Thermal Resistivity of Chemically Activated Calcined Clays-Based Cements

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Abstract. The study investigated the effects of selected potential chemical activators on thermal resistivity of calcined clay based cement mortars. 0.5 M Na_2SO_4 and 0.5 M NaOH were used as activator solutions. The chemical composition of sampled clays was determined by use of X-Ray Florescence (XRF) technique. Clays were incinerated at a temperature of 800 °C for 4 h. The calcined clays obtained were blended with OPC at replacement level of 35 percent by mass of the OPC to make the test cement labeled PCC35. The PCC35 mortar prisms measuring 40 mmx40mmx160mm were cast with activator solutions and cured in water. Compressive strength was determined at the 28th day of curing. As a control, OPC and PCC35 were similarly investigated without activator solutions. The 28 day cured mortars were exposed to a temperature of 700 °C for 2 h then cooled in water to room temperature and their compressive strengths determined. Chemically activated PCC35 and non-activated PCC35 exhibited lower loss in weight than OPC after exposure to the elevated temperatures. Chemically activated PCC35 and non-activated PCC35 exhibited higher residual compressive strength than OPC after exposure to the said temperatures. Na_2SO_4 activated mortars showed higher thermal resistance than NaOH activated mortars. Generally, chemically activated PCC35 exhibited the highest thermal resistance compared to non-activated PCC35 and commercial OPC mortars.

Keywords: Activators · Blended cements · Calcined clay · Cement · Compressive strength · Thermal resistance

1 Introduction

The durability of cement based structures is of great concern in construction industry globally. The structural integrity of cement based materials is guaranteed at ambient temperatures [1]. Hazardous fires are reported to destroy many cement based structures in the world annually resulting to enormous financial losses [2]. Emergence of domestic fires and electrical faults majorly contribute to hazardous fires that affect these structures. Hazardous fires expose these materials to elevated temperatures that are deleterious. High temperatures affect both physical and chemical aspects of the concrete / mortar matrix due to thermal effects on pore water and hydration products [3]. The service life of cement based structures thus reduced by hazardous fires.

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Production of Portland cement results in significant environmental damage due to raw material acquisition and production of carbon dioxide [4]. Carbon dioxide is the main greenhouse gas mainly responsible for global warming and climate change [4]. There is an increasing demand for eco-friendly cement in the world. Production of Portland cement is also an energy intensive process mainly due to the fact that temperatures in excess of 1300 °C are requires during clinkerisation [5]. This is mainly fuelled by petroleum or coal. The high energy demand during production of Portland cement makes it unaffordable especially in developing countries Kenya included [6].

Pozzolanic materials have been used to partly replace Portland cement to produce blended cements since antiquity [7]. Blended cements are commonly used in construction due to their high ultimate compressive strength and high durability of the cement structure as a result of the pozzolanic reactions increasing the amount of calcium silicate hydrates (CSH) while diminishing $Ca(OH)_2$ [8]. Hazardous fires and exposure to high temperature environments such in hydrothermal wells compromise both strength and durability of cement based structures [9]. Pouring of water on the structures on fire is the most common practice of cooling the cement based structures in case hazardous fires occur [10]. There is need therefore to develop high temperature resistant cementious materials.

The pioneering research conducted by [6] reported that Kenyan selected clay-Portland cement blends met the EAS 148-1(2000) when 35 percent of calcined clay was used as pozzolana in blended cement. The test cement used in this study was essentially blended cement prepared by mixing of Portland cement with 35 percent of calcined clay. This paper presents the research findings of the said cement on its resistance to high temperatures when mixed with Na_2SO_4 and NaOH as potential chemical activators.

2 Materials and Methods

2.1 Materials

Ordinary Portland cement (OPC 42.5 N) and standard sand used in this work was supplied by East Africa Portland Cement Company – Athi River, Kenya. Raw clays were sampled from three different places within Ugweri region (longitude 37 ^{0} 34′ 19.47″ E, latitude 0^0 25′ 20.44″ S) in Embu County- Kenya. In each place, three clay samples were obtained from a depth of 3 feet. Clays sampled from a given place were mixed mechanically to obtain a homogenous mixture and stored in labelled polythene bags.

2.2 Methods

2.2.1 Calcination of Clay

The sampled clay was dried to a constant weight at 105 °C to a constant weight in an oven. 6 kg of the dried clay, in a platinum clay trough, was placed in an electrical muffle furnace and allowed to heat for four hours at 800 °C. The resultant clay was cooled grounded in a laboratory ball mill until 95 percent of the calcined clay particles passed below 45 μm BS sieves.

2.2.2 Preparation of PCC35

350 g of calcined clay and 650 g of OPC were mechanically mixed in an automatic mixer for one hour to make 1 kg of PCC35 cement.

2.2.3 Chemical Analysis

X-ray Fluorescence (XRF) technique was used for the chemical analysis of the sampled clay. The samples were analyzed using a sequential X-ray spectrophotometer model number PW4025 in accordance with the instruction manual. The results were presented as a percentage of the oxides.

Loss on ignition of the cement sample was determined in accordance with EAS 148-2:2015. 1.0 ± 0.05 g of clay sample was placed in a crucible and covered with a lid. The covered crucible was transferred in the electric furnace controlled at 950 ± 25 °C for 1 h. The crucible was allowed to cool at room temperature in the desiccator. Loss on ignition was expressed in percentage as the difference between the original mass of the sample and the final mass.

2.2.4 Mixing Casting and Curing

Mortar preparation and curing was done in accordance to KS EAS 148–1:2000. However slight modifications were adopted. First, a w/c ratio of 0.55 was used to ensure a workable mix was achieved. Secondly, 0.5 M Na_2SO_4 and 0.5 M NaOH were also used in place of water.

2.2.5 Thermal Resistivity

The 28 day cured mortar prisms measuring 40 mmx40mmx160mm in size were weighed at the saturated surface in dry condition (W_1). Their compressive strength was determined and recorded as C_{S1}. The specimens were introduced in an electric furnace and heated at 700 °C for two hours with furnace temperature increment of 10 °C per min. After two hours of heating, the mortars were cooled to room temperature for two hours using cold water. Subsequently, the dry weight of the specimens was taken as W_2 and the residual compressive strength of the specimens was determined (C_{S2}). Finally, loss in weight was calculated as $(W_1 - W_2)/ W_1$ and the strength loss of the specimens due to the thermal effect was determined as $(C_{S1} - C_{S2})/C_{S1}$; where, C_{S1} is the compressive strength of the mortar before heating and C_{S2} compressive strength of the mortar after heating.

3 Results and Discussion

3.1 Chemical Analysis

The chemical analysis of clays is given in Table 1.

Table 1. Chemical composition of the sampled clays

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	Others	L.O.I
% Composition	55.26	15.35	11.43	0.54	2.13	4.7	3.19	4.4	3.0

EAS 148-5-2000; prescribes that the sum of SiO_2, Al_2O_3 and Fe_2O_3 should be above 70 per cent for the material to qualify for use as pozzolana. The sum of SiO_2, Al_2O_3 and Fe_2O_3 in the clay sample was 82.04 per cent. Alumina and silica react with calcium hydroxide produced during hydration of Portland cement to form secondary cementious materials. This reaction is referred to as pozzolana reaction. It is given in Eqs. 1 and 2.

$$2SiO_2 + 3Ca(OH)_2 + 5H_2O \rightarrow 3CaO.2SiO_2.8H_2O \quad (1)$$

$$Al_2O_3 + 4Ca(OH)_2 + 9H_2O \rightarrow 4CaO.Al_2O_3.13H_2O \quad (2)$$

3.2 Compressive Strength at 28th Day of Curing

The compressive test results are given in Fig. 1.

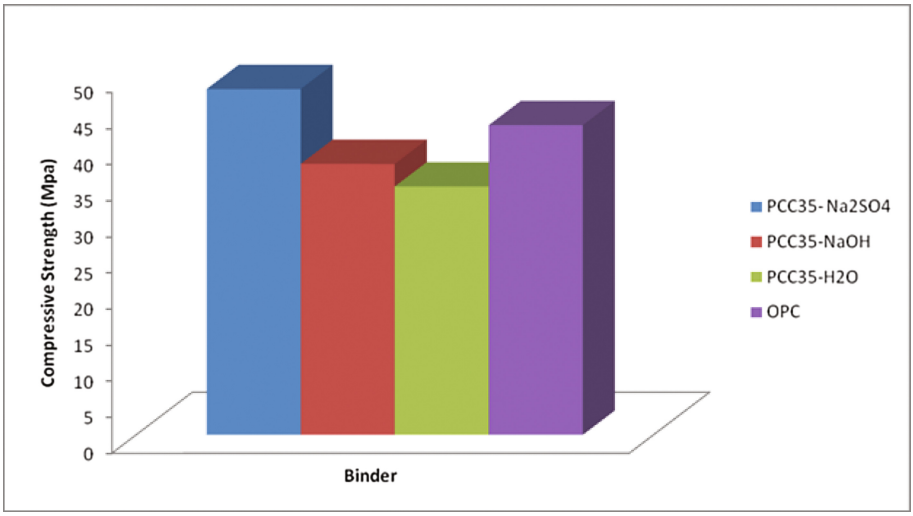

Fig. 1. Compressive strength of test cements on verses binder type on the twenty eighth of curing

It was observed that mortars with chemical activators (PCC35-Na_2SO_4 and PCC35-NaOH) exhibited higher compressive strength than the non-activated mortars (PCC35-H_20). This could be attributed to the fact that both Na_2SO_4 and NaOH accelerate the pozzolana reaction in blended cement leading to high compressive strength [11–13]. The lower compressive strength exhibited by non-activated PCC35 is possibly due to presence of large amount of unactivated pozzolana in PCC35 cement matrix due to the absence of chemical activators.

PCC35-Na_2SO_4 exhibited higher compressive strength than PCC35-NaOH. This can be attributed to the different modes of activation namely alkali and sulfate activation. Sulphate activation is based on the ability of sulfates to react with aluminium oxide in the glass phase of pozzolana to form ettrigite [14, 15]. Presence of ettrigite has been found to contribute to strength at early ages [14] More ettringite formation results in a significant solid volume increase hence forming a less porous structure and subsequently leads to higher early strength.

During alkali activation, the pH of pore water in cement matrix is greatly raised [16]. High pH has been reported to increase the dissolution of pozzolana materials hence improving pozzolanic reaction [13, 17–20]. This subsequently increases the early compressive strength of cement mortars. Shi and Day [14] examined the pozzolanic reaction mechanisms of fly ash in the presence of $CaCl_2$ and Na_2SO_4. The authors Shi and Day [14] reported that addition of Na_2SO_4 to fly ash cement increases the alkalinity of the solution and the dissolution of fly ash during initial stages, and accelerates the pozzolanic reaction. High 28-day compressive strength is normally achieved with improved pozzolana reaction.

3.3 Thermal Resistivity

Thermal resistivity was expressed as the change in weight/compressive strength of the mortars after exposure to 700 °C. Thermal resistivity of the mortars is presented by Fig. 2.

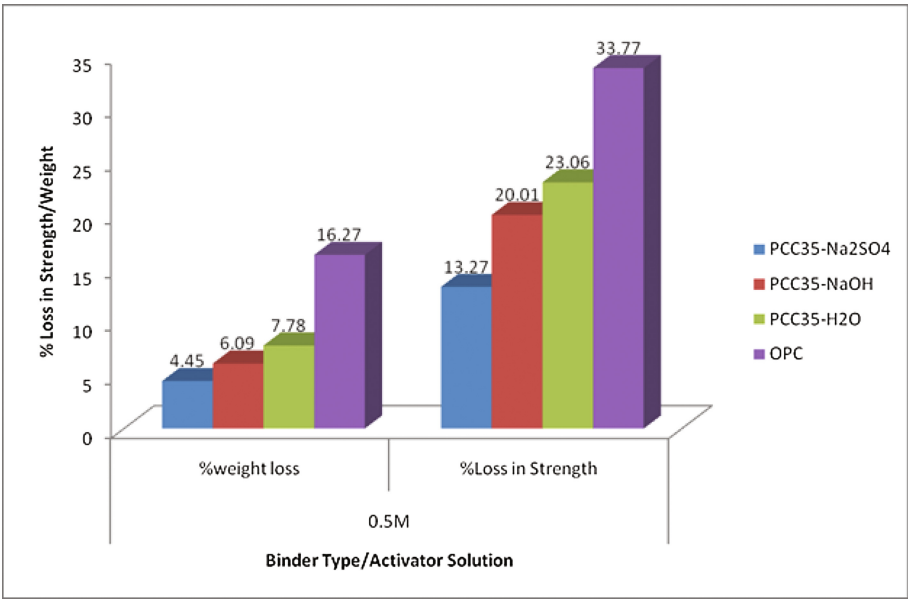

Fig. 2. Binder type/activator concentration verses percentage loss in compressive strength/ weight

Loss in weight and compressive strength was observed in all the cement categories after exposure to the elevated temperatures. This could be attributed to the decomposition of hydration products [10]. High temperatures have a significant influence on the thermal deformation, cracking, spalling and compressive strength losses [1]. High temperatures lead to the decomposition of CSH [3]. Decomposition of CSH due to elevated temperatures compromise the strength of cement based materials [9, 21].This could have led to the decrease in compressive strength of the mortars.

Hydrated mortars contain pore water that is, free, adsorbed or chemically combined in the mortar [21]. At elevated temperatures, the free and/or adsorbed water as well as combined water from CSH and CASH is removed [9, 21, 22]. This normally occurs at temperature range of 100–300 °C and leads to the collapse of the CSH gel that is mainly responsible for the strength of cement based materials the decreases in weight and compressive strength of the mortars [21]. Based on our study, a temperature of 700 °C was therefore sufficient to cause dehdroxylation leading to weight and strength loss in the specimens. $Ca(OH)_2$ in cement mortars has also been reported to undergo decomposition forming CaO and CO_2 at temperatures between 400–550 °C [22]. This is could have also led to the loss in weight of the mortars at high temperature observed in this study.

PCC35-H_2O exhibited higher loss in weight and compressive strength compared to and PCC35-Na_2SO_4. This could be attributed to the fact that PCC35-Na_2SO_4 exhibited higher compressive strength than PCC35-H_2O after 28 days of curing. High compressive strength offers buffering capacity to cement mortars when exposed to elevated temperatures [23]. Chemically activated mortars have been found to exhibit high resistance to high temperatures in other related studies [23].

4 Conclusion

Chemically activated cement mortars (PCC35-Na_2SO_4 and PCC35-NaOH) exhibit higher thermal resistance compared to non activated cement mortars (PCC35-H_2O and OPC) mortars.

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