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Cementitious Concrete Oil Containers Corrosion.

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ABSTRACT

This work is an experimental study that measures the effects of polymer on cementitious concrete (PLC) properties. Polymer serve as a super plasticizer admixture which may result to concrete's lower rate of water absorption, high-range water reducer, greater strength and excellent in elasticity. The experiments carried out on cement paste with the soluble polymer polyvinyl alcohol (PVA) that frequently used for the modification of concrete. PVA belongs to the class of the water nonionic polymers containing a vinyl group. The other is styrene-butadiene rubber (SBR) which is one of the bitumen modifiers that obtained from crude oil and improves low temperature performance at moderate concentrations. The polymers dissolved in water with five different proportions ranging from 2% to 20% with respect to cement's percent by weight in kg. The effects of water/cement ratio (W/C) and polymer concentration on the PLC density carried out and investigated. The effect of $CaSO_4$ that usually found in the crude oil on the density, pH, and corrosion of cementitious concrete carried out and investigated using three CaSO3 concentrations. SEM observations illustrated the effect of polymer in improving the cementitious concrete properties and the effect of CaSO4 on its ability to corrosion.

Keywords: polyvinyl alcohol (PVA); styrene-butadiene rubber (SBR); water/cement ratio (W/C); $CaSO_4$; density; pH, and corrosion.

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INTRODUCTION

Cruz et al. [1] concluded that polymer concrete is becoming increasingly popular due to many advantages that it possesses. It is very strong, durable and cures very rapidly, an important factor in most of the civil engineering applications such as transportation, utility, marine and building components. It has superior physical and chemical properties such as a short curing time, impact resistance, chemical resistance, electrical insulation, waterproofness, and freeze–thaw durability. Ribeiro et al. [2] decided that worldwide volume production and consumption of fiber- reinforced polymers (FRP) have increased in the last decades in several fields, mostly in the construction, automobile and aeronautic sectors. Ganiron Jr. [3] illustrated that an admixture of concrete is a material other than water, aggregates, cement, and fiber, added to plastic concrete or mortar to change one or more of its properties at the fresh or hardened stages. Mohamed et al. [4] investigated the effect of water/cement ratio, iron, lead and polypropylene on the mechanical properties of the cement paste taken into consideration the influence of mass percentages and age of cementitious composites. In addition, Mohamed et al. [5] applied cementitious composites to characterize the using of composites in both seismic and corrosion repair of structural systems. The effect of the number and conditions of the iron rods and the number of cans on the crushing loads of the cementitious composites carried out and investigated, [6]. Sivaarunkumar et al. [7] showed that the concrete with 9.5% of epoxy and 10% of silica fume showed better strength when compared with other mixes. Tutikian [8] evaluated the acoustic performance of lightweight concrete with ethylene vinyl acetate copolymer (EVA) residues to reduce impact noise on floors. Daud et al. [9], found that the replacements of modified binder (cement) with a thermoplastic material and the replacement of the gravel by the whisker of PET (Polyethylene Terephthalate) resulting in lighter products with a low of the wet ability by water. Nassar [10] used polystyrene packaging.

Hu et al. [11], investigated the microstructural properties of the mortar i.e. porosity, pore size distribution, were investigated by quantitative image analysis. Hu et al., [12], presented the effect of admixed polyethylene oxide-b-polystyrene (PEO113-b-PS70) micelles on corrosion behavior of reinforced mortar. Therefore, the presence of micelles further minimized and halted the corrosion process. Al-Ghamdi et al. [13] used the Atomic absorption spectroscopy method measure the corrosion effect of Na/Cl on the epoxy/aluminum composites. The aim of the present work is to discuss the effect of using two polymers; SBR and PVA with different concentrations on the effect of water/cement (W/C) ratio on the cementitious concrete is obtained. CaSO4 corrosion medium used with a concentration similar to that of the crude oil to discuss their effect on the density, pH and weight loss of the PLC. A metallographic examination carried out to illustrate the effect of both polymers and corrosion medium of PLC products.

EXPERIMENTAL WORK

Experimental Procedure

The research is a laboratory scale to determine the optimum composition of the manufacturing of cementitious concrete by replacing the gravel with two thermoplastic materials PVA and SBR. Specimen made up from constant sand ratio and different percentages of; W/C, and polymer weight ratios. This research involves compression, flexural, tension, density, porosity, and corrosion test. The apparent density of specimens measuring diameter 57 mm by 60 mm high was estimated by the Archimedes method using kerosene (ASTM C 380-79) according to the following relation;

$$\textbf{Density, } \rho = m/v$$

Where; m is the dry sample weight (Kg), v is the cylinder volume (m^3), and ρ is the concrete sample density (Kg/m^3). Portland cement used chemical with composition and physical properties shown in Table 1.

Table 1: Chemical compositions of Portland cement

Components	CaO	SiO_2	Al_2O_3	SO_3	Fe_2O_3	MgO	Na_2O	K_2O	TiO_2	P_2O_5	Mn_3O_4
Weight %	66.36	20.36	4.9	2.57	3.17	2.09	0.14	0.64	0.35	0.18	0.14

Test Specimens

The W/C (water cement ratios) of specimen was 40, 50, 60, 70 and 80% respectively. The mass ratio of the cement and sand was a constant value of 1:3. To initiate lightweight concrete corrosion, all samples were then ponded with the three different concentrations of $CaSO_4$ of 1.0, 5.0, and 10.0 %Wt. For each mix, three specimens prepared for each mix design to validate the reliability of test results. Ordinary tap water used in this work for all concrete mixes and curing of specimens. Styrene butadiene rubber (SBR) used as polymer modifier in this study. Styrene butadiene, an elastomeric polymer, is the copolymerized product of two monomers, styrene and butadiene. The soluble polymer polyvinyl alcohol (PVA) used for the modification of concrete. The polymers SBR and PVA used as a ratio by weight of cement of 2%, 5%, 10%, 15% and 20%. The pH of the solutions measured before immersing the specimens and after they removed. For each measurement, personal pH meter used. The specimens surface of were observed with a scanning electronic microscope (SEM) in a JEOL model JSM-5200 machine, in the backscattering-electron mode.

RESULTS AND DISCUSSIONS

Effect of (W/C) Ratio on the Concrete Density

Fig. 1 illustrates the effect of W/C ratio on the concrete density at various aging periods. As the different values of W/C lead to different size of micro voids within cement mortar, therefore, the effect of W/C on damage evolution is equivalent to the effect of average size of micro voids. For the cement mortar with high W/C, the average size of micro voids is large, so the density is low. This means longer time needed for the delayed ettringite to reach the boundary of the void, and this may delay the appearance of damage. It can be easily noticed that concrete mass density inversely affected by the increase of water cement ratio in agreement with [5] and [10].

Effect of Polymer %Wt. on the Concrete Density

Figure 2 shows the density values for both polymers. PVA has the lowest concrete density due to the PVA low weight. This shows that the additives reacted as binder between the raw materials when they mixed. The more additives applied, the stronger bonds were existed between them. Thus, it produced less porosity in the structure [8-9]. However, it is clear that as both SBR and PVA wt. % increases, the concrete density decreases due to the lower weight of both polymers that takes the place of water in the cement voids. It is clear that the SBR concrete has lower density compared to PVA.

Effect of the Corrosion Medium on the Concrete Density

Fig. 3 illustrated the effect of $CaSO_4$ concentration on the concrete density at various W/C ratio and aging periods. As the $CaSO_4$ concentration increases, the PLC density decreases due to the CaSO4 corroded effect in attacking that increases its micro voids a and leads to the lower PLC density. As the aging period increases, the water dissipation increases, and the density decreases, [21].

Effect of The Corrosion Medium on The Concrete pH

The changes in the pH with the aging period at different W/C ratios and $CaSO_4$ values are shown in Fig.4. In early stages, the pH increased with time in every $CaSO_4$ wt.%. Almost changes are remarkable for early stages from the aging periods. These changes are greatly near at the early stage of immersion. At, 1.0 wt.% CaO_4, the lower W/C has the higher pH due to the acidity increment, while at the higher W/C, the acidity decreases due to the water increment that leads to the acidity decrement. Also, as $CaSO_4$ wt.% increases for the same W/C values, the acidity increases as shown in Fig. 4.c.

Effect of the Corrosion Medium on the Concrete Weight Loss

Figure 5 illustrates that low W/C ratio is rich of cement component that induces intensive chemical reaction with sulphuric acid for all W/C concentrations. But with W/C = 0.4 at 1%$CaSO_4$, the mass loss% trends are reversal to those obtained at 5%wt. CaSO4 in agreement with the results obtained in Fig. 4. With long immersion term, the corrosion at a high W/C is larger than that at low W/C. Therefore, although a low W/C causes a large mass reduction than a high W/C due to the higher intensity of sulphur, it is regarded that low W/C is effective in preventing corrosion due to the lower porous structure.

SEM Observations

Effect of polymer

SEM observation of the cement paste shown in Fig. 6.a. The air void surfaces have a smooth surface, Fig. 6.b. The presence of polymers influence shown in Fig. 6.c and 6.d for both 1.0wt. Percentage of PVA and SBR respectively. It is clear that the rate of cement hydration, nature and morphology changed. The polymer acts as an admixture for concrete and no continuous polymer film formed. Because of the low amounts of water-soluble polymers added to the fresh mixture, these polymers generally considered as rheological additives and polymer film formation not mentioned. For polymer dispersions of 10% wt. percentage SBR shown in Fig. 6.e, an adequate film formation throughout the cement matrix, play an important role in sealing the high porosity of the adhesive layer and improve its cohesive strength. The gaps sealed in the contact surface and the bonding between the cement and polymer becomes more dense and firm.

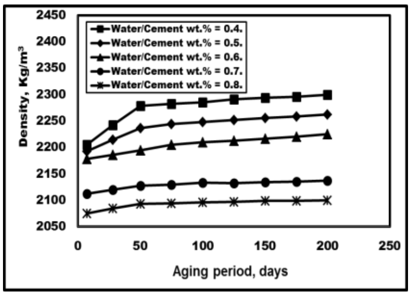
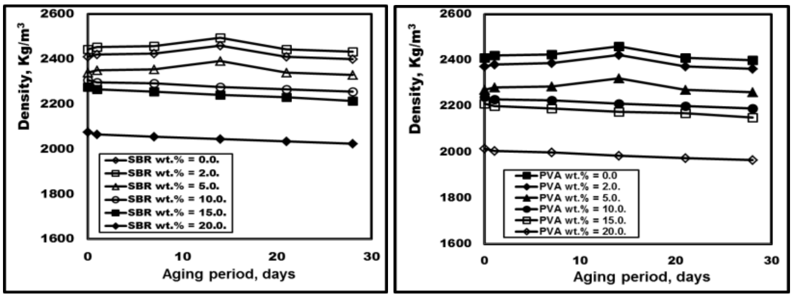
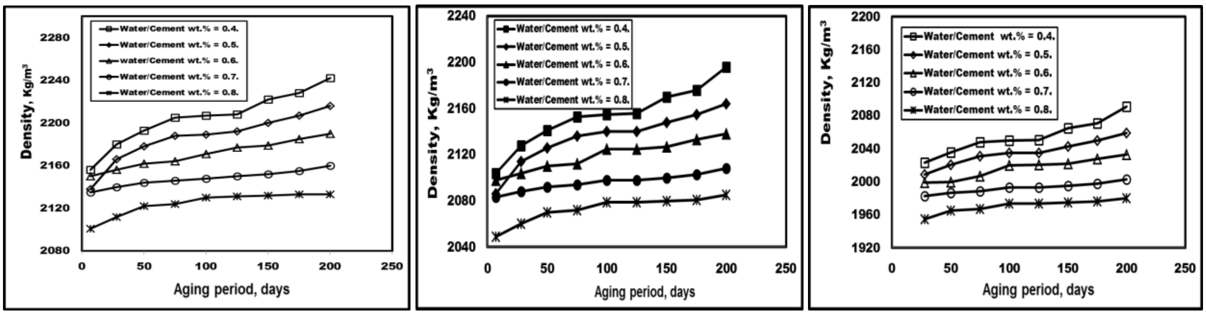


Fig. 1. Effect of W/C on concrete density.



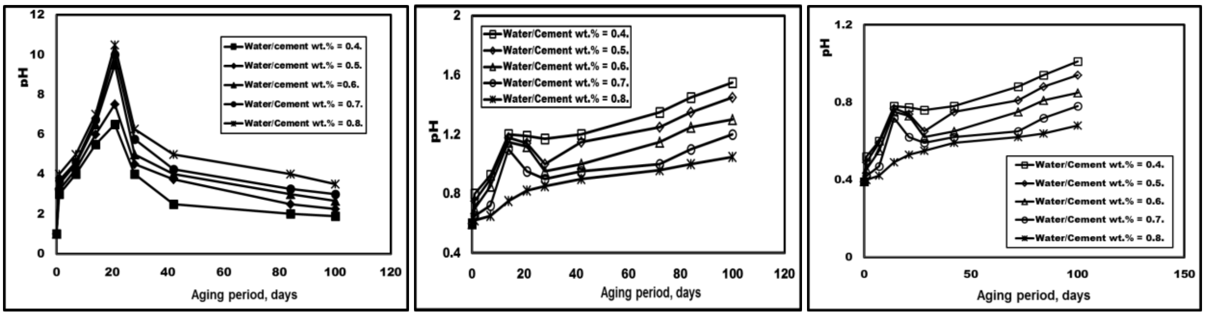
(a) SBR (b) PVA

Fig. 2. Effect of SBR and PVA wt.% on concrete density.



(3.a) 1.0wt% $CaSO_4$ (3.b) 5.0wt% $CaSO_4$ (3.c) 10.0wt% $CaSO_4$

Fig. 3. Effect of W/C ratio on concrete density at various aging periods and $CaSO_4$wt.% .



(4.a) 1.0 wt.% $CaSO_4$ (4.b) 5.0 wt.% $CaSO_4$ (4.c) 10.0 wt.% $CaSO_4$

Fig. 4. Effect of W/C ratio on pH of cementitious concrete at various aging periods and $CaSO_4$wt.% .

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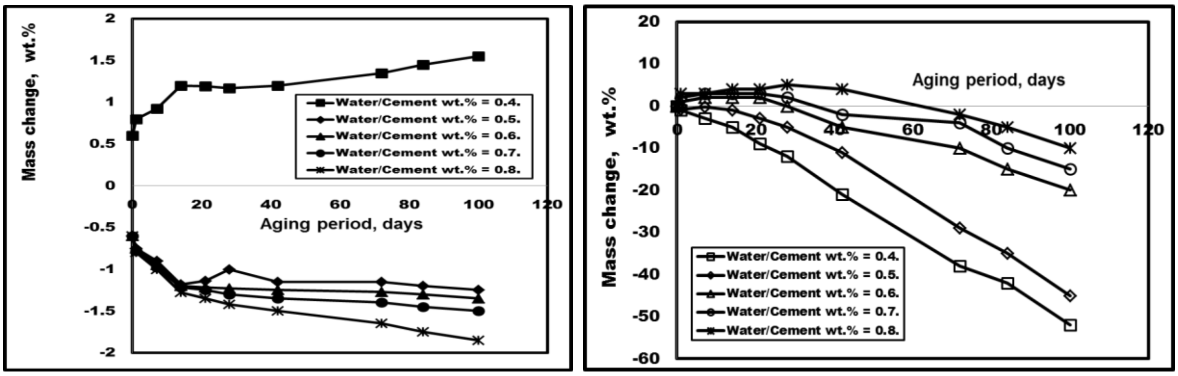


(5.a) 1.0 wt.% $CaSO_4$ **(5.b) 5.0 wt.% $CaSO_4$**

Fig. 5. Effect of W/C ratio on mass change of cementitious concrete at various aging periods and $CaSO_4$wt.% .

The admixing of $CaSO_4$ alter the morphology and microstructure of the cement-polymer interfacial region, as illustrated in Fig, 7.a, b, and c after being pounded by 10.0 wt.% $CaSO_4$ solution for 100 aging days. Fig. 7.a had a relatively homogeneous surface, featuring the presence of fine rod-like. For the samples with 10 wt.% SBR and 10.0 wt.% PVA at 10.0 wt.%$CaSO_4$ (7.b and 7.c), the exfoliated lamella crystals dominated the fracture surface, while delicate globular or whiskery minerals were also observed. The exfoliated lamella crystals reported to be responsible for expansion and subsequent cracking and spalling of mortar in agreement with [10], which might have aggravated the expansion due to the diffusion of mortar corrosion products into mortar at the polymer-mortar interfacial region.

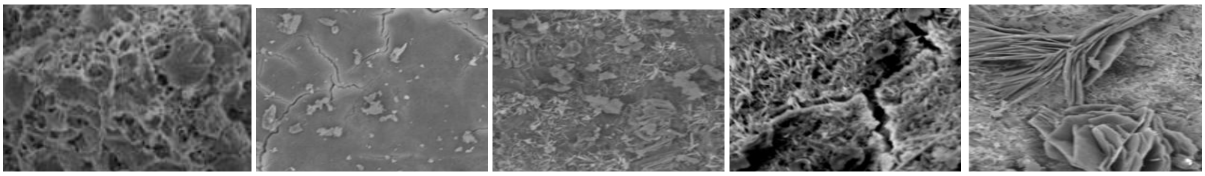
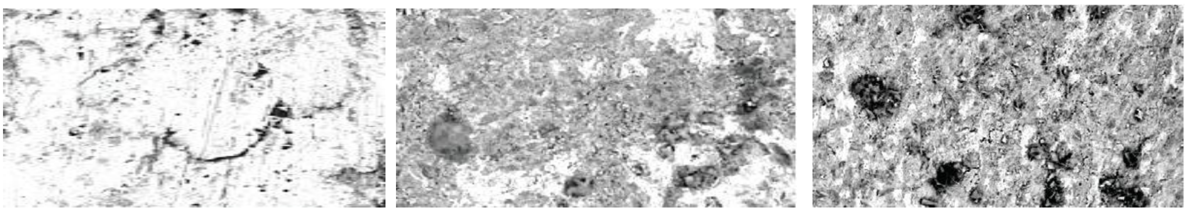


Fig. 6.a **Fig. 6.b** **Fig. 6.c** **Fig. 6.d** **Fig. 6.e**

Fig. 6. SEM observations of cementitious concrete.

(a) Cement paste, (b) 1.0 wt.%PVA, (c) 1.0 wt.%SBR, (d) 15wt.%PVA and (e) 10wt% SBR.



(7.a) 10.0 wt.% $CaSO_4$ **(7.b) 10.0 wt.% $CaSO_4$ and 10.0 wt.%SBR.** **(7.c) 10.0 wt.% $CaSO_4$ and 10.0 wt.%PVA.**

Fig. 7. SEM observation of cementitious concrete at 100 aging days and 10.0 wt.% $CaSO_4$.

CONCLUSIONS

Based on the results the following conclusions made:

- Both polymers types have a good effect on the produced concrete with an optimum SBR and PVA of 10.0 wt. percentage and 15.0wt. Percentage respectively.
- As the W/C increases, the cementitious concrete density decreases.
- The optimum W/C wt. percentage is 46% with respect to the cement weight.
- Both SBR and PVA have a good effect in reducing the rate of corrosion of the corroded medium.
- The metallographic examination showed the inhibition effect of SBR and PVA on the rate of corrosion of the polymer lightweight concrete.

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