Evaluation on physical and chemical properties of treated industrial wastewater sludge containing latex and heavy metals using ordinary Portland cement via stabilization / solidification technique

A L Abdul Rani¹, N A Rashid², M A H Abdullah² and M F Omar²

¹ Faculty of Engineering Technology, Department of Chemical Engineering Technology, Universiti Malaysia Perlis, Kampus UniCITI Alam Sungai Chuchuh, Padang Besar, 02100 Perlis, Malaysia.
² Faculty of Engineering Technology, Department of Civil Engineering Technology, Universiti Malaysia Perlis, Kampus UniCITI Alam Sungai Chuchuh, Padang Besar, 02100 Perlis, Malaysia.

E-mail: latifrani@unimap.edu.my

Abstract. Industrial wastewater sludge containing latex collected from rubber industry wastewater treatment plant has classified the waste as scheduled waste due to high concentration of selected heavy metals within it. Laboratory scale of special treatment via solidification/stabilization (S/S) technique has been performed to the waste by using ordinary Portland cement. The objective of this research is to evaluate the chemical properties of the raw waste using X-Ray Fluorescence (XRF) and physical properties related to unconfined compressive strength (UCS) performance of stabilised/solidified (s/s) cube specimens. Other factors took into consideration include the curing condition using air and water immersion curing technique, waste addition percentage, specimen age and density. The fresh mix prepared were cast in plastic moulds internal dimension of 50 mm³ producing cubical shape specimens and cured approximately 24 to 48 hours. The prepared specimen batches are A1 (90% OPC + 10% waste), A2 (70% OPC + 30% waste), A3 (50% OPC + 50% waste). Chemical analyses using XRF indicates that raw sludge contains approximately several heavy metals such as Aluminium (30%), Phosphorus, P (17.5%) and Zinc, Zn (11.7%). UCS testing were conducted on 7 and 28 days of specimen age. Positive average compressive strength results of 7 day air cured specimens reach 5.25 MPa, 5.28 MPa, and 2.16 MPa for A1, A2 and A3. Next, 28 days air cured specimens results are 9.59 MPa, 8.01 MPa, and 1.46 MPa for A1, A2, and A3 respectively. As for water immersion, the compressive strengths are 8.19 MPa, 4.93 MPa, and 1.90 MPa for 7 days, and 7.75 MPa, 10.10 MPa, and 2.11 MPa for 28 days at respective A1, A2 and A3 sequence. Based on the UCS performance, the tested specimens surpassed the minimum requirement for secured landfill disposal which is at 1 MPa.

1. Introduction
Industrial wastewater sludge containing latex and heavy metals classified as schedule waste under code of SW 321 have generate approximately 240 tonnes each year [1-2]. Moreover, the large waste volume also influence other problems associated with handling and storage of the waste prior to disposal [3].
Serious toxicity problem to human and ecosystem (includes animals and plants) was easily possible to occur as if the waste were washed off by rainfall and water runoff which act as transport media for the migration of toxic contaminants located from waste hold area into the drainage system and often directly connected to the water bodies (i.e. river and/or groundwater) [4]. An approach of treatment in laboratory scale was conducted via stabilisation and solidification (S/S) technique to treat the waste, as the ordinary Portland cement was found to be capable of treating and reducing the waste hazard toxicity potential [5].

Fundamentally, stabilisation was a technique aimed to chemically reduces the waste hazard by changing the properties of the contaminants into less soluble, mobile and toxic [6]. Meanwhile, solidification was a technique which incorporates mainly physical process that encapsulates the waste into solidified form or monolith. Solidification process truly does not necessarily involve a chemical interaction between the contaminants and solidifying additives [7]. The combination of both stabilisation and solidification were necessary to effectively immobilise the contaminants into an inert form with the assist of ordinary Portland cement as primary binder. Curing condition were crucial role in Stabilisation/Solidification (S/S) and mostly related to influence the unconfined compressive strength (UCS) performance of stabilised/solidified specimens. The initial (i.e. UCS 7 days) and final strength (i.e. UCS 28 days) basically reflects the key of evaluation in order to determine and compare the effectiveness of the S/S treatment. Strict minimum strength of 1 MPa should be achieved by stabilised/solidified specimens in order to be worthy disposed in a sanitary or secured landfill [7].

2. Materials and methods

2.1. Raw waste X-Ray Fluorescence analysis

The collected raw waste sludge was oven dried at 105°C for approximately 48 hours until it was fully dried with constant weight [8]. Prior to weighing process, the hot dried sludge were placed in a desiccators filled with granule silica gel to cool the raw sludge sample without moisture re-absorption [8]. Next, the dried sludge was ground using pestle and mortar and sieved at 63 microns aperture size. Approximately 3 g of the collected dried sludge were placed in an X-Ray Fluorescence (XRF) sample container prior to analysis. It took almost 30 minutes for the XRF instrument to analyse the waste. Finally, the composition data in form of percentage was obtained at the end of the analyses.

2.2. Preparation of fresh mix

Table 1 shows the factorial design for control batches, later abbreviated as “CB” composed as OPC and water only at different water to cement (w/c) ratio of 0.33 for CB01 and 0.50 for CB02. The fresh mixes were prepared according to factorial design method. Thus, each ingredient (i.e. unit of kilograms) was carefully weighted in order to achieve desired ratio of ordinary Portland cement (OPC) and waste in each specimen batch (refer to Table 2). All procedure conducted were referred to BS EN 196-1:2005 [9].

| Batch identity | Composition | OPC (kg) | Waste (kg) | Water (kg) | Water-cement (w/c) ratio |
|----------------|-------------|----------|------------|------------|------------------------|
| CB1            | OPC + water | 4.545    | 0.0        | 1.500      | 0.33                   |
| CB2            | OPC + water | 4.545    | 0.0        | 2.273      | 0.50                   |
Table 2. Specimen batches factorial designs

| Batch identity | Composition              | OPC (kg) | Waste (kg) | Water (kg) | Water-cement (w/c) ratio |
|----------------|--------------------------|----------|------------|------------|-------------------------|
| A1             | 90% OPC + 10% waste      | 4.770    | 0.530      | 1.860      | 0.4                     |
| A2             | 70% OPC + 30% waste      | 3.710    | 1.590      | 1.692      | 0.5                     |
| A3             | 50% OPC + 50% waste      | 2.650    | 2.650      | 1.782      | 0.6                     |

All weighted ingredients were carefully transferred into the mixer as in dry powdered form; the ingredients were slowly mixed well prior to water addition. Calculated amount of water were added into the mixture to achieve desired water-to-cement (w/c) ratio. Fundamentally, too much water generates adverse effect to the compressive strength of the stabilised/solidified specimen as ideal w/c ratio should be around 0.3 to 0.6 [10]. In consistent with the mixing process, water is added until certain consistency was achieved. An excessive of water was not be tolerated as it able to produced more porous specimen as the setting or hardening completed [7].

The fresh mix was transferred into mould in order to cast and produce 50 mm³ cube stabilised/solidified specimen. The size of 50 mm³ was selected due to minimise the waste generation in testing [7] as these specimens were classified as treated hazardous waste. As the moulds were continuously filled up, the moulds were vibrated at approximately 15s in order to remove any remaining air bubbles trapped in the fresh mix. For each batch prepared, approximately 20 to 25 specimens were able to be produced. The moulds were then placed in dry and dark room in order to allow hardening process of the fresh mix. The setting or hardening process usually took approximately 24 hours to completely harden which eventually depends on the composition of ingredients mixture on the specimens. Demoulding process (i.e. removing the specimens from the moulds) can be performed as soon as the specimens were stable and harden enough [10]. After the demoulding process completed, the specimens were stored in a closed large black plastic bag equipped with some wet tissue to preserve high humidity to aid the hydration reaction [7].

2.3. Unconfined compressive strength test

According to BS EN 196-1:2005, UCS test were performed at specific specimen age of 7 days for determining the initial strength and 28 days for final strength [7]. Prior to testing, triplicate of cube specimens were immersed in water for approximately 24 hours before the testing day at each specific specimen age correspond to respective 7 and 28 days, as these cube specimens represent the immersed cube specimen. Meanwhile, the dry or air cured specimens were taken directly from the storage bag and tested for UCS on the 7 and 28 days.

By means at every UCS testing, there are triplicate of dry and also immersed cube specimens which comprises of total of six (6) cubes to be tested (i.e. triplicate specimens for dry and immersed specimens respectively). The purpose of having triplicates is that an average value will be obtained represents the specimen strength at specific particular sample age.

The calibration of the concrete compression instrument was performed according to same standard (i.e. BS EN 196-1:2005) used to perform the UCS test [7]. Another routine steps prior to UCS testing, each air cured specimens dimension and weight is recorded for density calculation purposes. This is essential because density and UCS data are relatively correlated.
3. Results and Discussions
The initial and final strength of stabilised/solidified (s/s) specimens correlated with other factors (i.e. waste addition percentage, specimen age, density and also the curing methods) [7]. In order to evaluate the specimen batches prepared, control batches represented by CB1 (w/c ratio: 0.33) and CB2 (w/c ratio: 0.5) were prepared and tested. Control batch represent the baseline reference for comparison purposes in order to identify the effect of organic waste composition with respect to strength, density, water-to-cement (w/c) ratio of the specimens.

3.1. Analysis of raw waste using XRF
X-Ray Fluorescence (XRF) has been utilised to examine the heavy metals composition of the dried raw waste (i.e. industrial wastewater sludge containing latex). Figure 1 below indicates the composition of elementals in the waste.

![Figure 1. Raw waste elemental composition data in percentage using XRF](image)

According to figure 1, elemental composition data indicates that raw rubber sludge contains chromium (Cr) at 0.3%. Other elementals found at high percentage were as follow; Aluminium (30.3%), Phosphorus (17.5%), Zinc (11.7%), and Iron (7.1%). The toxicity problem associated with the waste was highlighted as large volume of waste generated each year can caused extreme harmful condition via direct disposed of the raw waste.

Example, at 240 tonnes of waste produced each year, approximately 72,000 kg of chromium was available within the waste. The same extreme toxic hazard condition was also possible for other elemental such as zinc (Zn) and iron (Fe). The raw waste also produced highly pungent rotten egg odour as it contains approximately 8.4% of sulphur (S) due to the formation of hydrogen sulphide (H2S). According to this finding, it is crucial to treat the waste in order to overcome toxic heavy metals and also odour problem.
3.2. Analyses of initial and final strength on air curing specimens

Air curing is one of the essential methods in hardening process applied in Stabilization/Solidification (S/S) technique due to prevent leaching of contaminants from the specimen [7]. The air cured specimens were sealed in large plastic bag together with some wet tissue to keep the internal bag moist condition. The sealing via large bag also purposely to exclude the intrusion of carbon dioxide into the specimens which could reduced the alkalinity of the internal specimens and leads to solubility of the heavy metals into surrounding available water [7]. The aim is to evaluate the performance of UCS in the presence of industrial rubber sludge at three different compositions (i.e. 10% waste in A1, 30% waste in A2 and 50% waste in A3). The initial strength analysis of air curing specimens in figure 2 illustrates almost linear decreasing of the initial strength from A1 to A3. The collapse trend of initial strength showed is clearly due to the increased of organic waste addition added into OPC. This findings supported by other studies which indicates that incorporation of OPC as an inorganic material with organic waste can be achieved a certain limitation of not more than 30% [7].

The final strength of control and sample batch specimens of air cured specimens illustrated in figure 3 whereby the UCS test was performed at 28 days specimen age. The findings in figure 3 indicate that there are strength increment occurred on the both control batches and also in A2 sample batch. This occurrence was normal towards the control batches because it do not contains any waste or impurities which can affect the hydration process [7], but an increase in strength of A2 specimen batch revealed the compatibility of the OPC matrix to accept the organic waste loading within the cement structure. The continual of strength development progress of A2 batch as can be seen from initial strength in figure 2 to final strength in figure 3 shows the optimum amount of waste which can be treated with OPC via stabilisation/solidification technique.

![Figure 2. Initial strength of air curing specimens](image1)

![Figure 3. Final strength of air curing specimens](image2)

An opposing condition in A1 and A3 specimen batch in figure 3 whereby decreasing in strength as compared to its initial strength (i.e. figure 2) was observed. The minimum waste composition in A1 batch (i.e. 10% waste) was not significant on the strength development. Clearly, the strength of the
specimens was significantly affected in A3 batch at 50% waste composition. Greater amount the organic waste affect the rigidity and compactness of the specimens due to the formation of heterogeneous specimen in A3 batch because both materials (i.e. inorganic and organic component) do not compatibility mixed well.

Analyses of water-to-cement (w/c) ratio between the control and specimen batches in figure 2, findings indicates higher water content contribute to lower strength development at initial strength. Data in figure 2 indicates A3 batch as the highest water-to-cement ratio (w/c ratio: 0.6), followed by A2 (w/c ratio: 0.5) and A1 with lowest w/c ratio of 0.4. The findings also revealed that the addition of organic waste (i.e. rubber sludge) have eventually increased the w/c ratio and leads to production of low strength specimens. The absence of waste in both control batches as shown in both figure 2 and figure 3 generally proved that organic waste does affecting the growth of strength in initial and final strength.

3.3. Analyses of initial and final strength on water immersion specimens

Water immersion curing method has also been applied for 7 and 28 days UCS which can be clearly observed in figure 4 and figure 5 respectively. In this water immersion curing method, triplicate of hardened specimens were immersed in water for 24 hour prior to the UCS test. The reason of having water immersion specimens was to prove that water does enhanced the hydration process within the internal structure of the specimens which in return aiding the strength development and not just a normal curing method [11]. Water is an important component in cement hydration reaction as it assist the growth of calcium-silicate-hydrate (C-S-H) formation at the beginning of initial strength [12].

![Figure 4. Initial strength of water immersion curing specimens](image1)

![Figure 5. Final strength of water immersion curing specimens](image2)

The formation of C-S-H usually occurred consistently as the specimen age increases. This can be observed in figure 5 as the final strength of all specimen batches at 28 days were found to be increased as compared to its initial strength at 7 days in figure 4. Outstandingly, A2 specimens show quite
remarkable average final strength as compared to A1 and A3 batch specimens at the same sample age (i.e. 28 days). The findings in figure 5 show the compatibility between the organic waste and inorganic material of OPC as all specimen batches were able to produce higher strength at 28 days.

However, in normal practiced of S/S treatment, water immersion can lead to leaching of contaminants within the specimen [7]. This is because water was capable to penetrate into the specimen via voids of the micro-capillaries presence in the specimen, which generally been produced during setting of the specimen. Due to this reason, only air curing method was applied in this S/S treatment. Comparison of initial strength between air curing method (i.e. figure 2) and water immersion (i.e. figure 4), indicates that initial strength was low in water immersion specimens. The reduction of initial strength was caused by water intrusion into the micro pores within the specimens leading to excess water within the specimens. At the initial strength stage, hydration reaction still occur in the presence of excess water, more micro-capillaries formation were produced during the process leading to the formation of more porous specimen. As the specimen’s porosity increases, the strength of the specimen was inversely decreased [13-15].

Water immersion curing method been applied also purposely to evaluate the stability and integrity of specimens under water immersion [11]. The stability of specimens under water immersion also examines matrix dissolution or detrimental swelling which can disrupt the physical of the specimen [7]. Observations of the immersed specimens’ condition were performed prior to UCS test. Based on the findings revealed by figure 4 and 5, all specimens are stable in water immersion and able to show significant compressive strength via UCS test from 7 to 28 days.

3.4. Relationship between unconfined compressive strength, density and waste compositions.

The correlation of initial strength and density of air cured specimens are demonstrated in figure 6. Density of the specimens also correlated with the water-to-cement (w/c) ratio and compressive strength. Analyses on figure 6 revealed that the density of control batch 2 (i.e. CB2) does slightly reduced, as the highest initial strength was obtained at the lowest w/c ratio batch (i.e. CB1). As w/c ratio increases, the strength and density decreases [13-14]. The water demand increases in the presence of organic waste (i.e. rubber sludge). Observation on all specimen batches (i.e. A1, A2 and A3 batches) clearly demonstrated that there was an increased of w/c ratio, as the amount of waste addition increases. The increment of w/c ratio was directly related to the additional water, needed to provide sufficient consistency to the fresh mix preparation. Fundamentally, as the organic waste compositions were increased, the strength and density also relatively decreases.

![Figure 6. Correlation of initial strength and density of air curing specimens](image-url)
The amazing outcome of this rubber sludge waste was that, even at 50% waste was added into the OPC, the initial strength of A3 batch specimens (figure 6) were able to surpass the minimum disposal limit required at 1 MPa, whereby an average strength of 2.16 MPa was obtained.

Observation on specimen A2 batch on both initial (i.e. figure 6) and final strength (i.e. figure 7) revealed that, there was an increased in strength development from initial to final strength. Ideally, the sludge at 30% composition in A2 reacts positively with OPC, and was able to produce sufficient strength at its final strength. One of the advantage of rubber sludge structure was its ability to absorb and retain water in its matrix, whereby these water were then been consumed by OPC to enhance hydration reaction resulting an increased in specimen strength. Contrary, the same occurrence was not appeared either in A1 or A3 batches in figure 6. It was due to A1 batch which contains quite low amount of rubber sludge (i.e. 10%) and the overall strength performance was dominantly governed by OPC as the majority component in the A1 specimen. Meanwhile, A3 specimens consist approximately 50% of rubber sludge and it was too much for the OPC matrix to sustain the integrity of the matrix strength. Good strength compatibility can be achieved if the organic was less than the OPC composition. This has been supported by previous studies which highlight the limitation of organic waste that can be added into OPC in Stabilisation/Solidification (S/S) treatment technique [7].

Analyses on figure 7 revealed that both control batches (i.e. CB1 and CB2) shows a positive increment in final strength density as compared to its initial strength density in figure 6. However, the final strength density of specimen batches which contains rubber sludge as in A1, A2 and A3 have revealed to be affected. The changes in the final strength somehow did some small changes in the density of specimen batches which can be clearly seen in figure 7. Strength and density are significantly correlated. Overall final strength performances of all specimen batches were found to be sufficiently above the minimum disposal limit at 1 MPa.

4. Conclusions
As conclusion, industrial rubber sludge which contains high level of heavy metals concentration was compatible and can be treated by the Stabilization/Solidification (S/S) technique. This study have proved that unconfined compressive strength (i.e. initial and final strength) and density were correlated and can be influenced by several factors such as organic waste addition, specimen age and curing conditions. The optimum condition revealed that OPC was able to react positively up to 30% of rubber sludge composition.
Acknowledgement
This research was funded by the Malaysian Government under the Fundamental Research Grant Scheme (FRGS), Grant no.: FRGS/1/2018/TK02/UNIMAP/02/7. The authors wish to acknowledge Ministry of Education, Malaysia for providing the research grant.

References
[1] Aja O C, Al-Kayiem H H, Zewge M G and Joo M S 2016 Chapter 5: Overview of Hazardous Waste Management Status in Malaysia, in Management of Hazardous Wastes (R.A.R. Hosam El-Din M. Saleh, Editor. InTech: Croatia. p. 186)
[2] Shorubber 2012 Annual report on scheduled waste production (SW 321) (Shorubber (M) Sdn Bhd: Kangar)
[3] Chen Q Y, Tyrer M, Hills C D, Yang X M and Carey P 2009 J. Waste Manag. 29 p 390-403
[4] Bozkurt S, Moreno L and Neretnieks I 2000 Sci. Total Environ. 250 p 101-21
[5] Hills C D, Sollars C J and Perry R 1993 Cem. Concr. Res. 23 p 196-212
[6] Guo B, Liu B, Yang J and Zhang S 2017 J. Environ. Manage. 193 p 410-22
[7] Stegemann J A and Zhou Q 2009 J. Hazard. Mater. 161 p 300-306
[8] da Silva Carneiro J, Nogueira R M, Martins M A, de Souza Valladão D M and Pires E M 2018 J. Biosci. 34 p 595-602
[9] Standard B 2005 BS EN 196-1:2005 in Methods of testing cement – Part 1: Determination of strength (British Standard Institution: London)
[10] Standard M 2012 MS EN 12390-2:2012: Testing hardened concrete - Part 2: Making and curing specimens for strength tests (Second revision) (SIRIM Berhad: Malaysia)
[11] Stegemann J A and Côté P L 1996 Sci. Total Environ. 178 p 103-10
[12] Bullard J W, Jennings H M, Livingston R A, Nonat A, Scherer G W, Schweitzer JS, Scrivener K L and Thomas J J 2011 Cem. Concr. Res. 41 p 1208-23
[13] Chen X, Wu S and Zhou J 2013 Constr Build Mater. 40 p 869-874
[14] Lian C, Zhuge Y and Beecham S 2011 Constr Build Mater. 25 p 4294-4298
[15] Matusinović T, Šipušić J and Vrbos N 2003 Cem. Concr. Res. 33 p 1801-1806