Oil palm ash as partial replacement of cement for solidification/stabilization of nickel hydroxide sludge

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Abstract

In this study, solidification/stabilization (S/S) of nickel hydroxide sludge using ordinary Portland cement (OPC) and oil palm ash (OPA) was carried out. The effects of increased substitution of OPA wt% in the S/S mix designs on the treated samples' physical and chemical characteristics were investigated. The physical characteristics studied were unconfined compressive strength (UCS) and changes in crystalline phases while chemical characteristics studied were leachability of nickel and leachate pH. Results indicated the optimum mix design for S/S of nickel hydroxide sludge using both OPC and OPA at $B/S_d = 1$ in terms of cost-effectiveness and treatment efficiency was 15 wt% OPA, 35 wt% OPC and 50 wt% sludge. The sufficient UCS and low leached nickel concentrations shown for this mix design indicate the viability of using OPA as substitute of OPC as it can significantly reduce cost normally incurred by usage of high amounts of OPC.
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1. Introduction

Solidification/stabilization (S/S) is an established technique used for treating industrial waste sludge prior to proper landfill disposal. "Solidification" refers to improving the physical integrity of waste sludge in order to facilitate handling while "stabilization" refers to reduce the mobility of contaminants via various mechanisms such as precipitation, chemisorption, encapsulation and ion exchange. S/S treatment generally consists of mixing of chemical binders with sludge with addition of water prior to dry curing of the cementitious mixture for several days. Established S/S binders include cement and lime, which contain high amount of calcium oxide, CaO, an ingredient essential to increase the pH of the mixture to facilitate precipitation. Research on S/S of industrial sludge are plentiful [1–4] and its high treatment effectiveness, especially for treating metal-based sludge, is well established.

The cementation mechanism of the waste/binder reaction which may be directly related to S/S of metal sludge is explained in the following. Cementation of the waste/binder mixture begins when water is added, either directly or as part of the waste. Once the cement powder contacts water, tricalcium aluminate immediately hydrates, causing the rapid setting which produces a rigid structure. In an idealized setting, the water hydrates the calcium silicates and aluminates in the cement to form calcium silicate hydrate (C-S-H). Thin, densely packed fibrils of silicate grow out from the cement grains and interlace to harden the mixture entrapping inert materials and unreacted grain. Hydration of tricalcium and dicalcium silicates results in the formation of C-S-H (also known as tobermorite and crystalline calcium hydroxide. C-S-H accounts for strength development after the initial setting of the mixture [5,6].

High costs mostly attributed to costs of cement and lime usually indicate that industrial waste sludge generators have to incur significant costs for S/S treatment. As such, most of them refuse to do so and opt to illegally store their sludge within their premises or dispose their sludge at nearby areas. This problem is especially rampant in developing countries. Therefore, S/S research in recent years have been focused on usage of recyclable waste materials to substitute cement and lime. In order to enable a more cost-effective S/S treatment design, S/S specialists often substitute portions of S/S binders

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with industrial wastes such as incinerator bottom ash [1] and coal fly ash [3]. Concrete technologists are beginning to find applications in OPA as partial substitute of cement for producing high-strength concrete [7,8] but there is no identified utilization of oil palm ash (OPA), a waste by-product of the palm oil processing industry, in S/S of metal hydroxide sludge. Therefore, usage of OPA for S/S of metal hydroxide sludge would represent a two-pronged approach in solving its disposal problem as well as providing a cost-effective cement replacement material.

The objective of this study was to utilize the OPA as a partial binder replacement for OPC to solidify/stabilize metal hydroxide sludge for safe disposal into a secure landfill and to determine the optimum S/S design. The effectiveness of the treatment was assessed by analyses of physical and chemical characteristics.

2. Materials and methods

2.1. Nickel hydroxide sludge and binder systems

Nickel hydroxide sludge was collected from a wastewater treatment system in a chemical manufacturing plant within Shah Alam Industrial Park, Selangor, Malaysia. The sludge was green in color, indicative of predominant presence of nickel hydroxide. The sludge was oven-dried at 105 °C overnight to remove moisture and repress microbial activity. Dried sludge was crushed to fine powders prior to storage in plastic containers. Treatment of the sludge was conducted using Type 1 ordinary Portland cement (OPC) as the main binder and supplemented by OPA. The OPC was obtained from Cement Industry of Malaysia (CIMA) while OPA was obtained from an oil palm mill at Segamat in the State of Johor, Malaysia. The precursor of the OPA was empty fruit bunches which was combusted at 800 °C to generate heat for a boiler in the mill.

2.2. Production of solidified/stabilized samples

The binder (OPC with OPA) was added to the sludge at binder-to-dry sludge (B/S_d) (w/w %) ratio of 1. Table 1 summarizes the mix design of the study. A control mixture consisting of 100% OPC was also included as part of the mix design. Mixing of these materials was conducted manually in a high-

Table 1
Mix design used in this study

Sample	Binder		Sludge	Water-to-mixture ratio
	Oil palm ash (wt %)	Ordinary Portland cement (wt%)		
A (Control)	0	100	0	0.45
B	0	50	50	0.45
C	5	45	50	0.45
D	10	40	50	0.45
E	15	35	50	0.45
F	20	30	50	0.50
G	30	20	50	0.50

density polyethylene (HDPE) basin. The mixture was briefly homogenized prior to addition of deionized water (<1 μS/cm) at water-to-mixture (W/M) ratio of either 0.45 or 0.50 after which mixing was carried out for 10 min. These ratios were selected to provide ample hydration effect for the mixtures to achieve minimum observable flowability and homogeneity. Higher W/M ratios were not used as higher water content may decrease hardening rate and ultimately reduce the treated samples' strength. The W/M for both samples F and G was stipulated at 0.50 instead of 0.45 as higher amount of OPA in the mixture required more water to achieve similar observable hydration effect. The mixture was cast into 50 mm × 50 mm × 50 mm steel cube molds (for unconfined compressive strength, UCS determinations) and 3 HDPE containers (approximately 100 cm³ each for leachability and characterization determinations) in three layers, with each layer compacted by manually shaking the molds and containers to yield good packing of the mixture. After the initial mixing, 1 day was allowed for setting before the solidified samples were demolded. A further 27 days were allowed for air drying of the solidified samples in a cabinet at a controlled condition (temperature = 25 ± 2 °C, humidity >70%).

2.3. Testing protocols

The 50 mm × 50 mm × 50 mm solidified cubic samples were subjected to the UCS test in accordance with BS 1881: Part 116: 1983 [9] after 7 and 28 days of air drying. Leaching tests were carried out for crushed samples after 28 days of air drying in accordance with the standard procedures prescribed by United States Environmental Protection Agency, toxicity characteristic leaching procedure (TCLP) Method 1311 [10]. The solution used in the method was acetic acid with initial pH 2.88. This method was used to simulate typical leaching conditions on disintegrated landfill wastes due to prolonged aging effects. In this study, one aspect of this method was altered in which the rotary agitation speed of the leaching process was 120 rpm instead of the stipulated 30 rpm. This was done to simulate a more adverse leaching condition which can be brought about by rapid disintegration of wastes and frequent rainfall (an aspect typical of Malaysian weather). Apart from the modified step, all other aspects of the method remained the same. Subsequent to completion of the 18-h extraction, the leachate was filtered and pH was measured at the end of the extraction period by using Seven Multi Mettler-Toledo pH meter. Metal concentrations of the leachate were determined via Perkin-Elmer 3110 Atomic Absorption Spectrometer (AAS).

The surface morphologies and elemental composition of the OPA was examined via PHILLIPS XL 30 electron microscope. Characteristics of reaction products attributed to the S/S process after 7 and 28 days of air-drying were analyzed via X-ray diffraction (XRD). The samples were manually ground to fine powders in a pestle and mortar prior to analysis. XRD analysis to determine the changes in crystalline phases of the samples was conducted using the Rigaku D/Max 2000 diffractometer operated at 40 kV and 30 mA for the reflection angle (2θ) in the range 3–70°.
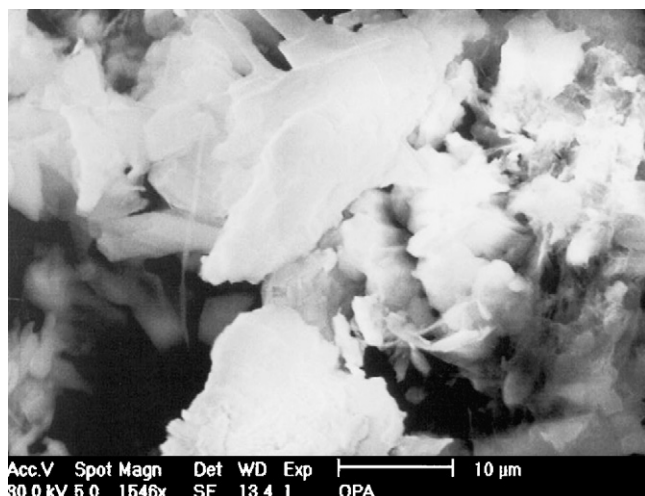
Fig. 1. Micrograph of oil palm ash.

3. Results and discussion

3.1. Surface morphologies and elemental composition of OPA

Fig. 1 shows the micrograph of OPA which illustrates the spongy and porous nature of the ash particles. The porous nature of OPA was also reported by Tangchirapat et al. [8]. Table 2 shows the elemental compositions of OPC and OPA used in the study determined by means of energy dispersive X-ray (EDX). A noteworthy observation with regards to both compositions is that OPA contains higher weight percentages of potassium and magnesium than OPC while on the other hand, calcium and iron weight percentages in OPA are lesser. Due to high wt% of oxygen of both OPC and OPA, it can be postulated that calcium, iron and aluminium may exist predominantly in oxide form. Calcium oxide (CaO) is perhaps the most essential substance in S/S treatment due to its strength building characteristic. The lack of calcium in the OPA composition (1.36 wt%) as compared to OPC (34.81 wt%) provides an initial indication that replacement of OPC with OPA in S/S treatment may create a stoichiometric imbalance which can entail some form of strength loss since calcium is one of the key elements in calcium silicate hydrate (C-S-H) required for hardening of cementitious mixtures.

Table 2
Elemental compositions of OPC and OPA used in the study

Element	OPC		OPA	
	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)
Oxygen (O)	43.83	59.56	56.30	64.22
Magnesium (Mg)	ND	ND	2.27	1.70
Aluminium (Al)	1.62	1.30	0.56	0.38
Silicone (Si)	5.78	4.48	4.65	3.02
Potassium (K)	0.68	0.38	16.04	7.48
Calcium (Ca)	34.81	18.89	1.36	0.62
Iron (Fe)	2.85	1.11	0.59	0.19
Zinc (Zn)	0.29	0.10	0.33	0.09
Other	10.14	14.18	17.90	22.30

Table 3
Stabilized/solidified waste acceptance criteria

Characteristic	Regulatory (acceptance)	Level
28-day compressive strength (N/mm^2)	Landfill disposal limit[a]	0.34
	Comparative mortar limit[a]	20
Leachability (mg/L)	Cadmium[b]	1.0
	Chromium[b]	5.0
	Lead[b]	5.0
	Copper[b]	100.0
	Nickel[b]	100.0

[a] Regulatory waste disposal limit at a disposal site in the UK [12].
[b] Waste Evaluation Guidelines, Kualiti Alam Sdn Bhd, Malaysia [11].

3.2. S/S waste acceptance criteria

Table 3 lists the S/S waste acceptance criteria which are utilized to assess the effectiveness of the treatment. The two characteristics selected for evaluation of the treated soils are UCS and leachability since the two are normally the predominant criteria assessed for the effectiveness of solidification/stabilization. The leachability limits are extracted from the Waste Evaluation Guidelines stipulated by Kualiti Alam Sdn Bhd (the only integrated scheduled wastes treatment center in Malaysia that provides comprehensive S/S treatment of industrial sludges) [11] while the UCS limits are extracted from regulatory waste disposal limit at a disposal site in the United Kingdom [12].

3.3. Metal components of sludge

In order to justify the need to solidify/stabilize the nickel hydroxide sludge, the TCLP Method 1311 as described in Section 2.3 was conducted on the sludge to determine the leachable metal concentrations. Table 4 lists the metal components of sludge as determined by TCLP method. All metal concentrations are within their corresponding leachability limits except for nickel of which its concentration of 1204 mg/L clearly exceed its leachability limit of 100 mg/L. This result justifies the need to treat the sludge prior to disposal.

3.4. UCS of treated sludge

Fig. 2 shows the UCS of treated samples at 7-day and 28-day of dry curing. UCS values of samples F and G were not shown as they did not harden sufficiently after curing at both times and disintegrated immediately upon UCS testing without providing any value. This implies that substitution of OPA into the mix

Table 4
Metal components of sludge as determined by TCLP method

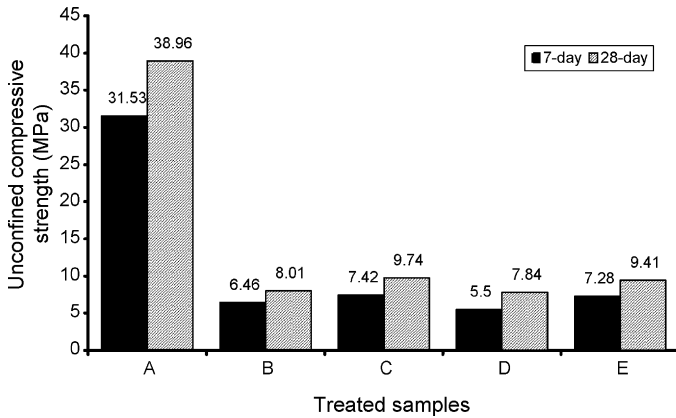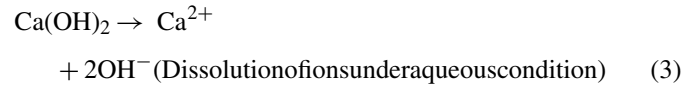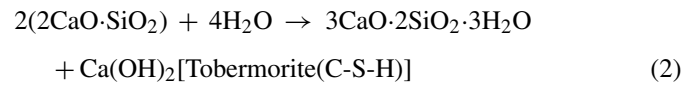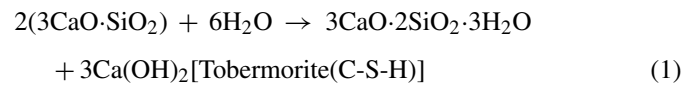| Metal element	Concentration (mg/L)
Cadmium	0.018
Nickel	1204
Lead	0.48
Chromium	0.01
Copper	0.31

Fig. 2. Unconfined compressive strength of treated samples at 7-day and 28-day of dry curing.

design should not exceed 15% of the total weight percentage. Samples F and G did not harden sufficiently as the mixture did not have ample CaO to sustain strength building throughout the curing periods due to higher OPA weight substitution. This is because OPA is deficient in CaO as compared to OPC as indicated in the EDX analysis. From the figure, it was observed that UCS values of samples A, B, C, D and E exceeded the landfill disposal limit of 0.34 N/mm². The UCS of control sample A (100 wt% OPC) at both curing times is clearly higher than the mortar limit while substitution of 50 wt% nickel hydroxide sludge for samples B, C, D and E constituted drastic decreases of UCS values. This is expected as presence of heavy metals such as nickel in S/S mixture can inhibit the cementation process, rendering significantly lower strength [6]. The UCS values for each sample at 28-day are higher than at 7-day of curing. This observation is also expected as hydration of the samples requires a certain period to enable diffusion of water molecules into pores of cementitious materials to form C-S-H necessary for strength building. The wt% increases of OPA in the mix design from 5 wt% OPA (sample B) to 15 wt% OPA (sample E) constitute UCS fluctuations rather than an apparent trend of decreasing UCS. This further implies that relatively constant UCS can be obtained within the allowable OPA substitution from 5 to 15 wt%.

3.5. pH and nickel leachability

The control of pH is a crucial factor in assessing leachability of S/S treated sludge, especially for metal-based sludges. Fig. 3 shows the pH and nickel leachability of TCLP leachate. The pH values of leachates of samples A, B, C, D and E are essentially alkaline at 11.65, 11.16, 10.46, 10.31 and 7.56, respectively, while leachate pH of samples F and G are slightly acidic at 6.82 and 6.15, respectively. These values clearly indicate a trend whereby increases of OPA wt% in the mix design actually constitute decreases in leachate pH of the treated samples. This result is consistent with the EDX analysis of the OPA whereby its very low calcium wt% may have contributed to lower leachate pH. This can be further elucidated by the following equations for

reaction of OPC with water:

$$2(3CaO \cdot SiO_2) + 6H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O$$
$$+ 3Ca(OH)_2[Tobermorite(C\text{-}S\text{-}H)] \qquad (1)$$

$$2(2CaO \cdot SiO_2) + 4H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O$$
$$+ Ca(OH)_2[Tobermorite(C\text{-}S\text{-}H)] \qquad (2)$$

$$Ca(OH)_2 \rightarrow Ca^{2+}$$
$$+ 2OH^- (Dissolution of ions under aqueous condition) \qquad (3)$$

For standalone OPC, both tricalcium and dicalcium silicates in the OPC reacted concurrently with water to produce strength-enhancing tobermorite or calcium silicate hydrates (C-S-H) and calcium hydroxide. Subsequently, hydroxide ions were released from calcium hydroxide under aqueous condition and contributed to the alkalinity of the leachates. As the OPC is partially substituted with OPA in this study, the calcium wt% is lower than the standalone OPC resulting in lesser dissolution of $Ca(OH)_2$ that produces OH^- ions and subsequently less alkaline.

It is shown in Fig. 3 that leached nickel concentrations all the samples are below the nickel leachability limit of 100 mg/L stipulated by Kualiti Alam Sdn Bhd. This shows that the S/S treatment of sludge using the OPC and OPA binder system is successful. Increases of OPA wt% from samples B to E constitute increases of nickel concentration in leachate of the same samples, a trend which is the opposite of leachate pH. This shows that with addition of OPA wt%, nickel is more easily leached out from the treated samples. This suggests that precipitation may be on of the main mechanisms in this study as nickel leachability is proven to be very much pH dependent. As such, at high pH, nickel may exist as nickel hydroxide complexes which are infused into the solidified/stabilized solid matrix. This leachability result coupled with determined UCS values of treated samples surmise that the optimum mix design for S/S of nickel hydroxide sludge using both OPC and OPA at B/S_d = 1 is 15 wt% OPA, 35 wt% OPC and 50 wt% sludge. Even though leachates
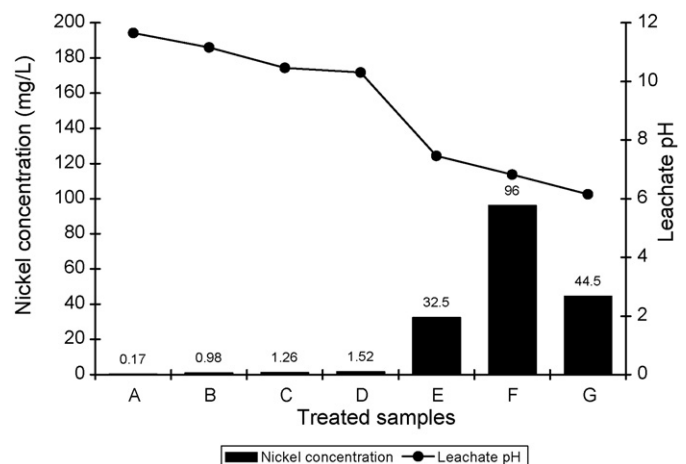

Fig. 3. pH and nickel leachability of TCLP leachate.

of samples F and G have permissible nickel concentrations (i.e., <100 mg/L), their mix designs should not be used since they do not exhibit sufficient hardening characteristics to reach the minimum UCS value of 0.34 N/mm^2 even after 28 days of air curing.

3.6. X-ray diffraction

The changes in crystalline phases of S/S treated sludge were determined by means of XRD. XRD patterns reveal phase, chemical and crystalline structure information data which afford better understanding on the reaction products of treated sludge. Fig. 4 shows the XRD patterns of samples A, B and E at 28 curing days. The diffraction intensities which were reflected by corresponding counts per second (cps) were used as the indication of changes among the patterns of various systems.

Major crystalline phases detected are unreacted di- and tricalcium silicates in all three samples in form of humps and peaks. Portlandite [Ca(OH$_2$)] is detected at prominent peaks of 2(of 28.80°, 47.20°, 50.90°, 54.40°, 62.50° and 64.40° for sample A. Portlandite was also reported to be present in standalone hydrated cement paste by Asavapisit et al. [13]. This indicates that for standalone hydrated cement paste, pozzolanic reactions are not over by the end of the 28-curing day period and that its UCS has not reached its maximum for this study. In contrast, portlandite is not detectable for samples B and E. This is due to the relatively lesser calcium element in the two samples as compared to pure hydrated cement paste which can be the limiting factor for strength development in the samples. Ettringite [Ca$_6$Al$_2$(SO$_4$)$_3$(OH)$_{12}$·26H$_2$O] is also detected in all three samples. Ettringite is a phase which is formed via the reaction of calcium and alumina in cement with sulfate either inherently present in the cement paste or introduced into the system through an outside source [14]. Ettringite normally present at high amount at curing age of 1–7 and gradually absent after 28 days of curing. Nickel complexes are not identified in the XRD patterns which indicates that these precipitated complexes are not contained as crystalline structures in the S/S matrix but rather present in an amorphous phase. This amorphous phase can be nickel silicate which is poorly crystallized. This is because the diffractometer is only capable of identifying crystalline structures and not substances that exist as amorphous.

3.7. Probable S/S mechanisms

The mechanisms involved in S/S of heavy metal wastes are generally accepted as a combination of precipitation, encapsulation, bonding, sorption and ion exchange [6]. In this study, it can be shown that an amalgamation of mechanisms may have contributed to the overall S/S treatment. In the mixing stage, hydration process due to addition of water may have ionized the nickel hydroxide and subsequently reprecipitated as amorphous nickel complexes due to high pH of the hydrated binder system. These complexes may gradually react with the silicate matrix as long as free silicate is available, i.e., before it reacts with other ions such as calcium in the system [5]. However, since the nickel complexes are likely to be amorphous, they may have adsorbed onto the S/S matrix as poorly crystallized precipitates and at the same time likely to be encapsulated inside the matrix.

4. Conclusions

The optimum mix design for S/S of nickel hydroxide sludge using both OPC and OPA at B/S$_d$ = 1 is 15 wt% OPA, 35 wt% OPC and 50 wt% sludge. The adequate strength and permissible leached nickel concentrations shown for this mix design indicate the viability of using OPA as substitute of OPC as it can reduce cost normally incurred by usage of high amount of OPC. One of the main mechanisms in this study is precipitation as nickel leachability is proven to be very much pH dependent.

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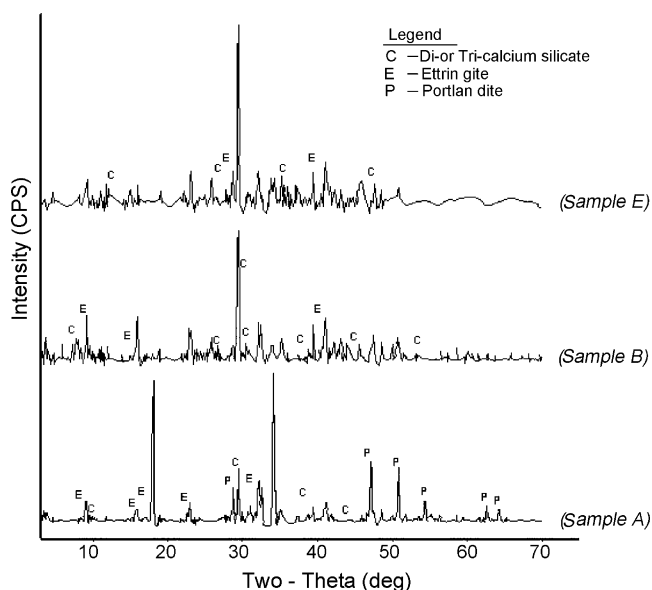

Fig. 4. XRD patterns of samples at curing age of 28 days.

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