cement-slag mortars, *Constr. Build. Mater.* 25 (2011) 30–38.
- [75] S. Boonjaeng, P. Chindapasirt, K. Pimraksa, Lime-calcined clay materials with alkaline activation: phase development and reaction transition zone, *Appl. Clay Sci.* 95 (2014) 357–364.

- [76] C. Shi, P.E. Grattan-Bellew, J.A. Stegemann, Conversion of a waste mud into a pozzolanic material, *Constr. Build. Mater.* 13 (1999) 279–284.
- [77] J. Sarfo-Ansah, E. Atiemo, K.A. Boakye, Z. Momade, Comparative study of chemically and mechanically activated clay pozzolana, *Mater. Sci. Appl.* 05 (2014) 86–94.
- [78] R.K. Datta, T. Raj, Estimation of pozzolana content in Portland pozzolana cement, *Cement Concr. Res.* 13 (1983) 861–868.
- [79] H. Uchikawa, R. Furuta, Hydration of C3S-pozzolana paste estimated by trimethylsilylation, *Cement Concr. Res.* 11 (1981) 65–78.
- [80] E. Opoku Amankwah, Influence of calcined clay pozzolana on strength characteristics of Portland cement concrete, *Int. J. Mater. Sci. Appl.* 3 (2014) 410.
- [81] S. Cara, G. Carcangiu, L. Massidda, P. Meloni, U. Sanna, M. Tamanini, Assessment of pozzolanic potential in lime–water systems of raw and calcined kaolinic clays from the Donnigazza Mine (Sardinia–Italy), *Appl. Clay Sci.* 33 (2006) 66–72.
- [82] M.M. Hossain, M.R. Karim, M.K. Hossain, M.N. Islam, M.F.M. Zain, Durability of mortar and concrete containing alkali-activated binder with pozzolans: a review, *Constr. Build. Mater.* 93 (2015) 95–109.
- [83] V.S.A. Sivakumar, Effect of calcium nitrate on the pozzolanic properties of high early strength concrete, *Res. J. Appl. Sci. Eng. Technol.* 6 (13) (2013) 2502–2508.
- [84] A. Neves Junior, M.M. Viana, J. Dweck, R.D. Toledo Filho, A comparative study between the early stages hydration of a high strength and sulphate resistant Portland cement and the type II F Portland cement through non conventional differential thermal analysis and thermogravimetry, *Mater. Res.* 18 (2015) 291–296.
- [85] A. Fernández-Jiménez, J.G. Palomo, F. Puertas, Alkali-activated slag mortars: mechanical strength behaviour, *Cement Concr. Res.* 29 (1999) 1313–1321.
- [86] G.C.H. Doudart de la Grée, Q.L. Yu, H.J.H. Brouwers, Assessing the effect of CaSO_4 content on the hydration kinetics, microstructure and mechanical properties of cements containing sugars, *Constr. Build. Mater.* 143 (2017) 48–60.
- [87] N.Y. Mostafa, P.W. Brown, Heat of hydration of high reactive pozzolans in blended cements: isothermal conduction calorimetry, *Thermochim. Acta* 435 (2005) 162–167.

- [88] C. Shi, R.L. Day, Acceleration of the reactivity of fly ash by chemical activation, *Cement Concr. Res.* 25 (1995) 15–21.
- [89] F. Sajedi, H.A. Razak, The effect of chemical activators on early strength of ordinary Portland cement-slag mortars, *Constr. Build. Mater.* 24 (2010) 1944–1951.
- [90] M.J. Pellegrini-Cervantes, F. Almeraya-Calderon, A. Borunda-Terrazas, R.G. Bautista-Margulis, J.G. Chacón-Nava, G. Fajardo-San-Miguel, J.L. Almaral-Sanchez, C.P. Barrios-Durstewitz, A. Martinez-Villafañe, Corrosion resistance, porosity and strength of blended Portland cement mortar containing rice husk ash and nano-SiO₂, *Int. J. Electrochem. Sci.* 8 (2013) 10697–10710.
- [91] M. Wu, K. Fridh, B. Johannesson, M. Geiker, Influence of frost damage and sample preconditioning on the porosity characterization of cement based materials using low temperature calorimetry, *Thermochim. Acta* 607 (2015) 30–38.
- [92] C. Shi, R.L. Day, Pozzolanic reaction in the presence of chemical activators: part I. Reaction kinetics, *Cement Concr. Res.* 30 (2000) 51–58.
- [93] C. Shi, R.L. Day, Some factors affecting early hydration of alkali-slag cements, *Cement Concr. Res.* 26 (1996) 439–447.
- [94] J.M. Marangu, J.K. Thiong'o, J.M. Wachira, Chloride ingress in chemically activated calcined clay-based cement, *J. Chem.* 2018 (2018) 1–8.