

Remediation of Heavy Metal Contaminated Soil by Using Chemical Stabilization

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ABSTRACT

The effectiveness of ordinary portland cement (OPC) in the immobilization of heavy-metal contaminated soil was investigated in this study. Heavy metal contaminated soil was collected from a scrap metal yard within the outskirts of Kuala Lumpur, Malaysia. Metal composition analysis indicated that the predominant heavy metals present in the soil were iron and aluminium with some composition of zinc and lead and little composition of copper and chromium. The contaminated soil was treated with OPC using cement-to-dry soil (C/S_d) ratios of 0.5, 1, 2, 4 and 8. The effectiveness of the treatment was evaluated by performing unconfined compressive strength (UCS) test and crushed block leaching on the treated soil. Crushed block leaching tests were performed in accordance with standard protocols of Method 1311: Toxicity Precipitation Leaching Procedure (TCLP) and Method 1312: Synthetic Precipitation Leaching Procedure (SPLP) of the United States Environmental Protection Agency (USEPA). The treatment results were compared to the solidified waste acceptance criteria which were compiled based on the regulatory waste disposal limit at a disposal site in the United Kingdom (UK) and the maximum concentration of contaminants for toxicity characteristic of solid wastes from USEPA. The UCS values of the solidified samples at 28 days under air drying for C/S_d ratios of 0.5 – 8.0, far exceeded the minimum landfill disposal limit of 0.34 N/mm² at a disposal site in the UK. Subsequent to leaching of the treated soils by three different leaching solutions (acetic acid, deionized water and nitric/sulfuric acid), metals in the leachates were either undetectable or appreciably below the proposed leachability limits.

Keywords : Land remediation, chemical stabilization, ordinary portland cement (OPC), heavy metal contaminated soil, unconfined compressive strength (UCS), leachability

INTRODUCTION

Chemical stabilization or chemical immobilization techniques which are more extensively utilized in the treatment of hazardous wastes, are increasingly finding applications in remediation of contaminated soil especially in developed countries such as the United States [1] and European Union [2]. Applications of established technologies for land remediation are scarce and still in its infancy in Malaysia due to the lack of specific contaminated land legislations that obligate land polluters to bear the clean up costs. Consequently, the disinclination of land polluters (mostly small and medium industries) to shell out exorbitant land remediation clean up fees had diluted specific pertinent stakeholders' effort in ensuring that remediation of numerous contaminated land are aptly carried out. Comprehensive researches on chemical stabilization technologies in Malaysia are only limited to treatment of industrial wastes prior to land disposal, most of which are undertaken at local academic institutions. Hence, there is a need to research novel remediation techniques or customize established ones for local applications in Malaysia in order to address the increasing exigency in remediating contaminated land to protect the public health as well as the environment.

Chemical stabilization is generally defined as a chemical alteration technique of reducing the mobility and solubility of contaminants present in waste or soil in order to convert that particular waste or soil into chemically innocuous form which may or may not include production of a monolithic matrix [3]. Chemical stabilization of contaminated soil may produce an end product of high strength which can be reused as construction-base materials. The objectives of this study were to evaluate the

effectiveness of OPC treatment for heavy metal-contaminated soil which was subjected to Malaysian weather and establish the most appropriate C/S_d ratio for the treatment based on the treated material's ultimate purpose or destination.

MATERIALS AND METHODS

Site and Soil Sample Description

An operational scrap metal yard located within the outskirts of Kuala Lumpur was selected as the study area (Figure 1). The scrap metal yard has been in operation for more than a decade and manages a variety of scrap metals ranging from construction steel bars to metal components of household appliances. Contaminated soil samples were collected at depths of 20 cm from the surface by using a stainless steel shovel and stored in cylindrical plastic containers. Based on visual inspection, the soil was dark in colour and contained fragmented metal pieces. All labware and sampling apparatus were pre-soaked in 5% nitric acid solution followed by distilled water for a day prior to sampling to remove trace concentrations of metals. Large plant debris and metal pieces were manually discarded from the contaminated soil samples before subjected to screening by using a 2-mm sieve.

Characterization of Contaminated Soil

Physical characteristics that include moisture content, soil particle density (specific gravity), soil pH, loss-on-ignition and particle size distribution were determined by using the *British Standard Methods for Test for Soils for Civil Engineering Purposes* [4]. The soil was acid digested by using *Method 3050B: Acid Digestion of Sediments, Sludges and Soils* [5] prior to chemical



Figure 1: Scrap metal yard

analysis by using the OPTIMA 3000 Perkin-Elmer Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES).

Production of Solidified Samples

Type 1 OPC obtained from Associated Pan Malaysian Cement was used throughout the study. The OPC was selected as binder in this study due to its relatively inexpensive cost and easy availability in Malaysia which may prove crucial should the technology be locally commercialized. The technical justification for its selection was due to the fact that composition of OPC was much more consistent, thus eliminating some of the many variables in studying chemical stabilization processes [6]. OPC was added to the contaminated soil at C/S_d ratios of 0.5, 1, 2, 4, and 8. Mixing of these materials was done in a 25-L SPAR type mixer. The sieved contaminated soil and cement were added into the mixer and homogenized for 15 minutes prior to the addition of ASTM Type II deionized water. It was ensured that the addition of water to the cement and soil was adequate to produce a mixture with a flow of 10% by using a K-slump tester specified in the standard test procedure given in ASTM Standard Method C 1362-97 [7]. The mixture was then cast into 50 mm × 50 mm × 50 mm cubic steel molds, 25.4 mm × 25.4 mm × 25.4 mm cubic perspex molds and 0.5-litre high-density polyethylene (HDPE) cylinder in three layers, with each layer compacted by using a vibrating table to yield good packing of the solidified samples. Solidified cubic samples for all the tests were prepared in triplicates. After the initial mixing, one day was allowed for setting before the solidified samples were demolded. A total of 27 days were allowed for air drying of the solidified samples in a cabinet at a controlled condition (temperature = 25 ± 2°C, humidity > 80%).

Unconfined Compressive Strength

The unconfined compressive strength (UCS) test measures the compressive strength of a material without lateral confinement [8]. This test was conducted on the solidified samples to indicate whether the treated material had adequate strength to support any overburden pressure. The 50 mm × 50 mm × 50 mm solidified cubic samples were subjected to the UCS test [9] at 1, 3, 7, 21 and 28 days.

Leaching Tests

Crushed block leaching tests were performed according to the standard US Environmental Protection Agency protocols of Method 1311: Toxicity Precipitation Leaching Procedure (TCLP)

[10] and Method 1312: Synthetic Precipitation Leaching Procedure (SPLP) [11]. The TCLP leaching solution was designed to simulate the worst-case leaching conditions on disintegrated landfill wastes due to prolonged aging effects while SPLP used a leaching solution that simulated acid rain. Although the TCLP test is principally used to determine hazardous characteristics, it is occasionally utilized to determine the impact of a waste on groundwater even when the waste is stored or disposed in non-landfill conditions [12].

For the TCLP test, 50 g of crushed samples (dry-cured for 28 days) which passed through a 9.5 mm sieve were placed in low-density polyethylene (LDPE) containers prior to addition of 1 litre of 0.1 M nitric acid (solution pH = 2.88) to provide a ratio of 20:1 mass ratio of leachant to solidified samples. The containers were then agitated using a rotating extractor at 30 rpm for 18 hours. Leachate pH was measured at the end of the extraction period prior to vacuum filtration (using 0.45-micron membrane filter) since the level and control of pH were extremely crucial factors in evaluating leachability of OPC-stabilized wastes, especially for metals [6]. The filtrate was then acidified with nitric acid to pH < 2 and stored under refrigeration (<4°C) prior to heavy metal analysis by using the ICP-OES. The SPLP test was slightly different from the TCLP as it required a leaching solution of diluted nitric/sulphuric acid (solution pH = 4.20) while other features remained the same. All TCLP and SPLP analysis were performed on sample triplicates and average values were used. A third leaching solution, deionized water (pH = 6.80) was used to examine the impact of a non-aggressive solution.

Table 1 : Soil physical characterization

Characteristic	Value
Particle Size Distribution (%)	Gravel = 22.68 Sand = 72.91 Silt & Clay = 4.41
Moisture Content (%)	14.48
Soil Particle Density	2.616
Soil pH	7.11
Loss-on-ignition (%)	7.63

RESULTS AND DISCUSSION

Characterization of Contaminated Soil

Results of contaminated soil physical characterization are shown in Table 1. The contaminated soil comprised of 22.68wt % of gravel, 72.91wt % of sand and 4.41wt % of silt and clay prior to sieving. The soil was classified as “gravelly sand” based on the British Soil Classification System [13]. The soil moisture content and particle density were 14.48% and 2.616 respectively while pH of the soil was determined to be slightly alkaline at 7.11. The soil consisted of 7.63% of organic content as determined by the loss-on-ignition (LOI) test [4].

Table 2 shows the result of the heavy metal analysis. High concentration of iron (108,290 mg/kg of soil) in the samples was observed because construction steel bars were the predominant type of scrap metal stored at the site. Zinc, lead and aluminium

were also present in the samples in excess of 1000 mg/kg of soil while copper and chromium were detected at concentrations of less than 1000 mg/kg.

Table 2: Heavy metal concentrations in contaminated soil

Heavy Metal	Concentration (mg/kg)
Fe	108,290
Cr	275
Cd	ND
Zn	2,315
Pb	1,005
Cu	559
Al	5,967

ND denotes "below detection limits"

Solidified Waste Acceptance Criteria

Table 3 lists the solidified waste acceptance criteria which were used to evaluate the effectiveness of the treatment. These criteria were compiled and used for evaluation purposes of the chemical stabilization treatment due to unavailability of soil and groundwater standards as well as solidified waste treatability criteria in Malaysia. The two characteristics selected for assessment of the treated soils were UCS and leachability since the two were the predominant criteria assessed for the effectiveness of solidification/stabilization treatment in the United States [14]. The regulatory UCS and leachability levels were extracted from two sources; regulatory waste disposal limit at a disposal site in the United Kingdom (UK) [15] and the maximum concentration of contaminants for toxicity characteristic of solid wastes from US Environmental Protection Agency [10,11].

Table 3: Solidified waste acceptance criteria

Characteristic	Regulatory (Acceptance) Level
Compressive strength at day-28 (N/mm ²)	Landfill disposal limit [†] :0.34
	Comparative mortar limit [†] :20
Leachability (mg/L)	Cadmium* :1.0
	Chromium* :5.0
	Lead* :5.0
	Copper [†] :5.0
	Zinc [†] :10.0

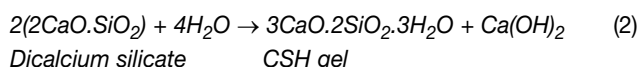
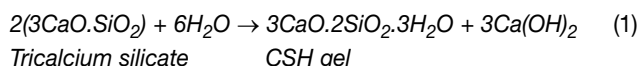
[†]Regulatory waste disposal limit at a disposal site in the UK (Sollars & Perry, 1989)

*U S EPA maximum concentration of contaminants for toxicity characteristic (SW-846)

Strength Development of Solidified Samples

Table 4 shows the UCS data of solidified samples throughout 28 days of air drying. Figure 2 shows the UCS development of solidified samples throughout 28 days of air drying while the correlation between UCS, C/S_d and curing age is depicted in Figure 3 as contour and surface profile which was created by utilizing Surfer 7.0. The UCS values of the solidified samples at 28 days of dry curing were in the range of 9.4 – 34.7 N/mm² for C/S_d ratio of 0.5 – 8.0, which far exceeded the minimum landfill

disposal limit of 0.34 N/mm² at a disposal site in the UK. It was observed that all solidified samples possessed UCS above 0.34 N/mm² even at the age of one day. This result indicates that by doubling the C/S_d ratio, the UCS of solidified samples had averagely increased by approximately 6 N/mm² from the preceding ratio at the age of 28 days. This effect was attributed to the fact that by increasing the C/S_d ratio, the amount of tricalcium silicate and dicalcium silicate (predominant elements in cement) increased in the stabilized soil enabling more production of tobermorite gel or calcium-silicate-hydrate (CSH) [16]. This, in turn, provided more strength to the solidified samples. The reactions of both tricalcium silicate and dicalcium silicate with water to produce CSH are shown in Equations (1) and (2).



Overall, higher UCS values were obtained when higher amount of OPC was used for the solidification process. It was observed that the high concentrations of heavy metals as well as organic content in the soil did not have a significant retardation effect on the hydration and initial strength development of the treated material, as indicated by the rapid strength development during the first three days of curing. A minimum C/S_d ratio of 2 was required to achieve the UK's typical UCS mortar limit of 20 N/mm², in which solidified contaminated soils had tremendous potential in construction material applications such as engineering fills, pavement blocks, bricks etc.

Table 4: UCS of solidified samples throughout 28 days of air drying

C/S _d	Unconfined Compressive Strength (N/mm ²)				
	1 day	3 days	7 days	14 days	28 days
0.5	1.2	5.8	9.4	9.3	9.4
1	6.0	12.6	13.8	16.3	15.4
2	11.8	16.4	19.5	23.7	21.0
4	13.5	25.2	25.9	32.1	29.2
8	19.4	34.0	31.4	32.8	34.7

Crushed Block Leaching

Figure 4 indicates the leachate pH of the three leaching solutions, deionised water, acetic acid and nitric/sulphuric acid subsequent to filtration. Figures 5 and 6 show the metal concentrations of TCLP leachates by using acetic acid and deionized water as leachants at various C/S_d ratios while Figure 7 indicates the metal concentrations of SPLP leachates at various C/S_d ratios. It was determined that the leachate pH of the three leaching solutions subsequent to leaching were essentially alkaline ranging from 12.34 to 12.49 (TCLP-deionised water), 11.41 to 11.94 (TCLP-acetic acid) and 12.37 to 12.53 (SPLP-nitric/sulphuric acid).

The results of TCLP and SPLP tests conducted on the solidified samples indicated that all analyzed metals in the three different leachates were either undetectable or appreciably below the proposed leachability limits as a direct effect of chemical stabilization by OPC. The only evident metal present in the three different leachates were aluminium with concentrations ranging from 1.27 to 0.107 mg/L. The high treatment efficiency may be attributed to the high pH value (>11) of the treated soils as

the precipitation of insoluble metal hydroxide. As a result of the high pH of the treated soils, the metals were retained in the form of insoluble hydroxide within the solidified matrix [1,6]. Equation (3) shows the generic reaction between metal in the contaminated soil with the free hydroxide ion when water is added into the mixture.

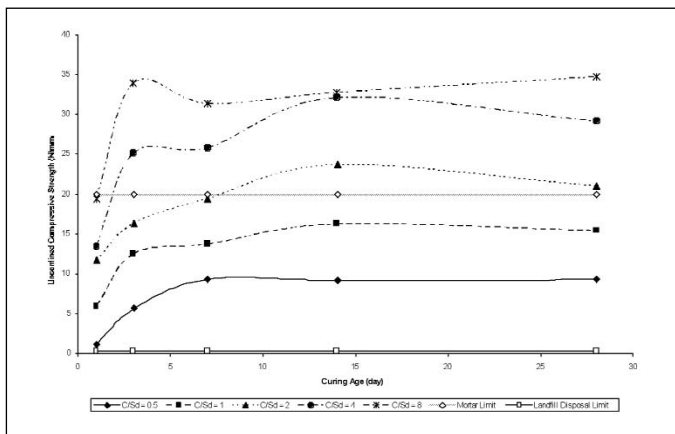
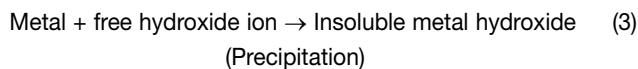


Figure 2: UCS development of solidified samples throughout 28 days

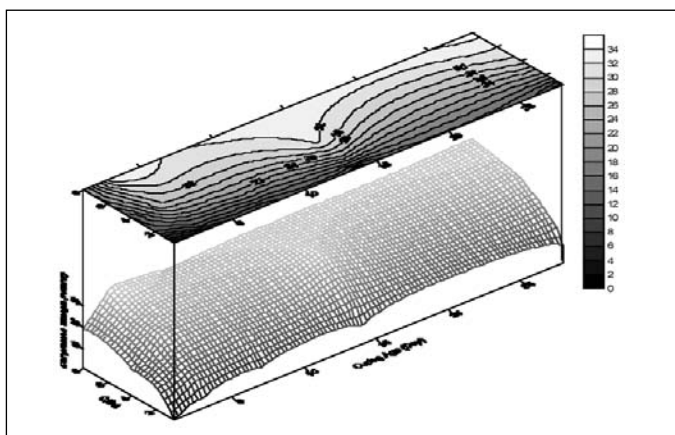


Figure 3: Development of UCS of solidified samples throughout 28 days corresponding to various C/Sd ratios

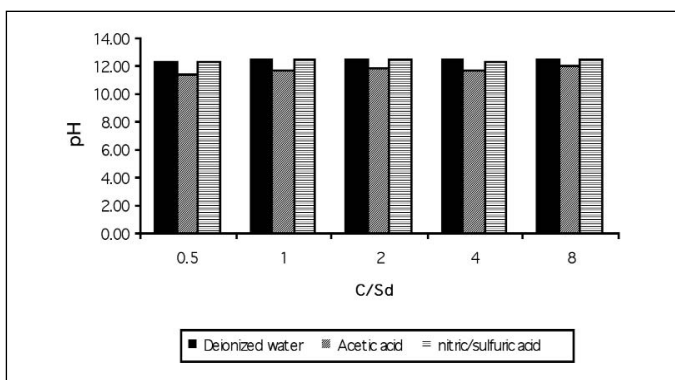


Figure 4: Comparison of leachate pH of the three leaching solutions subsequent to filtration

indicated by the pH of the leachates. It was postulated that the principal mechanism responsible for the effective treatment was hydroxide precipitation. Mass production of hydroxide ion due to hydration of OPC at the initial stage of treatment had facilitated

It was observed that there was no substantial effect of type of leaching solution used on the leachability of the metals with the exception that trace concentrations of aluminium were determined in each of the C/S_d ratio of which acetic acid was used as the leaching solution. In addition, it was noticed that

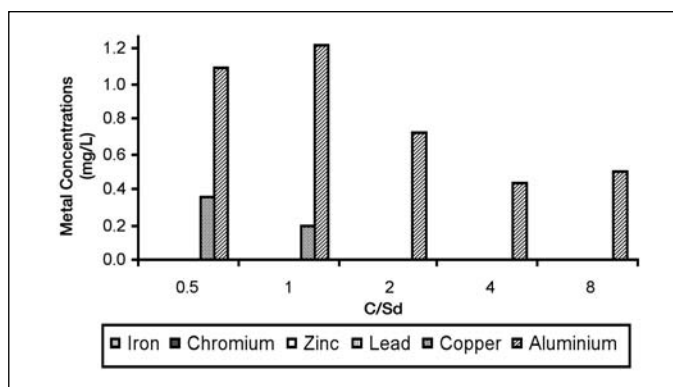


Figure 5: Metal concentrations of TCLP leachate (acetic acid as leaching solution) at various C/S_d ratios

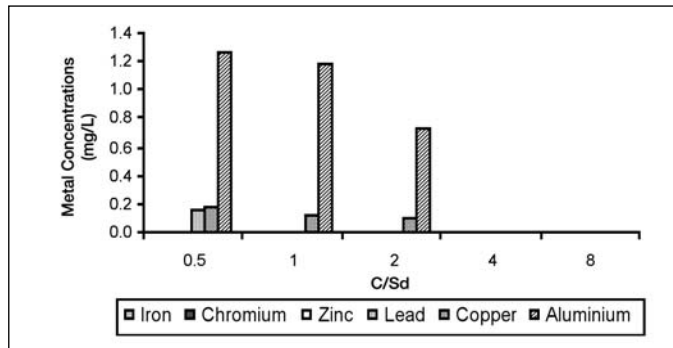


Figure 6: Metal concentrations of leachate (deionized water as leaching solution) at various C/S_d ratios

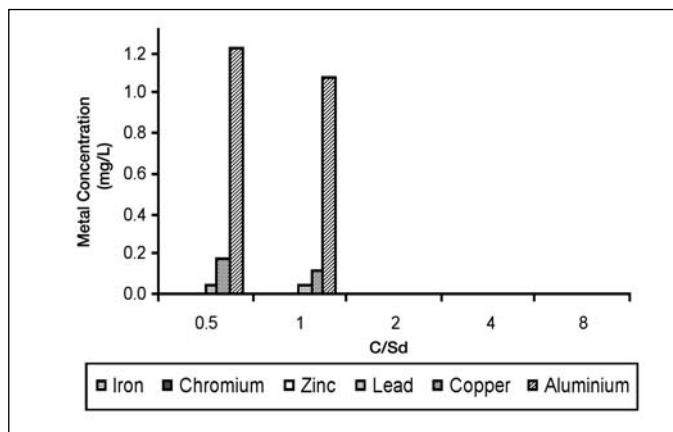


Figure 7: Metal concentrations of SPLP leachate (nitric/sulfuric acid as leaching solution) at various C/S_d ratios

increases in the C/S_d ratios were accompanied by meagre reduction of detectable metal concentrations except for the case of the deionized water and the nitric/sulfuric acid leaching solutions where no metals were detected at C/S_d ratios of 4 and 8. The results indicated that increasing the C/S_d ratios reduced the leachability of metals from the solidified samples.

Ultimate Purpose or Destination of Treated Contaminated Soils

Analysis of UCS development as well as leachability of solidified samples in this study indicated that the amount of OPC used to treat contaminated soils should be dictated by the ultimate purpose or destination of the treated soils; landfill disposal or construction material applications. If landfill is the ultimate destination of the OPC-treated soils, then treatment should be carried out by using the lowest C/S_d ratio of 0.5 in order to minimize treatment costs by which the treated product would adequately comply with the proposed UCS and leachability criteria. Alternatively, if the treated products are to be used as engineering fills or construction materials, then it is recommended that the treatment be carried out using the C/S_d ratio of 2 in order to comply with the comparative mortar limit of 20 N/mm².

CONCLUSIONS

Chemical stabilization is an effective land remediation method for heavy metal contaminated soils based on the compliance of the UCS and leachability of the treated material with the compiled solidified waste acceptance criteria. The strength development and heavy metal leaching from OPC treated contaminated soil had been evaluated and the following conclusions can be drawn:

- (1) Increasing the C/S_d ratio increased the strength of treated soils.
- (2) All solidified samples exhibited UCS above the minimum requirement for landfill disposal limit of 0.34 N/mm² even at the age of one day. A minimum C/S_d ratio of 2 is required to achieve the minimum UCS mortar limit of 20 N/mm² subsequent to 28 days of air drying.
- (3) Leachability tests conducted on the solidified samples indicated that all analyzed metals in the leachates as a result of leaching by using three solutions (deionized water, acetic acid and sulphuric/nitric acid) were either undetectable or appreciably below the proposed leachability limits.
- (4) There was no substantial effect of type of leaching solution used on the leachability of the metals.
- (5) The amount of OPC used to treat contaminated soils should be dictated by the ultimate purpose or destination of the treated soils:
 - landfill disposal (C/S_d ratio of 0.5)
 - construction material applications ($C/S_d = 2$).

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