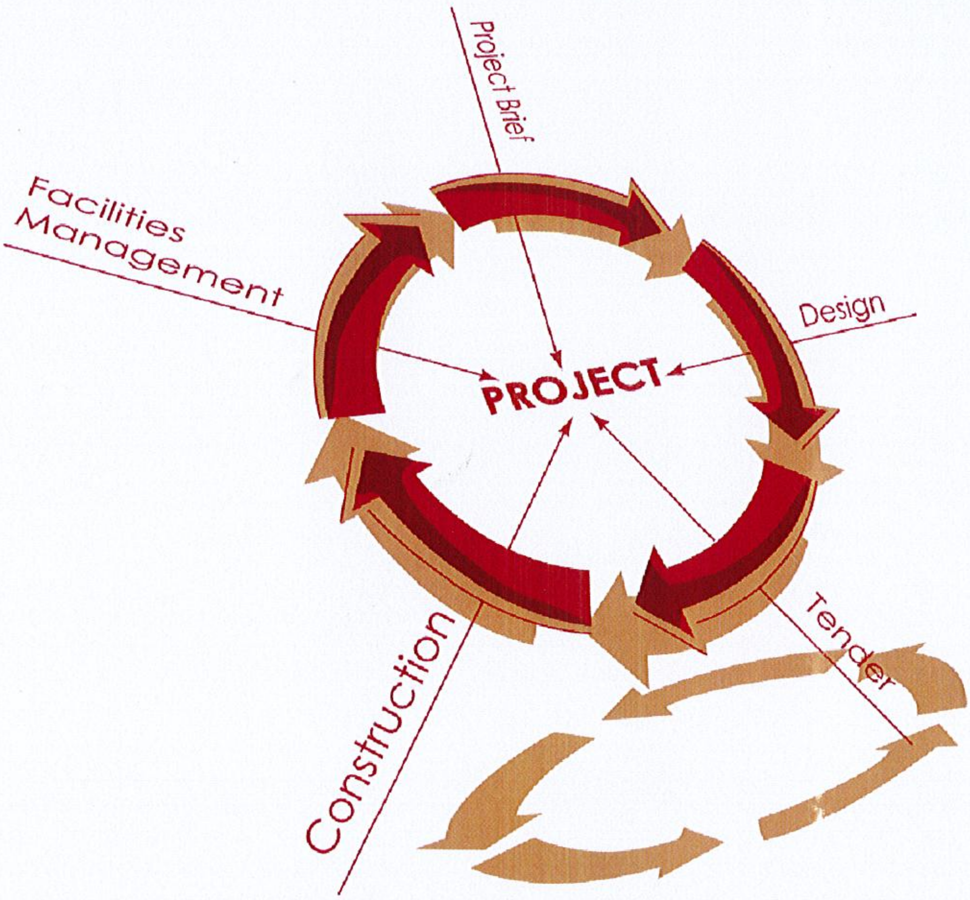
MCRJ SPECIAL ISSUE Volume 6 | No. 1 | 2019 eISSN 2590 - 4140

Malaysian Construction Research Journal

10TH ASIA PACIFIC STRUCTURAL ENGINEERING AND CONSTRUCTION CONFERENCE 2018



CREAM CONSTRUCTION RESEARCH INSTITUTE OF MALAYSIA
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MALAYSIAN CONSTRUCTION RESEARCH JOURNAL (MCRJ)

SPECIAL ISSUE Vol. 6 | No. 1 | 2019

10TH ASIA PACIFIC STRUCTURAL ENGINEERING AND CONSTRUCTION CONFERENCE 2018

The Malaysian Construction Research Journal is indexed in
Scopus Elsevier

eISSN No.: 2590 – 4140

Construction Research Institute of Malaysia (CREAM)
Level 29, Sunway Putra Tower,
No. 100, Jalan Putra,
50350 Kuala Lumpur
MALAYSIA

Contents

Introduction

Welcome to the Special Issue of Malaysian Construction Research Journal (MCRJ) in conjunction with the 10th Asia Pacific Structural Engineering and Construction Conference (APSEC) 2018.

This Special Issue of MCRJ for the APSEC 2018 consists of 20 selected papers by conference committees and expert reviewers. The selected theme of APSEC 2018, which is 'Sustaining the World with Better Structures and Construction Practices' is indeed consistent with the national agendas in gearing up the sustainability development towards economy, social and environment for Malaysia. Besides, sustainable in construction, material and structural building are important keys to reduce direct impact on the environment.

Hence, it is believe that this special issue will help and contribute to promote sustainable structures and construction practices in Malaysia. We are well concerned of the importance in incorporating the sustainable elements in the construction practices and keep on the exploration in this direction especially in research and development. This Special Issue volume is one of initiatives that shows we are ready to be the leader in this area. Therefore, we hope that this special issue can promote new knowledge and technology towards a sustainable future.

Editorial Advisory Board

Secretariat Special Issue

CLEAN STRENGTH, LEACHING AND MICROSTRUCTURE OF POLYMER MODIFIED CONCRETE INCORPORATING VINYL ACETATE EFFLUENTS

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Abstract
The increasing waste generation from paint industries accounts for the occupation of useful land spaces for disposal purposes. Waste products associated with these industries need attention during handling and treatment due to possible harmful effects on human health and the environment. This problem can be mitigated by incorporating it into concrete production. This study aims at investigating the effects of polymer vinyl acetate effluents on normal strength concrete. The incorporation of the effluents by weight of cement were 0%, 2.5%, 5%, 10%, 15% and 20%, and tested at 28, 56 and 84 days. The tests performed were compressive strength, leaching test and microstructure characterization of the specimen using FESEM and XRD. The results indicate that incorporation of polymer vinyl acetate waste in the range of 2.5% - 15% gave compressive strength of concrete comparable to that of the control specimen. The entire specimen in leaching test met the standard requirement for effluents. The FESEM of polymer modified concrete incorporating 5% effluents showed a well-dispersed morphology of the polymer. This concludes that the incorporation of vinyl acetate effluents up to 5% in normal strength concrete is beneficial to strength development and can consequently minimize pollution caused by these wastes.

Keywords: *Compressive strength; Concrete; Leaching; Vinyl acetate effluents; Polymer*

INTRODUCTION

Paint sludge is a hazardous waste that poses a serious risk for both human health and the environment. It is typically a final by-product resulting mainly from cleaning the paint of manufacturing facilities which accounts for about 80 % of the industry wastes (Lorton, 1988; Salihoglu and Salihoglu, 2016). The by-products contain several components of wastes such as solvent emulsion, pigment dust, rinsed water, paint sludge, and many more. Moreover, paint sludge is a complicated combination whereas polymeric compounds form approximately 50% - 90% of sludge weight which may be unbaked (Dabiri, 2006; Feng *et al.*, 2018). The production of paints, thus contributes significantly to the amount of waste generated annually. This problem becomes worse with improper management of solid wastes that leads to serious environmental pollution and the disruption of the ecosystem, as well as short or long-term impact on human health.

In Malaysia, paint wastes have been grouped under category of scheduled hazardous waste which is toxic to the populace and impacts negatively on the environment. Wastes generated from paint industries have increased tremendously due to rapid development and urbanization resulting from increase in economic activities. The volume of waste generation is connected to paint consumption estimated to have increased from 140,000 tonnes in 2009 to 166,000 tonnes in 2014 (Reg, 2010). This consumption increases the volume of wastes generated by paint industries and in turn increases land space for recovery and disposal purposes. Due to many negative impacts to the environment, water-based paint is commonly used to replace the solvent paint. Water-based paint commonly uses polymer vinyl acetate as the main ingredient in the production of emulsion paint for interior application. Polyvinyl acetate emulsions are milky white liquids containing 30-55% polymer solids, water, small amounts of emulsifiers, protective colloids and other additives (Erbil., 2000). Compared to other polymers, paints containing vinyl acetate are more durable, flexible, adhere strongly, dry quickly, colourless, as well as low cost (Randall, 1992; Miller, 2005). In general, paint effluents are alkaline, having high BOD, COD, and contain some heavy metals, suspended solids and coloured materials (Dey *et al.*, 2004). However, the increase in production of this type of paint is responsible for the increase in wastes in the form of effluents for disposal and this enhances the necessity for utilisation of this waste material for environmental preservation. Concrete is the largest man-made material with global productions of 3.8 billion annually (Abukersh and Fairfield, 2011). Ease of application, low cost and strong compressive strength have become the main reasons for universal acceptance (Muthukumar and Mohan, 2004).

However, some properties of concrete manifest its shortcomings specifically concerning low chemical resistance, delayed hardening, low tensile strength and higher drying shrinkage. These shortcomings of concrete can be solved by introducing polymer as modifiers. Such a polymeric compound is polymer latex, redispersible polymer powder, water-soluble polymer or liquid polymer (Ohama, 1995). The synergic action between polymers and concrete gives better performance for durable and sustainable construction materials (Gemert, 2013). There is a growing concern to recycle waste materials from paint production by using it to modify concrete mixes. Several works have been done in the utilization of paint waste in concrete as addition or replacement by weight of cement to improve the strength and durability properties of concrete (Almesfer *et al.*, 2012; M. Ismail *et al.*, 2011; Ismail and Al-Hashmi, 2011; Nehdi and Adawi, 2008; Nehdi and Sumner, 2003). However, there is scanty information on researches utilising vinyl acetate effluents in liquid form as an addition in normal strength concrete. This research aims at investigating the effects of incorporation of vinyl acetate effluents on strength, microstructure and leaching of the concrete.

MATERIALS AND METHODS

Materials

Ordinary Portland Cement (OPC) complying with BS EN 197-1: 2000 specification was used. Table 1 presents the chemical compositions and physical properties of the cement. Vinyl acetate effluents used as an admixture in concrete were waste generated from the production of polymer dispersion factory in southern Malaysia. The chemical properties of vinyl acetate effluents are shown in Table 2.

Table 1. Composition of cement

Constituents	Percentages (%)	Constituents	Percentages (%)
SiO_2	20.1	CaO	65
AlO_3	4.9	SO_3	2.3
Fe_2O_3	2.4	MgO	3.1
Loss on Ignition	2	Lime Saturated Factor	0.85

Table 2. The composition of waste latex paint (all values in mg/l except for pH)

Parameter	Units	Parameter	Units	Parameter	Units
pH	7.12	Cl^{-1}	56.23	Mn	0.91
BOD	13363.00	NO_3^{2-}	27.53	Ni	0.08
COD	77800.00	Zn^{2+}	1.04	Hg	3.50
TSS	8200.00	Fe^{2+}	1.70	Pb^{2+}	0.13
TDS	5460.00	Ca^{2+}	72.75	P_2O_5	222.00
DO	2.72	Mg^{2+}	9.72	SO_4^{2-}	4514.00
Cr^{3+}	0.14	Na	1199.00	Cu^{2+}	2.69

Mixture Proportion of The Samples

Table 3 shows the mix design used in this study. Concrete sample containing vinyl acetate effluents were cured in accordance to JIS A1171: 2000, and the control following BS 12390-2: 2009.

Table 3. Mix proportion

Specimens	Vinyl acetate effluents (kg/m^3)	Cement (kg/m^3)	Fine aggregate (kg/m^3)	Coarse aggregate (kg/m^3)	Water (kg/m^3)
WLP 0%	-	380	824	1009	209
WLP 2.5%	9.5	380	824	1009	204
WLP 5%	19	380	824	1009	198
WLP 10%	38	380	824	1009	187
WLP 15%	57	380	824	1009	176
WLP 20%	76	380	824	1009	165

Compressive strength

The compressive strength test was conducted in accordance with BS EN 12390-3:2000. Concrete specimens were prepared by addition of vinyl acetate effluents by weight of cement, as well as control specimen in 100 mm size cubes. Average values of three samples were taken.

FESEM

Field emission scanning microscopy (FESEM) was used to produce morphological photographs, in order to study the microstructural features of polymer modified concrete vinyl acetate waste and control specimen using GEMINI FESEM instrument. The analyzer was fitted to energy dispersive X-ray detector for elemental analysis (EDX). In order to develop a good morphological photograph, the specimens were spotted with platinum gold in an Auto Fine coater instrument. The analyzer utilizes low magnetic field outside the objective lens enabling investigation of magnetic materials and devices. It has magnification in the range of 12-900,000X and a working distance in the range of 1-50 mm, depending on the working condition.

X-Ray Diffraction (XRD)

The hydration of the specimens was analyzed using x-ray diffraction technique. In this study, a Siemens Diffractometer D5000 with X-ray source of Cu Kα radiation was used. The scan step was 0.02° using a scanning rate of 0.5°/min and in the range 2-theta-scale from 5°C to 80°C. The scale on the x-axis (diffraction angle) of usual XRD pattern gives the crystal lattice spacing, and y-axis scale (peak height) shows the intensity of the diffraction ray.

Leaching Test

Leaching test was carried out according to the Montgomery method (Montgomery *et al*, 1988). The mix with 2.5%, 5% and 10% of vinyl acetate effluents were prepared in cement paste. Samples of cube size 25 mm x 25 mm x 25 mm were cast and cured in air at room temperature for 28 days before immersed in 100 ml distilled water in the sealed high-density polyethylene bottle. The water leaching samples were tested at 1, 3, 5, 7, 15 and 31 days, and the parameters studied were copper - Cu (II), lead - Pb (II) and Zinc - Zn (II).

RESULTS AND DISCUSSION

Compressive Strength

The mix proportion of concrete is designed to achieve grade 25 concrete with a target mean strength of 33 MPa. However, the control specimen achieves a mean strength of 35 MPa at 28 days. Compressive strength shows remarkably higher value when 2.5% of vinyl acetate effluents is added into the mix. However, the incorporation of 5% - 15% of vinyl acetate effluents in concrete still achieves a substantial compressive strength at 28 days. The one-way Analysis of Variance (AoV) indicates the population means of control mix and 2.5% vinyl acetate effluents are significantly different. However, the population mean of control mix is not significantly different from the mix with 5% vinyl acetate effluents specimen. The implication is that the incorporation of 5 % vinyl acetate effluents can be said to yield compressive strength which is not statistically different from the control mix. While 2.5% vinyl acetate effluents is observed to improve the compressive strength, addition of up to 5 % may provide strength not significantly different from the control mix. The objective of adding latex is not mainly enhancing the compressive strength, although some increases in compressive may be achieved with addition of latex as a result of reduction in water/cement ratio by the total solid content of the waste (Ramakrishnan, 1992). Figure 1 illustrates that the compressive strength of polymer modified concrete increases with prolonged curing period. As the water is withdrawn by hydration process or evaporates, the closed packed polymer particles coalescent into continuous film to form a co-matrix intermingled with the hydrated cement paste and binding aggregates (Beeldens *et al*, 2005; Kardon, 1997; Ramakrishnan, 1992). Similar results are also observed by other researcher (Kim *et al*, 1999), where the addition of small amounts of poly (vinyl alcohol) up to 2% by weight of cement causes significant change in the properties of the concrete. Higher concentration of waste latex paints consisting of vinyl acetate effluents in concrete leads to gradual decrease in compressive strength. This trend of results is comparable to other findings (Almesfer *et al.*, 2012; Ohama, 1995; Ribeiro *et al.*, 2008). The observed decrease in compressive strength with increase in polymer effluent could be associated with combination of phenomena which may include delay in hydration of cement as well as increased air content leading to reduction in density in gel forming the reacted cement skeleton (Ribeiro *et al.*, 2008).

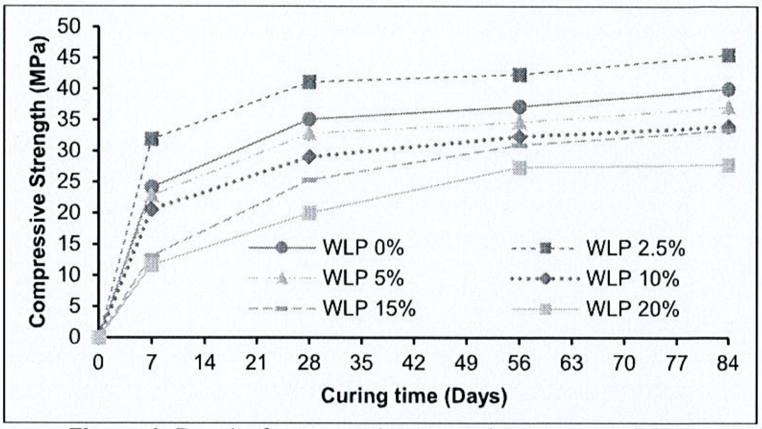

Figure 1. Result of compressive strength at respected days

Morphology

Incorporating polymer vinyl acetate effluents with cement as polymer admixture interacts with the microstructure as evident in Field Emission Scanning Electron Microscopy (FESEM) micrographs at 28 days as shown in Figure 2. The coalescence polymer particles are seen to reside on the surface of cement gel, as well as occupy some spaces in the voids of the cement gel leading to the formation of a polymeric film at the interface with other constituents of the microstructure. The mix with 2.5 % vinyl acetate effluents is observed to reveal minimal cluster of the polymer particles which tends to fill the voids contained in the microstructure and the thin polymeric film may be responsible for its improved strength performance. However, this cluster of polymer particles increases with increase in percentage of vinyl acetate effluents and tends to create more spaces within the gel particles. The diminishing compressive strength as the vinyl acetate effluents addition increased beyond 5 % is attributable to the formation of the thick film of vinyl acetate effluent particles that weaken the interfacial transition zone. The results found are similar to other findings (Mansur *et al.*, 2007; Silva *et al.*, 2001; Silva *et al.*, 2002; Silva and Monteiro, 2005). EDX results show that there are possible chemical interactions between polymer and hydration products of Portland. In Figure 2, the weight percentages of calcium carbonate show decrease with increase of polymer cement ratio content. Some polymers containing vinyl acetate group can suffer hydrolysis when dispersed in alkaline medium. The product of this hydrolysis is the acetate anion $(CH_3COO)^-$ which reacts to Ca^{++} ion from C_2S and C_3S hydration, and forms an organic salt (Calcium acetate). The formation of calcium acetate $Ca(CH_3COO)_2$ increases the loss of weight of the carbonate phases (Gomes and Ferreira, 2005).

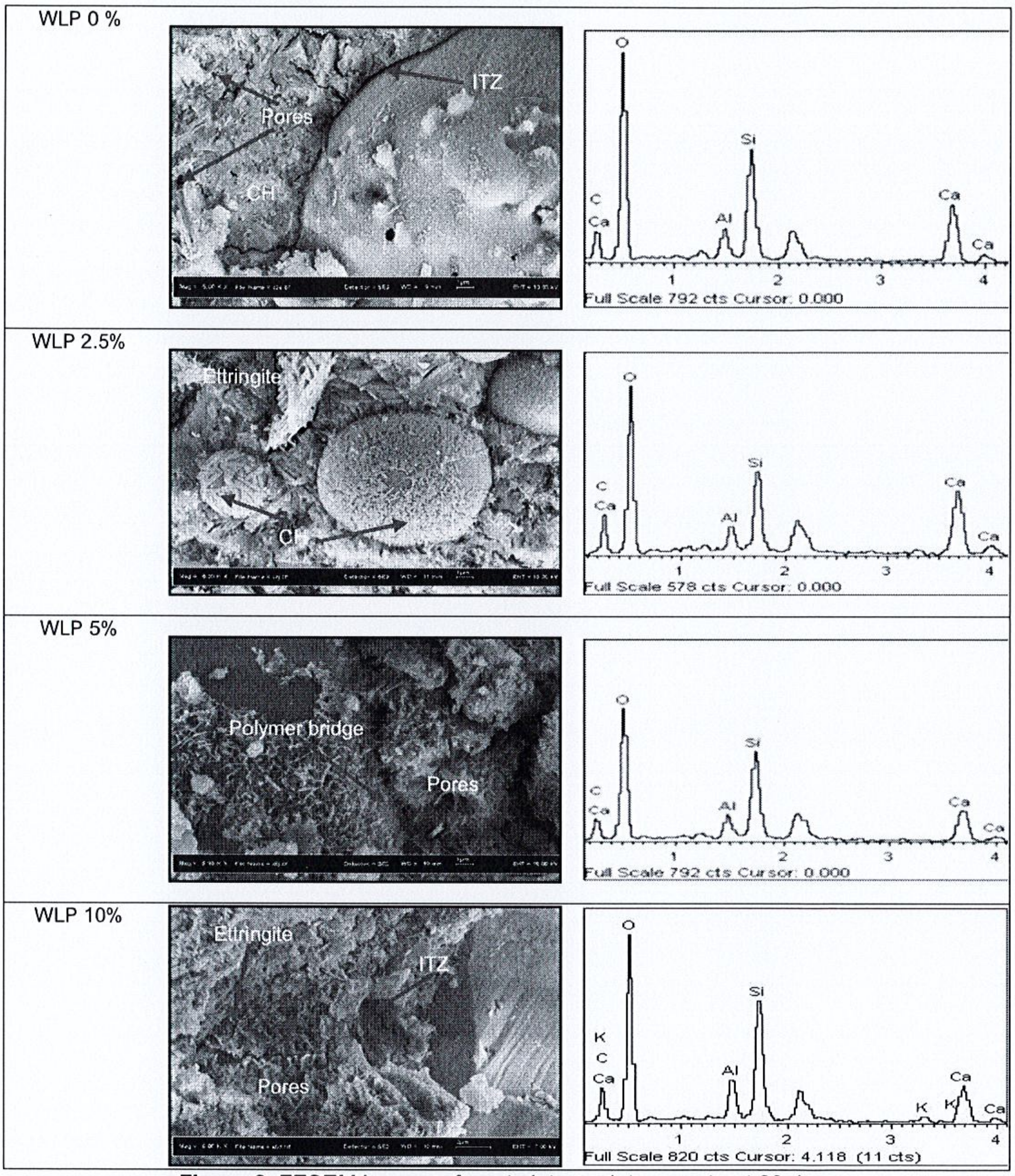

Figure 2. FESEM images of waste latex paint concrete at 28 days

X-ray diffraction (XRD) Analysis of Polymer Effluents

Figure 3 shows the typical XRD curves obtained from vinyl acetate effluents sample. The XRD curve presents the characteristic pattern of amorphous materials with some crystalline peaks associated with an inorganic material, which is calcium carbonate. This inorganic part, known as anti-blocking agent, is added to the formulation to prevent adhesion between polymer particles during manufacturing, transporting and storage.

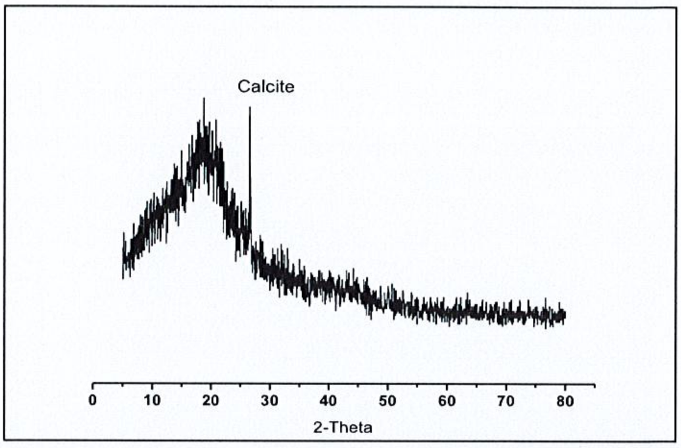

Figure 3. X-ray diffraction (XRD) results of the polyvinyl acetate effluents

X-ray diffraction (XRD) Analysis of Waste Latex Paint Concrete

In order to investigate the influence of the polymer on the cement hydration in the modified paste, XRD patterns of the pastes with and without polymer vinyl acetate effluents are obtained and displayed in Figure 4. Upon hydration of the Portland cement main phases, C_3S (tricalcium silicate-alite) and C_2S (dicalcium silicate-belite) produce mainly portlandite $Ca(OH)_2$ and amorphous calcium – silicate – hydrate (CSH). The degree of hydration could be estimated by comparing the peaks corresponding to Ca(OH) and C_3S. With more hydration, the relative surface area of the peak associated with portlandite will increase and the C_3S will decrease (Wang *et al.*, 2005). It is seen that $Ca(OH)_2$ peak for specimen incorporating polymer vinyl acetate effluents 2.5%-10% are similar to the control on the same spectrum. However, the incorporation of vinyl acetate effluents sample shows smaller peak of $Ca(OH)_2$ with 10% modified sample. These indicate lesser hydration has occurred in this sample. This is possibly due to the surfactant layer at the cement granules surface that prohibits the hydration of water.

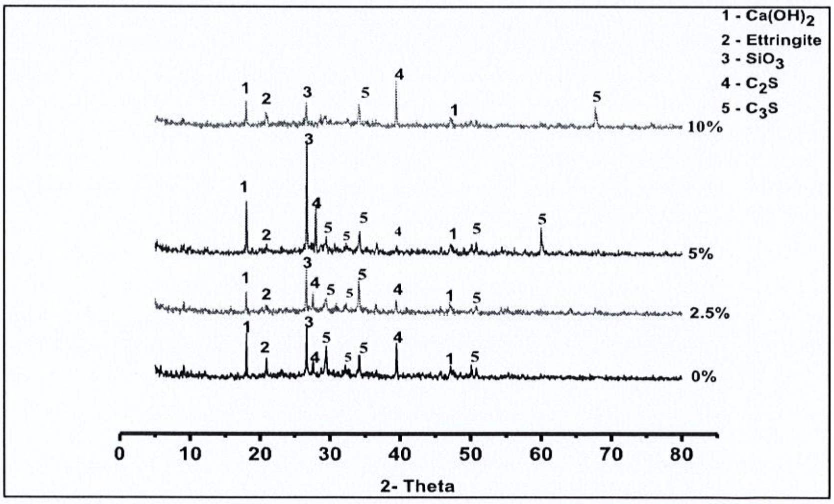

Figure 4. X-ray diffraction (XRD) results of waste latex paint concrete

Heavy Metal Analysis

Table 4 shows the results of leaching test from the incorporation of vinyl acetate effluents in cement paste. Heavy metal compounds such as ions of copper, zinc and lead from vinyl acetate effluents were observed to be reduced after a one-month period. According to the World Health Organization (WHO) data, the maximum contaminant levels for Cu (II), Zn (II) and Fb (II) are 0.5, 3.0 and 0.01 mg/l, respectively, while the Department of Environment Malaysia (DOE) reveals the tolerable limit for the substances are 1.0, 1.0 and 0.5 mg/l, respectively. All the metals are within the prescribed limits. These results were found similar to previous work by Avci *et al* (2017) using paint sludge with cement and lime at 3 days. On the other hand, it was also shown that high content of vinyl acetate effluents, for instance 10% in cement paste reduced the concentration of heavy metal compounds, which could probably be due to the waste ion immobilization. The properties of hardened cement matrix have been used for many years as an effective way and a safe material to solidify hazardous wastes (Kuterasińska-Warwas and Król, 2017).

Organic particles are among the factors that affect cement hydration by adsorption as chemical precipitate forms surface compound on any several cement component surface, forms inclusions, or is chemically incorporated into the cement structures or has simultaneous occurrence of several of these situations (Cocke and Mollah, 1993; Spence and Shi, 2004). Stabilization/solidification using cement based or cementitious material is common worldwide for disposal of hazardous, mixed waste and radioactive material (Gougar *et al*, 1996). The production of solidified waste reduces the surface area available for leaching and the high alkaline environment produced by cementitious binders which ensures that heavy metals are effectively immobilized (Asavapisit *et al*, 1997).

Table 4. Results of the leaching test

Samples	**Day**						**Tolerable Limits**	
							DOE	**WHO**
CP 2.5%	Initial	1	3	7	15	31	Mg/l	Mg/l
Cu (II)	1.344162	0.001226	0.003038	0.003455	0.003512	0.003005	1	0.5
Zn (II)	1.969869	0.002017	0.003054	0.002725	0.002842	0.002594	1	3.0
Pb (II)	0.401441	0.000057	0.000034	0.000073	0.000049	0.000031	0.5	0.01
CP 5.0%	Initial	1	3	7	15	31	Mg/l	Mg/l
Cu	0.062261	0.000383	0.000339	0.000531	0.000474	0.000469	1	0.5
Zn	0.121488	0.000296	0.000323	0.000288	0.000318	0.004699	1	3.0
Pb	9.139098	0.014657	0.034297	0.008525	0.003075	0.001950	0.5	0.01
CP 10.0%	Initial	1	3	7	15	31	Mg/l	Mg/l
Cu	0.059383	0.000464	0.000258	0.000347	0.000369	0.000468	1	0.5
Zn	0.119482	0.000288	0.000311	0.000290	0.000363	0.000577	1	3.0
Pb	7.795460	0.021127	0.024180	0.024629	0.010561	0.040921	0.5	0.01

(Source: (MDC, 1997; WHO, 2008)

CONCLUSIONS

While the addition of 2.5 % vinyl acetate effluent increases the compressive strength above the control, the addition of up to 5 % vinyl acetate effluent achieves strength comparable to the control mix. However, incorporation of waste latex paint (vinyl acetate effluent) above 5% tends to reduce the compressive strength of concrete. The utilisation of 5 % of waste latex paint in concrete would be beneficial to the objective of waste minimisation.

The incorporation of vinyl acetate effluents interacts with the concrete microstructure. Polymer film formation does exist in the interfacial transition zone layer that provides network structure between cement hydration and aggregate bonding which could prevent microcrack propagation. While the thin polymer film observed in the 2.5 % effluent mix is responsible for strength increase, an excessive thickening of the polymer film in the specimen with higher effluent content weakens the interfacial transition zone, hence leading to a reduction in strength.

The XRD patterns of the vinyl acetate effluent sample confirms its amorphous nature, and its ability to interact in the hydration process. The interaction is confirmed in the concrete specimens with the $Ca(OH)_2$ peaks that reduce with increasing effluents as a result of reduced hydration reaction. The patterns of the control sample and varying waste latex paint mixes are not significantly different in terms of the types of hydration products (ettringite, portlandite, alite, belite and silica) identified. It is observed that the XRD patterns show little difference in the quantity of hydration products between the mixes.

Leaching tests show that the incorporation of waste latex paints in cement paste up to 10% meets the tolerable limit provided by the relevant standard.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the cooperation and financial supports from RMC, GUP grant No 03H35, as well as technical support from the School of Civil Engineering, Faculty of Engineering, Universiti Teknologi Malaysia.

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