Effect of a Modified Pozzolan on the Sulphate Attack Resistant of Mortar

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Abstract—**Durability of mortar/concrete is a vital property that affects its serviceability. One of the factors that affect concrete durability is sulphate attack, which can result to expansion, cracking, deterioration, and deformation of concrete structures. The effect of a modified pozzolan (PWC) on the sulphate attack resistant of mortar was investigated in this study. The additive, a blend of selected alkaloids and zeolite, is commercially available and effectively used in soil stabilization for road construction. The additive pozzolanic behaviour had been observed in previous study in terms of strength and permeability. However, the present study focuses on its resistant to sulphate attack as a pozzolan. PWC additive was used in the proportions of 0 %, 0.4 %, 0.6 % and 2.5 % by weight of cement. Samples were subjected to both internal and external sulphate attack tests, according to ASTM C1038 and ASTM C1012 respectively, after being cured for 14, 28, 60, 90, 120, 180, and 295 days. The results showed that PWC additive when used at low dosages of 0.4 % and 0.6 % PWC causes reduction in expansion due to external sulphate attack. At higher dosages of PWC additive, greater external expansion occurs when compared to control samples.**

Index Terms—**Durability, expansion, modified pozzolan, mortar, resistant, sulphate attack.**

I. INTRODUCTION

Sulphate attack is one of the most aggressive environmental factors that affect long term durability of concrete structures. It can result in cracking, expansion and deterioration of concrete structures [1]. Sulphate attack is the reaction of sulphate ions with calcium hydroxide and calcium aluminate hydrate to form ettringite and gypsum, these products are voluminous and lead to expansion, cracking, deterioration, and deformation of concrete structures [1]-[4] when formed after concrete has hardened.

Sulphate attack can also lead to leaching of calcium compounds, degradation of calcium silicate hydrate (C-S-H), and overall deterioration of cement paste matrix [1]. One of the most severe conditions for durability of concrete is the sulphate or acid environment caused by industrial wastes or chemical residues at re-claimed grounds [5]. Deterioration of concrete as a result of sulphate attack can be in form of internal attack due to sulphate content of the cement, and external attack due to exposure of concrete to sulphate environment. Both forms of sulphate attack are manifested by expansion and cracking of concrete.

External sulphate attack may occurs due to penetration of sulphate in solution (for example ground water), which is in return have contact with concrete. The reaction will change the composition and microstructure of the concrete to which it has contact. The effect of the change might result to external cracking, expansion or loss of bond between the cement paste and aggregate. The general effect of the changes will be loss of concrete strength.

Internal sulphate attack occurs when source of sulphate, for example, sulphate-rich aggregate or excess gypsum content is incorporated during concrete mix. The sulphate phases transformation of over-sulphated cement is from anhydrite to gypsum and ettringite, and then to thaumasite. This will finally result to concrete mush [6]. Delayed ettringite formation (DEF) is a form of ettringite that occurs in hardened concrete that has been cured at elevated temperature and contains excess sulphate, which reacts with calcium- and aluminium- containing phases of the cement paste and leads to increase in volume and expansion. Concrete composition, curing conditions and exposure conditions affect the potential/degree of DEF. Thaumasite form of sulphate attack requires adequate supply of sulphate and carbonate and it continues to form until the calcium silicate hydrate is completely decomposed. It is relatively unusual form of sulphate attack; it is associated with low temperatures and very wet environments [6]. The oxide compositions of ettringite and thaumasite as reported by Hooton [6] are shown below:

Ettringite: $Ca_3Al_2O_6.3CaSO_4.32H_2O$
       (no silica)
Thaumasite: $CaSiO_3.CaCO_3.CaSO_4.15H_2O$
       (no alumina)

Quite a number of studies have been done to investigate ways of increasing concrete resistance to sulphate attack through incorporation of extenders (pozzolans) in mortars and concrete mixes [1], [2], [7], [8].

Consumption of calcium hydroxide produce during hydration by cement extenders and less presence of C_3A due to reduced quantity of cement content when extender is incorporated [4], [8], can help in increasing the resistance of concrete to sulphate attack. This emanates from reduction in gypsum and ettringite formation within the cementitious system. PWC additive has been investigated to be a pozzolanic reaction [9]; its effects on the sulphate resistant of mortar are explored in this paper.

II. BRIEF REPORT FROM PREVIOUS WORK

The previous investigation on the PWC additive as it affects concrete strength, permeability, sorptivity reported by

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Ikotun and Ekolu [9] and alkali silica reaction reported by Ikotun [10] are summarized below:

The use of PWC in concrete generally increases both early and late compressive strengths when compared to strength results of the control. At 28 days curing period, PWC concrete samples exhibited a decrease in split tensile strength compared to control, but at 180 days their split tensile strength increased to values higher than that of control samples. It was found that the effect of PWC additive on concrete strength improves significantly when it is used in conjunction with fly ash (FA). When 30% FA was used with 0.6% PWC additive in concrete, there was 21.3% increase in compressive strength at 180 days when compared to the control. With 0.6% PWC additive alone, a small increase of 7.5% in compressive strength was observed at 180 days. Accelerated compressive strength test done at 28 days on mortar samples also showed 22.7% increase in strength for 0.6% PWC + 30% FA compared to 12.6% strength increase for only 0.6% PWC additive. Oxygen permeability of concrete improved only when PWC additive was used in conjunction with FA. PWC additive improves concrete porosity and sorptivity but further effective reductions in the properties are observed when PWC is used together with FA. Results show that PWC additive is most effective when used in the presence of FA.

The use of PWC additive in reducing expansion due to alkali-silica reaction might be adverse. Higher expansions than for control were observed with PWC additive samples. This is explained by the very high alkali contents of PWC of 21 % Na2Oe. When PWC additive was used together with FA in mixes, lower ASR expansions than for control were observed, this shows that PWC additive is most effective in reducing alkali silica reaction in the presence of FA.

III. EXPERIMENTAL PROCEDURE

A. Materials

The binding materials used for this study consisted of modified pozzolan (PWC) and ordinary Portland cement (OPC). PWC additive was commercially available and obtained from PowerCem Technologies, described as ConcreCem, micronized. The Portland cement used was the CEM 1 42.5N, produced by the Afrisam cement South Africa. Silica sand produced by Rolfes silica, South Africa was used as aggregate in mortar mixes. Silica sand was locally graded to conform to the requirement of SABS EN 196-1[11]; the locally graded silica sand (LGSS) was compared to the commercially available European standard silica sand (ESSS). The grading analysis of both LGSS and ESSS is shown in Fig. 1. Both LGSS and ESSS show similar trend, hence, LGSS is appropriate for the test. Calcium hydroxide $(Ca(OH)_2)$ and sodium sulphate (Na_2SO_4) were used as reagents.

B. Sulphate Resistance

According to ASTM C 1038 [12], expansion of samples due to their internal sulphate content was examined based on ASTM C 1038 [12]. The purpose of the test is to determine the amount of expansion of mortar bar samples when stored in water. PW WC additive was used as additive to OPC in the following proportions 0 %, 0.4 %, 0.6 % and 2.5 % by weight of cement. Details of all the mixes are shown in Table I.

According to ASTM C 1012 [13], expansion of samples when exposed to sulphate environment was examined based on ASTM C 1012 [13]. This test method provides a means of assessing the external sulphate resistance of mortars made using Portland cement, blends of Portland cement with pozzolans, and blended hydraulic cement. PWC additive was used as additive to OPC in the proportions of 0 %, 0.4 %, 0.6 % and 2.5 % by weight of cement. Details of all the mixes are shown in Table II.
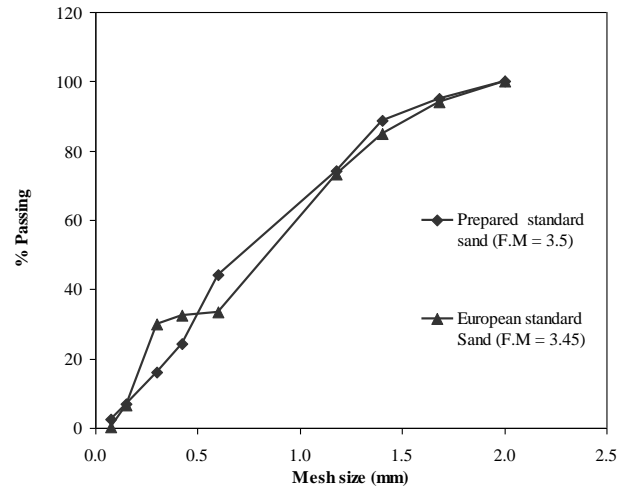

Fig.1. Grading curve of locally graded silica sand (prepared standard sand) and European standard sand.

C. Moulds Preparation

25 × 25 × 280 mm prism moulds and 50mm cubes (for external resistance test) were cleaned and sparingly covered with a lubricant, before mortar mixing operation. The lubricant was used as a releasing agent, so as to allow easy removal of hardened samples. The studs were attached at ends of 25 x 25 x 280 mm prisms moulds as shown in Fig. 2.

Fig. 2. 25 × 25 × 280 mm prism mould with attached studs.

D. Mixing Procedure

OPC, PWC and locally graded silica sand of size 0.4 – 0.85 mm (medium), were weigh batched and mixed in a HOBART mortar mixer for 3 minutes according to SABS EN 196-1[11]. Water and binder were mixed for 30 seconds at low speed, after which standard silica sand was then added over another 30 seconds. The mix was then allowed to stand for another one minute, while rubber scraper was used to remove the mortar adhering to the wall of the mixing bowl into the main mortar at the middle of the mixing bowl. The mixer was then adjusted to a medium speed and mixing run for another 1 minute. Constant water/binder (w/b) ratio of 0.485 was used as stipulated in ASTM C 1012 [13] (for external resistance test).

TABLE I: MIXTURE PROPORTIONS FOR 1M3 OF MORTAR FOR SULPHATES RESISTANCE TEST TO C 1038 [12]

Samples	Cement (Kg)	Silica sand (Kg)	PowerCem (Kg)	Water (Kg)	w/b	Flow (mm)
Control	714.00	1964.00	0.00	350.00	0.49	110.02
0.4% PWC + Cement	714.00	1964.00	2.86	351.00	0.49	110.04
0.6% PWC + Cement	714.00	1964.00	4.28	352.00	0.49	111.24
.5% PWC + Cement	714.00	1964.00	17.85	358.00	0.49	115.90

TABLE II: MIXTURE PROPORTIONS FOR 1M3 OF MORTAR FOR SULPHATES RESISTANCE TEST TO C 1012 [13]

Samples	Cement (Kg)	Silica sand (Kg)	PowerCem (Kg)	Water (Kg)	w/b	Compressive Strength (N/mm²) At day 1
Control	714.000	1964.000	0.000	346.300	0.485	24.200
0.6 % PWC + Cement	714.000	1964.000	4.280	348.400	0.485	22.800
5 % PWC + Cement	714.000	1964.000	17.840	354.900	0.485	20.160

E. Casting and Compaction

Mortar was cast by filling the already prepared $25 \times 25 \times 280$ mm prisms moulds in two layers and compacting with tamping wooden plate of size $10 \times 25 \times 150$ mm. For external resistant test, 50 mm cube moulds were also filled and hand-held on a mechanical vibrating table for 10 seconds. Sufficient mortar was added to fill the 50 mm cubes mould, held on the vibrating table for further period of 10 seconds.

F. Curing

After casting, the moulds were covered with moist cloth for 24 hours to preserve the initial moisture condition of the sample, after which the hardened prisms were removed from their moulds and properly labeled. The samples were then placed in saturated lime (calcium hydroxide) solution for 30 minutes prior to making the initial measurement.

After the initial measurement, the samples were immersed in a saturated lime solution placed in a storage container. Bottom of the container was lined with plastic mesh to allow for easy expansion measurement. The container was covered tightly with a lid during sample storage. Periodically, the calcium hydroxide solution was re-filled to cater for the loss of solution which occurred as a result of evaporation or during removal of samples.

For external resistance test, immediately after molding, the filled mortar moulds were covered with a rigid plastic plate, and placed in a water curing tank. The temperature of curing water was maintained at 38 ± 2 °C with a built in thermostat and a small circulation pump, until the mortar cube strength reached a value of 20 MPa. This strength value was reached after one day of curing for all cube samples tested. Initial measurement was then recorded, after which the bar samples were immersed in 5 % Na_2SO_4 solution in a storage plastic container. The samples rested on plastic mesh placed at the bottom of container to allow for free expansion movement.

The container was covered tightly with a lid during samples storage period. The storage container was periodically re-filled with 5 % Na_2SO_4 solution to maintain constant volume of solution.

G. Testing

Expansion was measured at different curing ages using length comparator as shown in Fig. 3. The initial measurement was recorded after one day of casting, while other expansions were measured at 14, 28, 60, 90, 120, 180, and 295 days curing period. For external resistance test, the initial measurement was recorded after compressive strength value of 20 MPa has been confirmed. Other expansions were measured after 7, 14, 28, 60, 90, 120, and 180 days curing period.

Fig. 3. Length comparator.

H. Expansion Calculation

The change in length of the samples at any age was calculated as follows:

$$\Delta L = \frac{L_x - L_i}{L_g}.100 \qquad (1)$$

where:

ΔL = change in length at any age, %

L_x = comparator reading of samples at any age

L_i = initial comparator reading of samples (reading at day 1)

L_g = nominal gage length, 250 mm

The change in length at any age was recorded as the expansion of the samples at that age. Results recorded are average of four samples.

IV. RESULTS AND DISCUSSION

A. Effect of PWC Additive on Internal Sulphate Attack of Mortar.

Expansion of the samples when stored in lime water is directly related to the amount of sulphate in the cement according to ASTM C 1038 [12]. Fig. 4 shows the percentage expansion of samples due to sulphate attack when immersed

in lime solution according to ASTM C 1038 [12]. There was an increase in expansion at the early days of curing between 14 and 28 days for control and 0.6% PWC samples, which might be as a result of incomplete hydration. Samples containing 0.6 % PWC have highest expansion value of 0.033 % at 28 days. Relatively moderate expansion was however observed for 0.6 % PWC sample between 60 and 120 days. A similar expansion trend was also observed for all the samples between 120 and 295 days with higher expansion observed with samples containing PWC. This is an indication that the sulphate contents in blended samples (samples containing PWC) are higher than that of the control sample. This observation does not necessary explain the effect of the samples when exposed to sulphate environment. Internal Expansion may become excessive when the cement contains too much sulphate.

B. Effect of PWC Additive on External Sulphate Attack of Mortar.

Resistance of concrete to external sulphate environment is directly affected by how dense and permeable the concrete is. A dense and low permeable concrete will have good resistant to external sulphate environment than a porous and high permeable concrete. Fig. 5 shows the percentage expansion of samples due to sulphate attack when immersed in 5% Na_2SO_4 solution according to ASTM C 1012 [13]. At all ages observed, the expansion of 0.4% PWC and 0.6 % PWC samples were less than the expansion observed in control samples. It was also observed that the higher dosage of 2.5% PWC additive resulted in a higher expansion. Expansion is seen to decrease for 0.4 % PWC and 0.6 % PWC samples at ages 28, 60, and 90 days. Further relative decrease in expansion was also observed for 0.4 % PWC and 0.6 % PWC samples at the late ages of 120, 180, and 260 days.
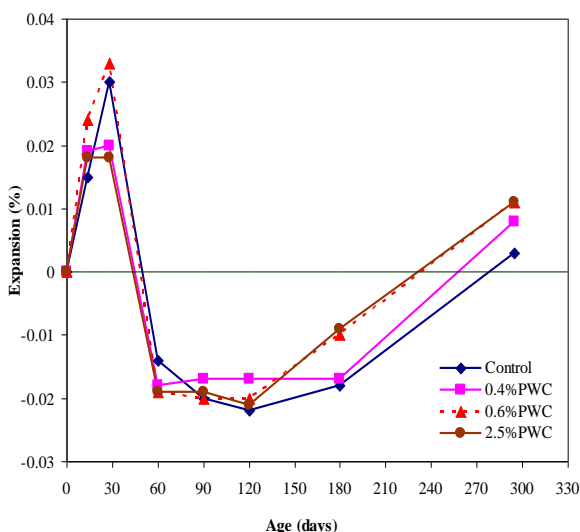

Fig. 4. Expansion due to internal sulphate attack as per ASTM C 1038 [12].

The influence of PWC additive on sulphate attack may partially be attributed to the pozzolanic reaction between the additive and $Ca(OH)_2$ formed during hydration process. This reaction results into secondary C-S-H and forms more dense mortar and pores of similar diameter. Consumption of excess calcium hydroxide due to pozzolanic reaction is reported by Sideris *et al.* [3] to render it unavailable for the formation of ettringite and gypsum compounds. The formation of ettringite and gypsum compounds in hardened cementitious systems is responsible for expansion.
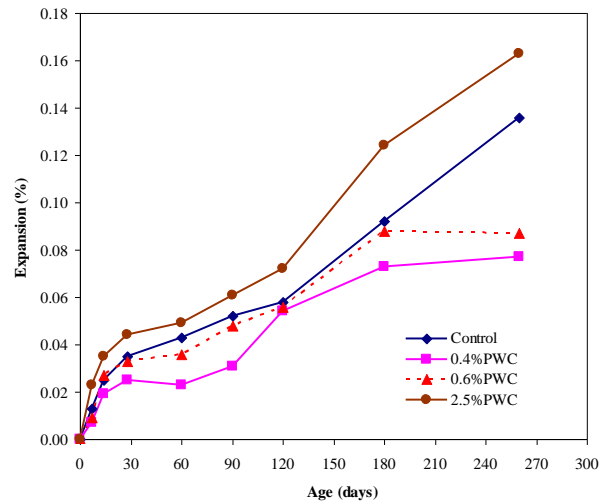

Fig. 5. Expansion due to external sulphate attack as per ASTM C 1012 [13].

V. Conclusion

It was found that when PWC additive is used at low dosages of 0.4 % and 0.6 % PWC, it causes reduction in expansion due to external sulphate attack. Though blended samples seems to have higher sulphate content, they exhibited better resistant to external sulphate attack when used optimally (0.4%PWC and 0.6%PWC). At higher dosages of PWC additive, greater expansion occurs when compared to control samples. Again this result indicates that the optimum proportion of PWC additive to be used may lie in the range between 0.4 % and 0.6 %.

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