

# Effect of a Synthetically Modified Natural Zeolite Additive on Properties and Durability of Cement Mortars

**Bolanle Deborah Ikotun, Stephen O. Ekolu, Victor de Freitas**

School of Civil and Environmental Engineering, University of the Witwatersrand,

Private Bag X3, WITS 2050, Johannesburg, South Africa

[Bolanle.Ikotun@students.wits.ac.za](mailto:Bolanle.Ikotun@students.wits.ac.za), [Stephen.Ekolu@wits.ac.za](mailto:Stephen.Ekolu@wits.ac.za)

## ABSTRACT

Durability characteristics of cement mortars and concrete are of interest to various researchers and practitioners in the field of construction materials engineering. This study evaluated the potential use of a semi-synthetic zeolite additive for improvement of cement mortar properties. The product, a blend of selected alkaloids and zeolite is commercially available and effectively used in soil stabilization for road construction. However, its influence and effectiveness on properties of cementitious systems has not been explored. Emphasis of this study was on durability of cement mortars. This was assessed using the durability index approach being advanced in South Africa. The additive was added to standard mortars of 0.5 water-cement ratio, prepared according to EN 196, in proportions of 0%, 0.4%, 0.6%, 0.8%, 1.0%, and 2.5%. Tests carried out include compressive strength, oxygen permeability, sorptivity and resistance to sulphate attack. It was found that the additive significantly improves durability characteristics while increasing strength and workability when used at optimum proportions. Its use in proportions between 0.4 to 0.6% additive gave optimum results in most tests. Further increase in the additive proportion tends to be counter effective, especially at above 1% additive. The low optimum proportions found also favour economic considerations.

**Keywords:** Durability; Zeolite; Additive; Cement mortar; Compressive strength

**Corresponding author:** [Bolanle.Ikotun@students.wits.ac.za](mailto:Bolanle.Ikotun@students.wits.ac.za)

## Introduction

Durability of cement mortars and concrete is an important property which determines their long term existence. Though strength has been rated as the most important property that determine concrete quality because it can be measured without difficulty and other properties can be related to it but it cannot be used to assess concrete durability, because concrete of the same strength but different water/cement ratio (w/c), mix design, pore structure and compositions will have different performance characteristics. The most important property that affects concrete

durability is its pore structure [9]. This property can be affected by the following factors w/c, materials used, rate of hydration and paste- aggregate bond.

Various researches had been carried out on improving concrete durability by addition of mineral admixtures, this mineral admixtures are referred to as Pozzolana. Widely investigated Pozzolana are fly ash, volcanic ash, silica fume and slag powder [6], [7], [10]

Natural Zeolite is also a mineral admixture which had been investigated as cement mortars and concrete improver by few researchers [12], [13]. Natural Zeolite contains large quantities of reactive  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  [13] that offer large (internal and external) surface areas. These elements combine with  $\text{Ca}(\text{OH})_2$ , a by-product of cement hydration to form further calcium silicate and calcium aluminate. This reaction is called Pozzolanic reaction and it is responsible for increasing strength and reducing pore size of blended cement mortars and concrete.

It has been observed [13] that pozzolanic reactivity of natural Zeolite is higher than that of fly ash but lower than that of silica fume. This make natural zeolite blended mortars and concrete to have higher early strength compared to fly ash blended mortars and concrete. The oxide compositions of some selected Zeolite are shown in Table 1.

Table 1. Oxide composition of selected natural zeolites

Oxides (% by mass)	Natural Zeolite		
	A	B	C
$\text{SiO}_2$	69.1	65.8	65.7
$\text{Al}_2\text{O}_3$	11.9	14.3	12.5
$\text{CaO}$	0.7	3.4	2.0
$\text{Fe}_2\text{O}_3$	0.7	2.6	1.7
$\text{MgO}$	0.4	1.3	0.9
$\text{Na}_2\text{O}$	3.5	2.5	1.5
$\text{K}_2\text{O}$	3.8	2.7	1.7
$\text{MnO}$	4.9	0.04	0.9

Source: Yan Fu et al.[16]

Studies carried out on Natural Zeolite show that natural Zeolite blended mortars and concrete improve strength, prevent expansion due to alkali- aggregate reaction, reduce porosity and improve the interfacial microstructure properties between the blended paste and the aggregate [6], [13]. According to Niu and Feng [11], the effect of natural Zeolite can be improved if it is modified. Due to its large surface area and water adsorption ability, more water and superplasticizer will be needed to maintain slump. The modified Zeolite will have the advantage

of enhancing cement mortars and concrete properties better and also reduce the dosage of the modified Zeolite that will be needed.

The product, being referred to as PowerCem (PWC), a blend of selected alkaloids and natural Zeolite will be used in this study, this product is commercially available and effectively used in soil stabilization for road construction. Its influence on cement mortars properties, especially durability will be investigated, this will prove the sustainability of the product as cement mortar improver.

## Experimental procedure

### Materials

The cement used was commercially available Portland cement CEM I 42.5N ( equivalent of a ASTM type 1), synthetically modified natural Zeolite additive (PowerCem) was obtained from PowerCem holdings in Netherlands, Silica standard sand according to SABS EN -196 [14] was used and mortar was prepared according to SABS EN 196-1 [14]. The chemical composition of the cement used had already been recorded in another work [5].

### Sample preparation

**Compressive and flexural strength test:** Cement mortars were prepared for the determination of flexural and compressive strength test. PowerCem was used as additive to cement in the following proportions 0%, 0.4%, 0.6%, 0.8%, 1.0% and 2.5% by weight of cement. The sand: cement ratio was 3 and water: cement ratio was 0.5. Details of all the mixes are shown in Table 2, flow test was carried out using the flow table as described in ASTM C230 [2]. The cement mortar was mixed for 3 minutes, following the procedure in SABS EN 196-1: 1994 [14] and then cast in 40x40x160mm prisms. The samples were demolded after 24hrs and water cured at 23°C. The flexural and compressive strength were determined at 3 and 28 days curing periods according to SABS EN 196-1: 1994 [14].

Table 2. Mixture proportions for 1m<sup>3</sup> of mortar for flexural and compressive strength test

Binder	Cement (kg)	Silica sand (kg)	PowerCem (kg)	Water (kg)	w/b	flow (mm)
Control	586.00	1758.00	0.00	293.00	0.5	112.97
0.4% PWC + Cement	586.00	1758.00	2.34	294.17	0.5	112.46
0.6% PWC + Cement	586.00	1758.00	3.52	294.76	0.5	112.55
0.8% PWC + Cement	586.00	1758.00	4.69	295.35	0.5	113.48
1.0% PWC + Cement	586.00	1758.00	5.86	295.93	0.5	119.06
2.5% PWC + Cement	586.00	1758.00	14.65	300.33	0.5	135.03

**Sulphate attack resistance test:** The sulphate resistance was determined by measuring the expansion of mortar samples according to ASTM C1012 [3] using 25x25x280mm prisms. The cement: Sand: water ratio used was 1:2.75:0.485, samples were steam cured at 38°C until the mortar cube strength reached a value of 20MPa, after which the samples were immersed in a 5% Na<sub>2</sub>SO<sub>4</sub> solution. PowerCem was used as additive to cement in the following proportions 0%, 0.4%, 0.6% and 2.5% by weight of cement. Details of the mix proportions are shown in Table 3. The length readings of the samples before immersing in Na<sub>2</sub>SO<sub>4</sub> are taken as the initial readings and expansions were observed at ages 7, 14 and 28 days after immersing in Na<sub>2</sub>SO<sub>4</sub>.

Table 3. Mixture proportions for 1m<sup>3</sup> of mortar for sulphate resistance test

Binder	Cement (kg)	Silica sand size 0.4-0.85 (kg)	PowerCem (kg)	Water (kg)	w/b
Control	714.00	1964.00	0.00	346.30	0.485
0.4% PWC + Cement	714.00	1964.00	2.86	347.70	0.485
0.6% PWC + Cement	714.00	1964.00	4.28	348.40	0.485
2.5% PWC + Cement	714.00	1964.00	17.84	354.90	0.485

**Permeability, sorptivity and porosity test:** The gas permeability was measured using a falling head permeameter developed by Ballim [4] at the University of the Witwatersrand, Johannesburg South Africa. The method is based on the Darcy coefficient of permeability by monitoring a falling pressure head. The samples are cores of diameter 68±2mm and thickness 25±2mm, which were cut from 100mm cubes (parallel to the casting direction). The samples were cured for 7 and 28 days and put in oven which was maintained at 105°C for 7 days after curing.

The samples were cooled on a steel tray in a dessiccator in a room maintained at 23°C, for 2hrs, the thickness and the diameter of each sample were measured with vernier at 4 points equally spaced around the perimeter of the specimen. The samples were placed in a compressible collar with the test face (outer face) at the bottom, the collar was placed in a PVC sheath with wooden ring on top of the permeability cell, this is to provide adequate seal.

The cover plate is placed in position and tightened. Oxygen was passed through the pressure with both cylinder inlet and outlet valve open for 5secs, in order to purge the test chamber. The outlet valve was then closed and pressure was allowed to rise to approximately 100KPa, then the inlet valve was closed and time and pressure recorded. The reduction in pressure was recorded at intervals of approximately 5KPa until the decrease in pressure reached approximately 60KPa or 6hrs after starting of test. The outlet valve was then opened and sample removed. The schematic permeameter test arrangement is shown in Fig 1.

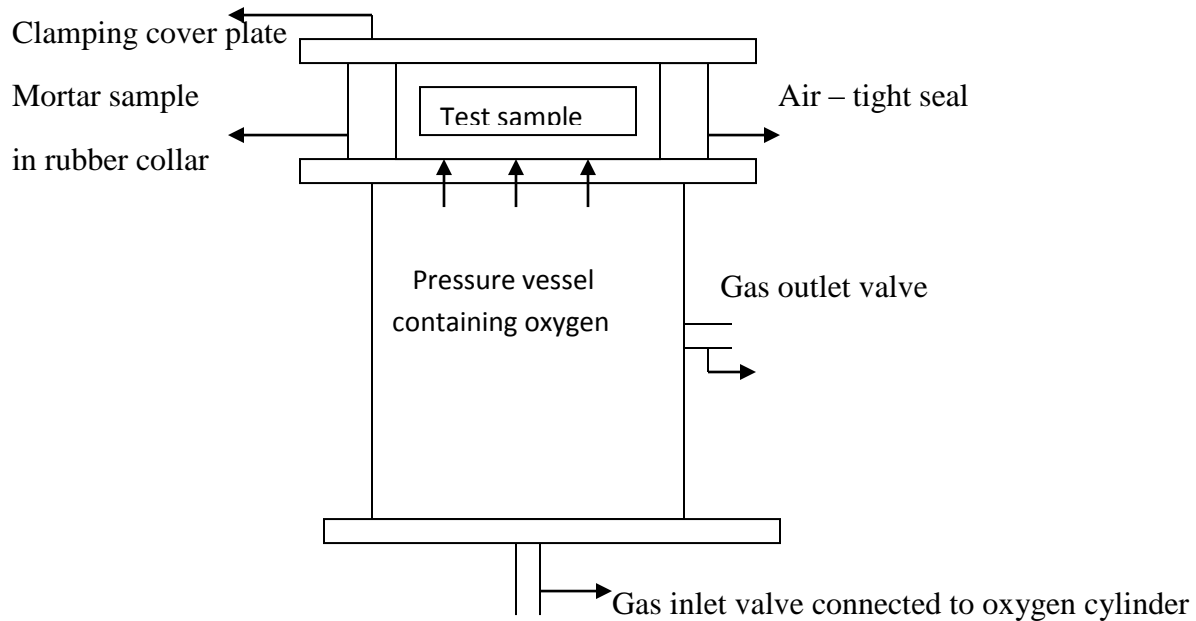


Fig 1: The schematic permeameter test arrangement.

The coefficient of permeability (m/s) was calculated from the equation:

$$K = \frac{WVg}{RA} \left( \frac{d}{\theta t} \right) \ln \left( \frac{P_0}{P} \right) \text{----- (1)}$$

K = coefficient of permeability (m/s)

W = molecular mass of oxygen = 32g/mol

V = volume of oxygen under pressure in permeameter (m<sup>3</sup>)

g = acceleration due to gravity (9.81m/s<sup>2</sup>)

R = universal gas constant = 8.313(Nm/Kmol)

A = superficial cross- sectional area of sample (m<sup>2</sup>)

d = average sample thickness (m)

$\theta$  = absolute temperature (K)

t = time (s) for pressure to decrease from P<sub>0</sub> to P

P<sub>0</sub> = pressure at the beginning of test (KPa)

P = pressure at the end of test

The same samples were used for water sorptivity test, but a packaging tape was wrapped around the circumference up to approximately 5mm above the front face, this is to allow the capillary rise of water to occur within the surface of the sample alone. The samples were placed back to the oven at a temperature of 105°C for 24hrs to allow the drying of moisture that might have been acquired during permeability test. The test was performed according to the procedure described by Alexander et al [1].

The samples were then removed from the oven, and the oven dry mass was recorded. After cooling, the samples were reweighed. Calcium hydroxide solution was poured in a 10 layers of paper placed on a tray such that at least 10mm gap was left between the sides of the tray and the edge of the paper. The level of the solution was approximately 2mm up the side of the samples. The samples were placed on the prepared tray and the mass of the sample was recorded at regular intervals for 25mins after the initial introduction of Ca(OH)<sub>2</sub> solution, after weighing, the samples were placed in a vacuum saturation tank, the lid was sealed with petroleum jelly.

The vacuum tank was evacuated between -75 and -80KPa and samples were maintained under vacuum of between -75 and -80KPa for 3hrs. After 3hrs the tank was isolated and calcium hydroxide saturated water was allowed to flow into the chamber until the water level was approximately 40mm above the top of the samples. The vacuum pump was reconnected to the tank and vacuum was maintained for 5hrs at between -75 and -80KPa. After 5hrs the vacuum was released and air was allowed to enter. The samples were allowed to soak for a further 18hrs, after which the samples were removed from the solution and weighed immediately. The Porosity was first calculated from the equation:

$$n = \frac{M_{sv} - M_{so}}{Ad\rho_w} \text{ ----- (2)}$$

M<sub>sv</sub> = The vacuum saturated mass of the samples to the nearest 0.01g

M<sub>so</sub> = Mass of the specimen at t = 0 to the nearest 0.01g

A = Cross- sectional area of the samples to the nearest 0.02m<sup>2</sup>

d = Average samples thickness to the nearest 0.02mm

P<sub>w</sub> = Density of water

Then the mass of the water absorbed at each weighing period was calculated from:

$$M_{wt} = M_{st} - M_{so} \text{ ----- (3)}$$

Where M<sub>st</sub> = Mass to the nearest 0.01g of the sample at time t.

The sorptivity was calculated from the slope of the graph of water absorbed (M<sub>wt</sub>) versus the square root of time (in hr).

$$S = \frac{Fd}{M_{sv} - M_{so}} \text{ ----- (4)}$$

Where F = The slope of the best fit line obtained by plotting M<sub>wt</sub> against t<sup>1/2</sup>

## Results and discussion

### Effect of the additive on strength

The flexural and compressive strength data obtained at ages 7 and 28 days are given in Fig 2-5. Results are the average values of three samples for each mix at a particular period. Highest flexural strength is observed in 0.6% PWC mortar samples at 28 days, while increase in additive dosage beyond 0.6% shows decrease in flexural strength except for 1.0%, this behaviour is beyond our understanding, on the other hand, the compressive strength of control shows to be higher than other samples but 0.4% and 0.6% PWC mortar samples have higher results at 28 days than other PWC mortar samples, the behaviour of 1.0% PWC mortar samples is still unclear.

There is no specific relationship between the flexural and compressive strength results obtained, this confirms the observation of Fulton [8]. The reduction in strength beyond 0.6% dosage of additive may be as a result of increase in flow, since flow increases as additive increases with constant w/c ratio. Increase flow will result in less strength as a result of excess water that is present in the mortar after hydration has taken place and through evaporation, the mortar will be left with more voids.

Higher rate of increase in strength is also observed with 0.6% PWC mortars samples in both flexural and compressive strength compare to control mortars samples with no additive. This may be as a result of pozzolanic reaction between the  $\text{SiO}_2$  in the additive and  $\text{Ca(OH)}_2$ , a by product of cement hydration to form more C-S-H gel which is responsible for strength development.

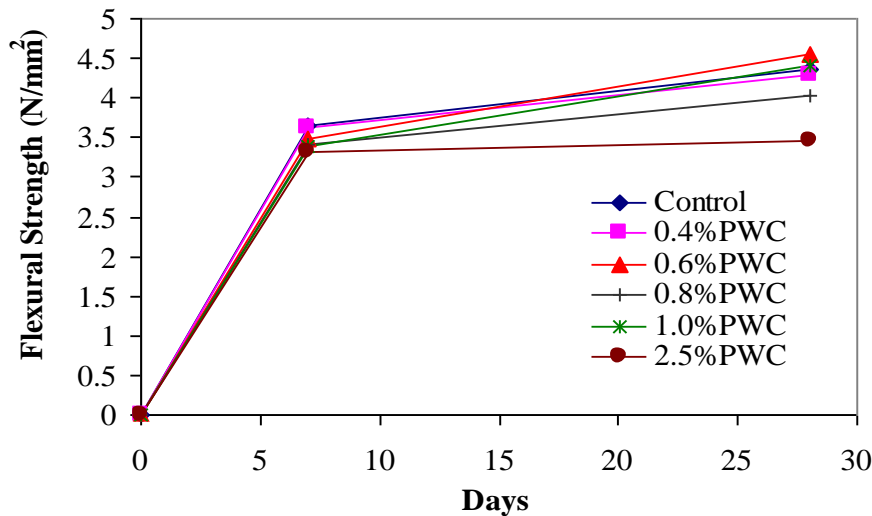


Fig 2: Flexural strengths obtained at ages 7 and 28 days

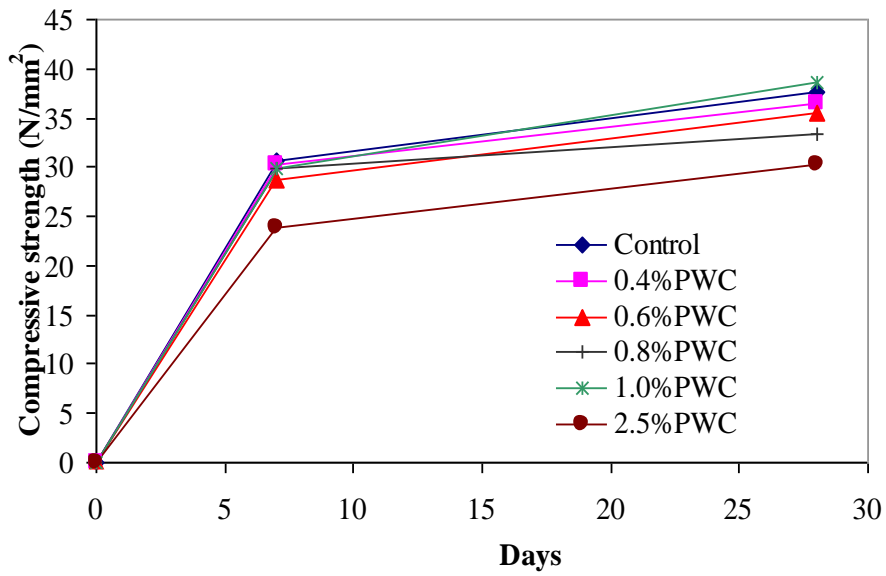


Fig 3: Compressive strengths obtained at ages 7 and 28days

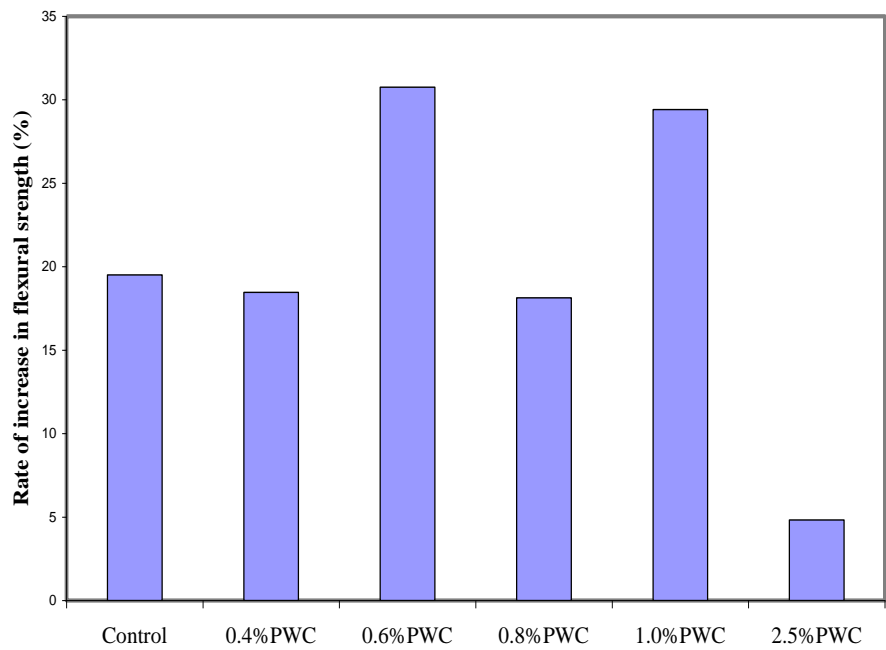


Fig 4: Rate of increase in flexural strength



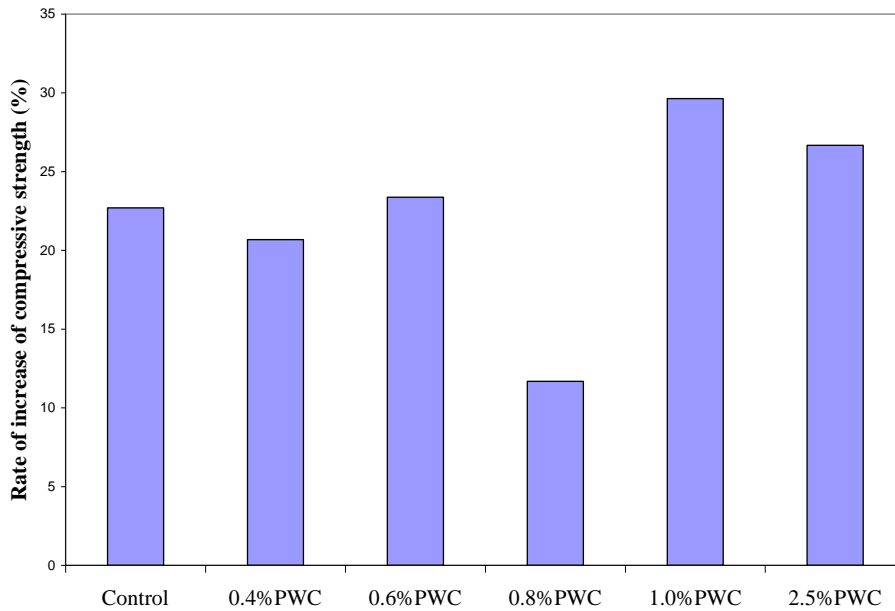


Fig 5: Rate of increase in compressive strength

### Effect of the additive on sulphate resistance

The results of sulphate resistance behaviour of samples are shown in Fig 6-8

Expansions observed in 0.4% and 0.6% PWC mortars samples are lower than that observed in control mortar at 28days, higher dosage of additive shows higher expansion. Lower rate of expansion was also observed with 0.4% and 0.6% PWC mortar samples between ages 14 and 28 days.

The behaviour of this additive can be attributed to the pozzolanic reaction between the additive and  $\text{Ca}(\text{OH})_2$  formed during hydration process, which result into secondary C-S-H and form more dense mortar and pores of smaller diameter. According to Sideris [15], secondary C-S-H produces a layer on the reactive phases of mortar which hinders the formation of secondary ettringite. On the other hand, increase dosage of additive beyond 0.6% can result in high content of calcium-silicate because of high content of  $\text{SiO}_2$  in the additive, this will produce more  $\text{Ca}(\text{OH})_2$  during hydration and can lead to more formation of gypsum when exposed to sulphate. Gypsum is also an expansive product apart from ettringite and therefore leads to high expansion.

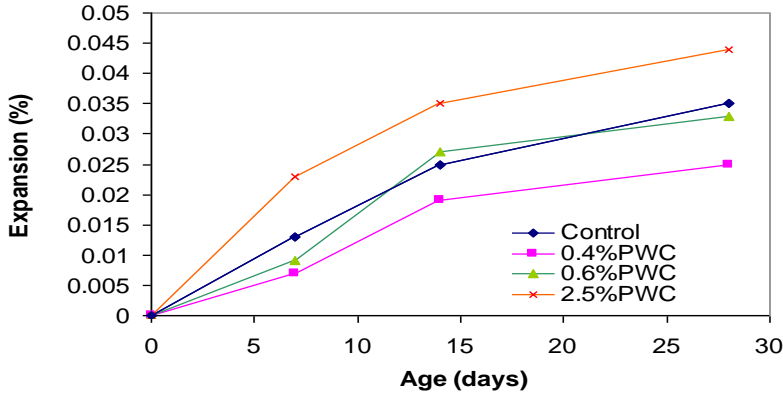


Fig 6: Expansion due to sulphate attack

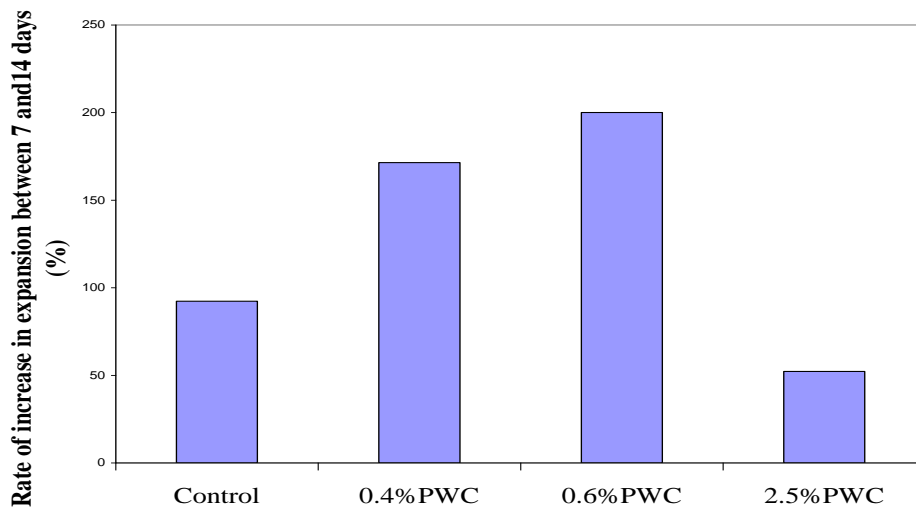


Fig 7: Rate of increase in expansion between 7 and 14 days

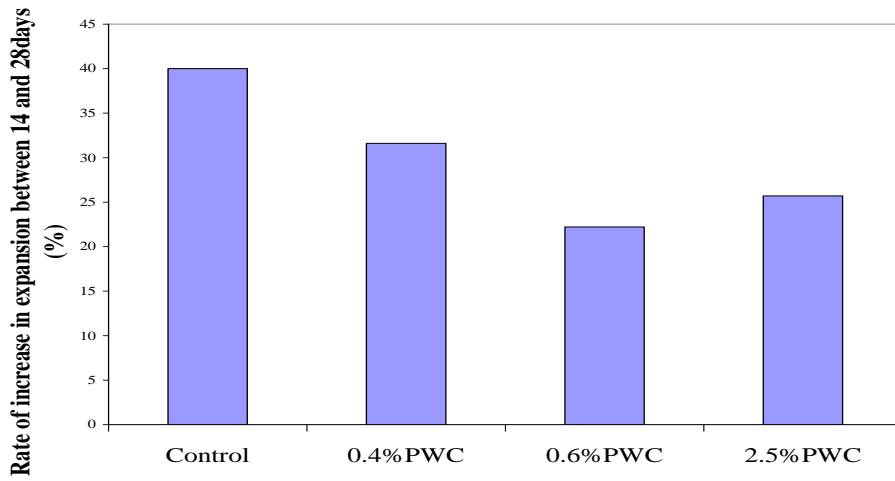


Fig 8: Rate of increase in expansion between 14 and 28 days

### Effect of the additive on permeability, sorptivity and porosity

The results of permeability, sorptivity and porosity for ages 7 and 28 days are shown in Fig 9-11. Results are average values of three samples for each mix at a particular period. Reduction in permeability was observed with mortar of low dosage of additive (0.4%, 0.6% and 0.8%) at 28 days compare to control mortar. However, increase in the dosage of additive beyond 0.8%, shows increase in permeability.

Sorptivity of control mortar is higher than PWC mortar at 28 days for all dosages, increase in sorptivity was however observed with control mortar sample from day 7 to 28 days while otherwise was observed in PWC mortars samples.

In the case of porosity, control mortar samples shows lower porosity at 28 days than all PWC mortar samples and decrease in porosity was observed between ages 7 and 28 days, while increase porosity was observed in all PWC mortar samples.

No significant change was seen between the results at ages 7 and 28 days of 1.0% and 2.5% PWC mortar samples for both sorptivity and porosity.

Addition of the additive at all levels, shows reduction in sorptivity at 28 days compare to control mortar samples and this is very important to durability because it will reduce the filtration of chloride-containing or sulphate-containing water (this can cause serious damage) into mortar.

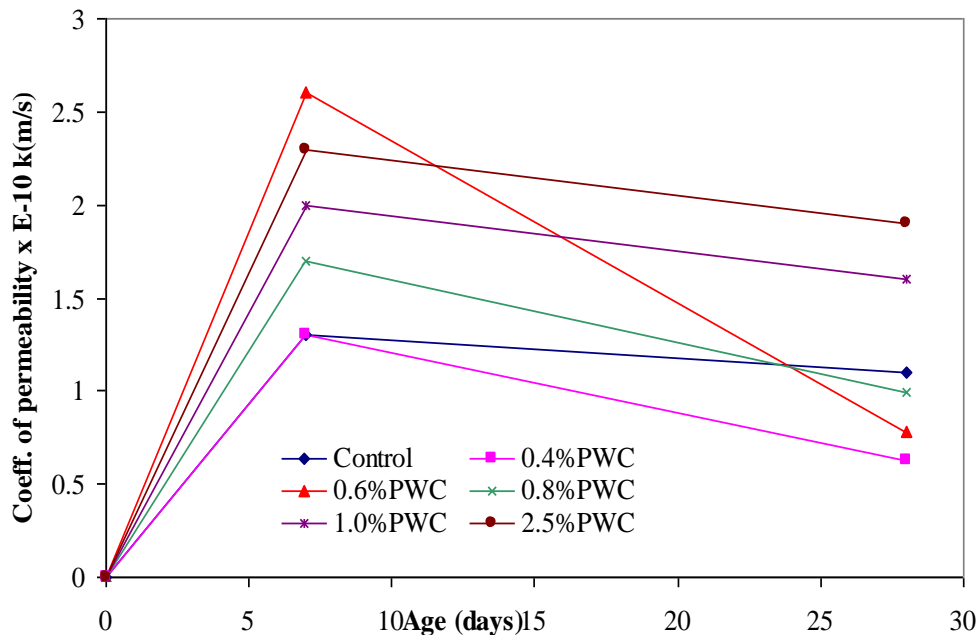


Fig 9: Coefficient of permeability of samples

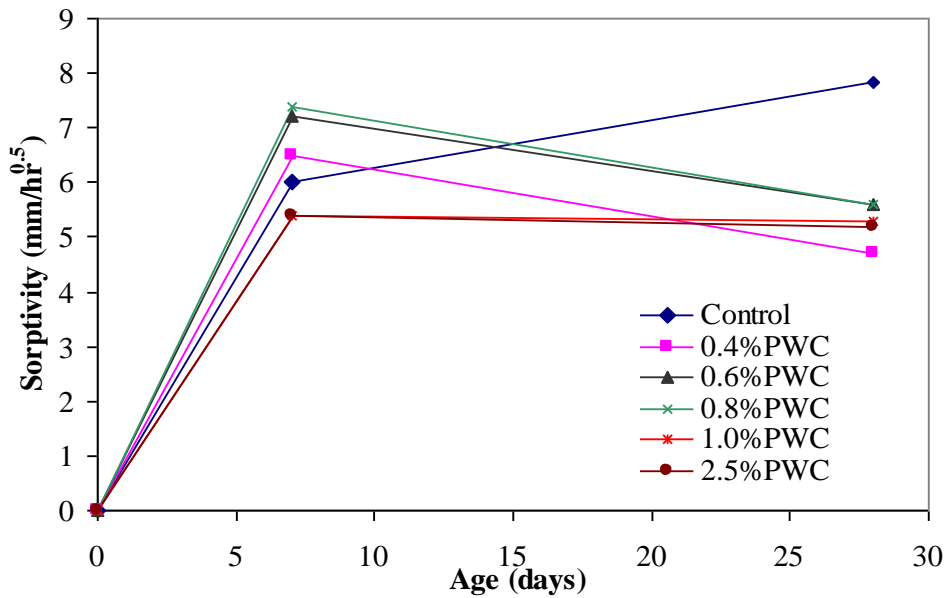


Fig 10: Sorptivity of samples

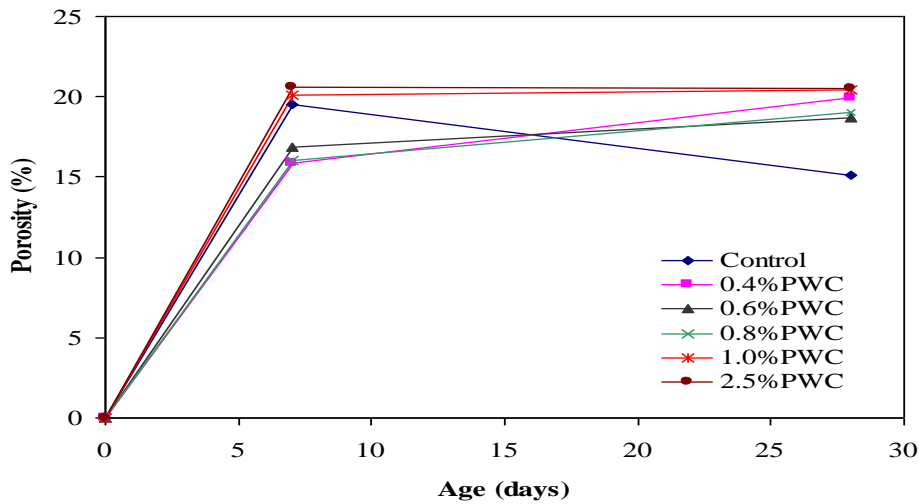


Fig 11: Porosity of samples

## Conclusion

The following conclusions can be drawn from this study.

- The additive has a positive effect on flexural strength, compressive strength, permeability, sorptivity and expansion due to sulphate attack of mortar samples when used at optimum proportions (0.4% and 0.6%), while the porosity of the mortar samples increased at 28days curing period.

- Addition of additive beyond the optimum proportions results in decrease flexural and compressive strength, increase permeability, expansion to sulphate attack and porosity at 28days curing period.
- Rate of increase in flexural and compressive strength is higher in 0.6% PWC mortar samples than control samples, showing that 0.6% PWC mortar samples might still maintain its high strength values for long term test, compare to control samples.
- The positive effect of the additive on the permeability, sorptivity and expansion to sulphate attack at optimum proportions shows that the additive improved the durability behaviour of mortar.
- Low optimum proportions favour economic considerations.

## **5. Recommendations**

- Further investigation is needed on the long term effect of the additive on mortar.
- Effect of the additive on concrete should also be investigated so as to compare the trend with that of mortar

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