



pH-dependent leaching behaviour and other performance properties of cement-treated mixed contaminated soil

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Abstract

Portland cement has been widely used for stabilisation/solidification (S/S) treatment of contaminated soils. However, there is a dearth of literature on pH-dependent leaching of contaminants from cement-treated soils. This study investigates the leachability of Cu, Pb, Ni, Zn and total petroleum hydrocarbons (TPH) from a mixed contaminated soil. A sandy soil was spiked with 3000 mg/kg each of Cd, Cu, Pb, Ni and Zn, and 10,000 mg/kg of diesel, and treated with ordinary Portland cement (CEM I). Four different binder dosages, 5%, 10%, 15% and 20% (*m/m*) and different water contents ranging from 13%–19% dry weight were used in order to find a safe operating envelope for the treatment process. The pH-dependent leaching behaviour of the treated soil was monitored over an 84-day period using a 3-point acid neutralisation capacity (ANC) test. The monolithic leaching test was also conducted. Geotechnical properties such as unconfined compressive strength (UCS), hydraulic conductivity and porosity were assessed over time. The treated soils recorded lower leachate concentrations of Ni and Zn compared to the untreated soil at the same pH depending on binder dosage. The binder had problems with Pb stabilisation and TPH leachability was independent of pH and binder dosage. The hydraulic conductivity of the mixes was generally of the order, 10^{-8} m/sec, while the porosity ranged from 26%–44%. The results of selected performance properties are compared with regulatory limits and the range of operating variables that lead to acceptable performance described.

Key words: diesel; heavy metals; hydraulic conductivity; porosity; Portland cement; stabilisation/solidification

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Introduction

Portland cement has been widely used for stabilisation/solidification (S/S) treatment of contaminated soils and it has been applied to a greater variety of hazardous wastes than any other binder (Spence and Shi, 2005). Cement is frequently deployed for S/S works generally, due to its ability to (1) chemically bind free liquids, (2) reduce the hydraulic conductivity of the waste form, (3) encapsulate waste particles surrounding them with an impermeable coating, (4) chemically fix hazardous constituents by reducing their solubility, and (5) facilitate the reduction of the toxicity of some contaminants (Conner, 1997).

The combined process of stabilisation and solidification usually results in increasing the strength, and decreasing the leachability, compressibility and hydraulic conductivity of the treated material (LaGrega et al., 2001). The extent to which the above are achieved would depend on the binder and water proportions used in the S/S treatment. Furthermore, it is well-known that the pH of

S/S treated materials is progressively lowered over time by a number of factors including carbonation by CO₂ uptake, and natural leachants like rainwater or landfill leachate with slightly acidic pH. This in turn leads to increased leachability of contaminants from the treated material. However, there is a dearth of literature on pH-dependent leaching of contaminants from cement-treated soils, although there are a number of studies for a range of similar hazardous waste materials (van der Sloot, 2003; van der Sloot et al., 2003; Vítková et al., 2009). Most of previous works evaluated leachability using the Toxicity Characteristic Leaching Procedure (TCLP) (USEPA, 1986) and the batch-leaching test with de-ionised water extraction, BS EN 12457 (BSI, 2002). Similarly, very few studies have considered the effect of variability in water and binder proportions, especially the water content, on the performance of treated soils. Previous studies have mainly dealt with the variability in both parameters for the unconfined compressive strength (UCS) of uncontaminated soils (Heathcote, 1991; Yoon and Au-Farsakh, 2009; Reddy and Kumar, 2010) and variability in binder dosage on the leachability of particular contaminants (Lin et al.,

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1996; Yilmaz et al., 2003; Moon et al., 2010).

Therefore, in response to these gaps in the literature on CEM I S/S of contaminated soil, the initiation work on the development of process envelopes – the range of operating conditions for acceptable performance – for stabilised/solidified contaminated soils was presented in an earlier conference paper (Kogbara et al., 2010). This included selected performance parameters on CEM I treated soil such as compaction behaviour, UCS and cadmium leachability. This paper builds on the information presented in Kogbara et al. (2010) and goes further to present more information on the treated soil used in the aforementioned study. This includes the pH-dependent leaching behaviour of other contaminants studied, monolithic leaching, and some geotechnical properties such as hydraulic conductivity and porosity. The study was aimed at investigating in depth the granular leachability of contaminants at different pH conditions, in a mixed contamination scenario, to help characterise chemical immobilisation of contaminants and also the chemical durability of the S/S matrix. It was also the aim of the study to test the effectiveness of the binder over a range of binder dosages and water contents, and hence, define the range of operating variables that lead to acceptable performance of the treated soil in order to provide insights for S/S treatment of similar soil types.

1 Experimental

With the exception of the monolithic leaching test, the materials and experimental methodology used in this work have been documented in an earlier conference paper (Kogbara et al., 2010) as well as in previous related publications (Kogbara, 2011; Kogbara and Al-Tabbaa, 2011; Kogbara et al., 2011). However, they are summarised here to provide a complete picture of the work carried out.

1.1 Contaminated soil and binder

A clayey silty sandy gravel, with a natural water content of ca. 12%, from a petrol station in Birmingham, UK, contaminated with low levels of heavy metals and total petroleum hydrocarbons (TPH), and with a pH of 11.64 was used. It had very low organic carbon content (0.22%, *m/m*). The soil did not contain significant concentration of contaminants and was therefore spiked with 3000 mg/kg of each of cadmium (using $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), copper (using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), lead (using PbNO_3), nickel (using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and zinc (using ZnCl_2), and 10,000 mg/kg of diesel in order to increase the contaminant levels to relatively high values for monitoring during the course of the study. The addition of contaminants reduced the pH of the soil to 9.83. CEM I was employed in 5%, 10%, 15% and 20% dosages in paste form. Unspiked samples were also stabilised for use as the control, only with 5% and 10% binder dosage.

1.2 Preparation of S/S products

The diesel was added to the soil first and thoroughly mixed, followed by the five metals in solution form, using part of the added water, while the remaining water was used

to form the cement paste. Compaction, using a 2.5 kg rammer, was then carried out on the prepared S/S mixes, at 4–5 different water contents, ranging from 13% to 22% dry weight. It should be noted that the terms, water content and water/solid ratio of the samples are synonymous in this study. Following this, the same mix material was then broken up and cast into cylindrical moulds, 50 mm diameter and 100 mm high, to the same compaction density determined above for a given water/solid (W/S) ratio, and cured at 95% relative humidity and 20°C.

1.3 Testing of S/S products

Testing was carried out mainly on day 28 and 84, representing the standard and extended curing ages, respectively, in the cement and concrete industry. However, performance properties were not determined on the higher binder dosages used (15% and 20%) on day 84 since testing started with low binder dosage (5%) and granular leachability of contaminants assessed until most leaching criteria were met. It is for the same findings of preliminary investigations that performance parameters were determined on only optimum moisture content (OMC) mixes at 84-day, and only OMC mixes of 5% and 10% binder dosages were used in the monolithic leaching test. UCS (ASTM, 2000) was determined on triplicate samples before they were crushed and mixed together for the ANC test (Stegemann and Côté, 1991). The three-point ANC test with pH measurements at 0, 1 and 2 meq/g acid addition based on Environment Canada method was used. Crushed samples sieved past 1.18 mm were placed in 1 L glass bottles and de-ionised water and HNO_3 added to give a liquid-to-solid (L/S) ratio of 10 and the desired acid addition. The bottles were then rotated end-over-end for 48-hr and the leachate extracted was analysed for pH and contaminant concentrations using gas chromatography-flame ionisation detector (GC-FID; Agilent 6850 series, UK) for TPH and inductively coupled plasma-optical emission spectrometry (ICP-OES; Perkin Elmer Optima 7000, UK) for heavy metals. Diesel in the water phase was directly extracted with hexane and the diesel extract in hexane analysed on the GC-FID in line with the method described by Vreysen and Maes (2005). Metal concentration was measured on the ICP-OES. The wavelengths used for the analysis were 327 nm for Cu, 220 nm for Pb, 232 nm for Ni and 206 nm for Zn.

The monolithic leaching test was determined according to NEN 7375 (Environment Agency, 2004) on 49-day old OMC mixes. The ratio of the volume of leachant to the volume of the specimens was kept constant at 3.5 and the leachant was renewed at 8 time intervals of 0.25, 1, 2.25, 4, 9, 16, 36 and 64 days after commencement of the test. The leachate pH and conductivity were also measured at the end of every interval. Thereafter, the leachate was analysed for heavy metal content; the TPH content was not investigated as the leached concentrations were negligible.

1.4 Statistics

One and two-way ANOVA, with and without replication, was used for data analysis to test for statistically significant

differences in performance parameters due to the effects of water content, binder dosage and curing age.

2 Results and discussion

As mentioned earlier, the compaction behaviour, UCS and Cd leachability of the treated soil has been presented elsewhere (Kogbara et al., 2010). Hence, these are excluded from the results here. It should be noted that the compaction behaviour showed OMC (the same as water/solid) values of 17% and 19% for all binder dosages in the spiked and unspiked soil, respectively (Kogbara et al., 2010).

2.1 Hydraulic conductivity and porosity

The hydraulic conductivity of all the spiked mixes and OMC mixes of the unspiked soil at 28-day is shown in Fig. 1a. The hydraulic conductivity of some spiked OMC mixes at 84-day is also shown. The hydraulic conductivity of OMC mixes decreased with increasing binder dosage corroborating the findings of Al-Rawas et al. (2005). The hydraulic conductivity was optimum around the OMC. Unspiked mixes had lower hydraulic conductivity than spiked mixes at 28-day; hence, the presence of contaminants could be responsible for the higher hydraulic conductivity of the spiked soil. Increases in hydraulic conductivity due to the presence of contaminants have been reported (Trussell and Spence, 1994; Bone et al., 2004). The hydraulic conductivity at 84 days also increased in relation to those at 28 days for the few spiked samples studied, differing from the position of Glasser (1997) probably due to the presence of contaminants. The increase in hydraulic conductivity could be caused by interactions of the contaminants with the soil-binder material superseding the effect of the continued hydration of the cementitious materials (Al-Tabbaa and Evans, 2000).

The porosities of spiked and unspiked mixes at 28-day and 84-day are shown in Fig. 1b. Generally, the porosity decreased with increasing water content. This is probably a reflection of the compaction behaviour of the mixes

with changes in water content. It is well known that the compactability of soil or soil-cement samples improves with increasing water content up to an optimum point. Well-compacted samples are very likely to have lower porosities than poorly compacted samples, which provide reason for the porosity behaviour observed. Spiked mixes generally had lower porosities than unspiked mixes, differing from the position of Bone et al. (2004) on the effects of high quantities of soluble salts on porosity. The trend in porosity between 28-day and 84-day varied between 5% and 10% binder dosages, and differences in porosity was independent of binder dosage. The range of porosity recorded was similar to those of Reddy and Kumar (2010) for cement-treated uncontaminated soils.

2.2 ANC and leachability of contaminants

The contaminant concentration results are based on single tests, however, duplicates tested for a few samples showed maximum margins of error of $\pm 7\%$, $\pm 13\%$, $\pm 2\%$, $\pm 4\%$ and $\pm 5\%$ for Cu, Pb, Ni, Zn and TPH, respectively. The effect of water content and binder dosage on leachate pH and contaminant leachability at 28-day and 84-day for Cu, Pb, Ni, Zn and TPH is shown in Fig. 2. Each mix on the graphs has three points, from right to left representing the leachate pH values measured at 0, 1 and 2 meq/g acid additions. The bold solid line on the graphs is the theoretical solubility profile of the metal hydroxide (Stegemann, 2005). The theoretical concentrations of the metal contaminants were calculated on the basis of equilibrium with hydroxide in dilute solution at 25°C (without adjustment for ionic strength), based on data in the MINTEQA2 database, a chemical equilibrium model for predicting metal speciation and solubility in natural waters. While the dashed line with stars is that of the untreated contaminated soil at the aforementioned acid additions and at two additional acid and two base (NaOH) additions (apart from TPH). It should be noted that the untreated contaminated soil data was taken straight after contamination and not at the same curing ages as the treated soils. The additional acid and base for the uncontaminated soil was meant to cover a wide

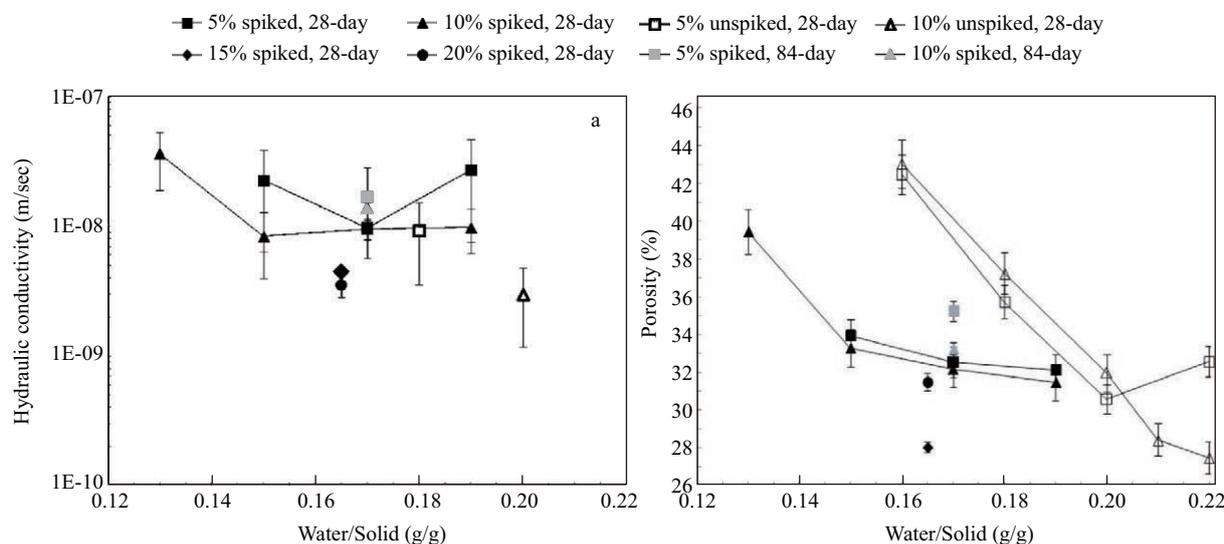


Fig. 1 The 28 and 84-day of hydraulic conductivity (a) and porosity of cement-treated mixed contaminated soil (b).

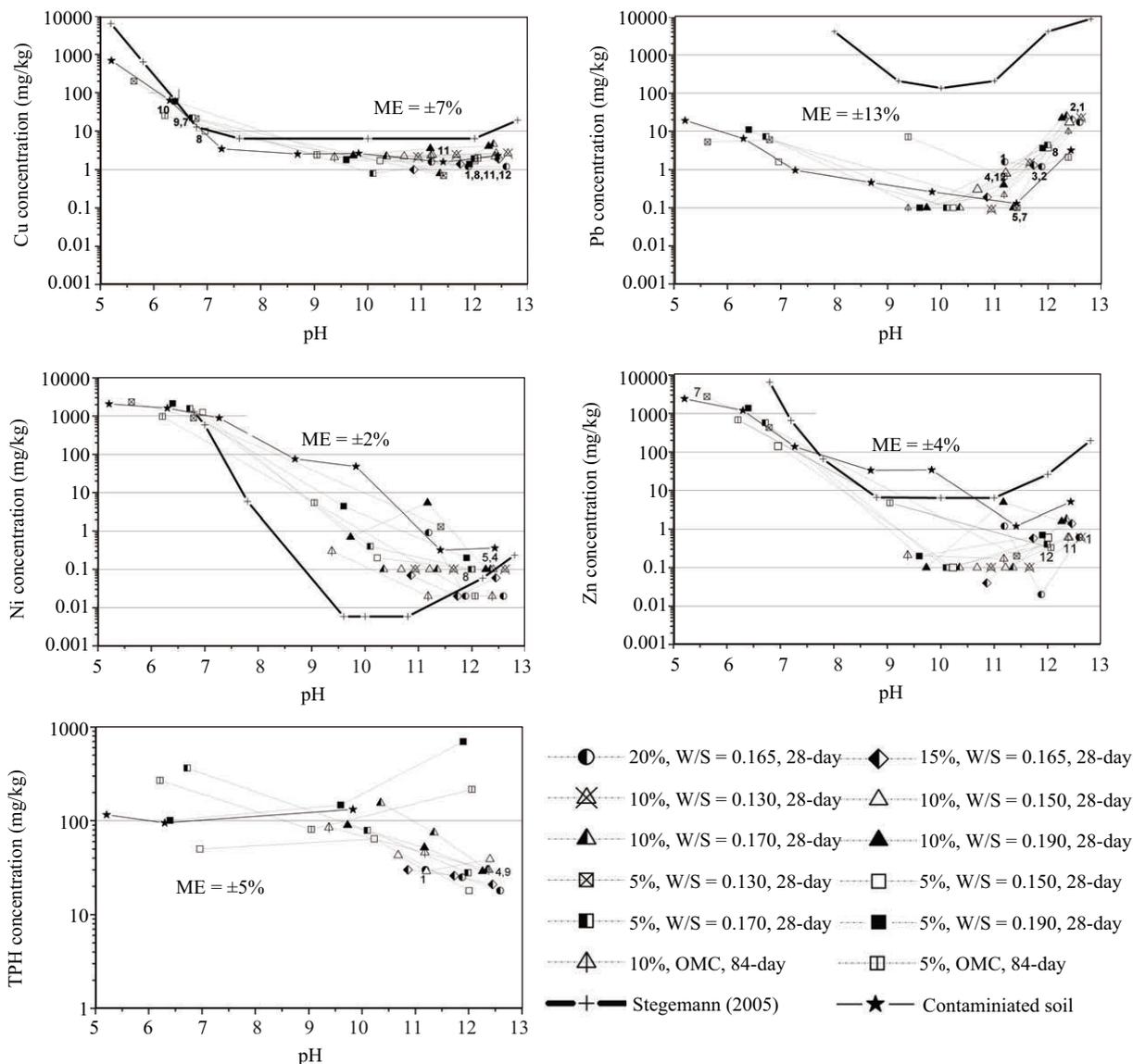


Fig. 2 Leachability of Cu (a), Pb (b), Ni (c), Zn (d), and TPH (e) at 28 and 84 days in cement-treated mixed contaminated soil. W/S: water/solid.

pH range (5–12) so that chemical immobilisation of metals within a given pH zone could be evaluated. Furthermore, TPH leachability was determined on only three of the four water contents of 5% and 10% CEMI dosages: the OMC and the next successive water content on the dry and wet side of OMC based on initial findings of the study. For comparison, it should be noted that the pH of the binder alone (without contaminated soil) was 12.80, 12.66 and 12.53 at 0, 1 and 2 meq/g acid additions, respectively.

Figure 2 shows that the leachability of the metals from the mixes demonstrated the well-known effect of leachate pH on metal solubility in the literature since the pH governs the solubility of the metal hydroxides. Small changes in pH caused large differences in leachability. There was insignificant influence of dissolved organic carbon (DOC) on the leaching patterns observed as the soil contained very low amount of organic carbon and preliminary investigations showed that the contribution of the spiked diesel to DOC was negligible. Generally, variations in water/solid ratio did not cause significant differences in the leachability of the contaminants at any given acid addition.

Further, there was no significant difference in the amount of metals leached between 28-day and 84-day ($p > 0.3$ in all cases), especially for Cu and Pb.

Copper leachability closely followed its hydroxide profile (Stegemann, 2005). Hence, the leachability was similar in both treated and untreated soils since the pH of the untreated soil fell in the region for minimum Cu solubility (Fig. 2a). This corroborates Li et al. (2001) on the leaching behaviour of Cu being controlled by $\text{Cu}(\text{OH})_2$ since it is the dominant species formed in cement hydration process.

Similarly, Pb leachability followed that of its hydroxide and the leachate concentrations of the metal were well below the estimated limits of Stegemann (2005) (Fig. 2b). This corroborates reports by Stegemann (2005) that the concentrations of the metals used in this study in near-equilibrium laboratory leachates from S/S products generally do not exceed the theoretical solubility limits when metals precipitate as their single-metal hydroxide. The leaching pattern of Pb could be either due to the incorporation of the metal in the undissolved C-S-H matrix or its precipitation as Pb silicate compounds (Halim et

al., 2003). The metal exhibited the usual characteristic amphoteric behaviour reported in the literature (Sanchez et al., 2000). The leachability of Pb in the mixes was at a minimum in the pH range 9.5–11.5, and it increased at pH > 11.5 (Fig. 2b). Hence, Pb leachability increased with increase in binder dosage in the highly alkaline pH region, which corroborates reports by Akhter et al (1990) on problems with Pb immobilisation using CEM I. Further, in the pH range 5.5–7.0, there was no marked difference between treated and untreated soils. Apart from pH 9.8, where the leachability of the treated soils was slightly less than that of the untreated soil, a comparison of treated and untreated soils does not show clear evidence of chemical immobilisation of Pb by CEM I (Fig. 2b). Sanchez et al. (2000) reported a similar observation.

The leachability of Ni did not strictly follow its hydroxide profile as the leachate concentrations of the metal was higher than the estimated limits of Ni(OH)₂ solubility profile in majority of the mixes (Fig. 2c). It is documented that the presence of complexing agents or dissolved organic matter could sometimes lead to unexpectedly high metal solubility. A similar behaviour also occurs when metals do not precipitate as their single-metal hydroxides but form other phases or other mixed hydroxides (Stegemann, 2005). In the light of the above, it is likely that Ni did not precipitate as its single hydroxide in most of the mixes. Christensen et al. (1996) reported that at high pH values, chloro-complexes were negligible but carbonate complexes accounted for > 90% of soluble Ni. Thus, the higher solubility of NiCO₃ over that of Ni(OH)₂ may probably be responsible for the higher solubilities of Ni in the mixes. However, there were exceptions to the above in 15% and 20% CEM I dosage mixes at 0 and 1 meq/g acid addition (pH 12–13), where probably due to incorporation into the crystalline phases of the cementitious material, the leachate concentrations were lower than the estimated limits of Ni(OH)₂ (Stegemann, 2005). In support of the probable chemical immobilisation mechanism above, the leachability of the said mixes and that of some lower binder dosage mixes was also less than that of the untreated soil by up to an order of magnitude at the same pH (Fig. 2c).

Zinc leachability clearly followed its hydroxide profile with concentrations well below the estimated solubility limits. This corroborates reports by Poon et al. (1985) that in cement-based fixation processes, most of the Zn is precipitated as the hydroxide. The leachability of the metal in treated soils increased at pH > 11 in line with the solubility profile of Zn(OH)₂ (Fig. 2d). There was evidence of chemical immobilisation of Zn at pH ≥ 9.8, when the leachability of most mixes of the treated soil was less than that of the untreated soil at roughly the same pH. This was probably by incorporation of the metals into the crystalline phases of the cementitious matrix. The same behaviour was observed for Ni at pH 9.8 (comparing Fig. 2c with Fig. 2d), especially as the leachability of the metals in the wettest mix of 10% binder dosage was lower than that of 5% dosage at pH 9.8. Interestingly, Ni and Zn have minimum solubility in that pH zone.

There was no significant effect of pH and binder

dosage on TPH leachability although the 15% and 20% binder dosage mixes, whose values were the same, was marginally better than the lower binder dosage mixes (Fig. 2e). Besides being soluble in one another, petroleum hydrocarbons are generally characterised by insolubility under different conditions in single solvents. Hence, the leaching of TPH is not expected to be governed by the pH of the leachant. However, cement treatment reduces TPH leachability as generally, higher concentrations were leached from the untreated soil than treated soils especially in the alkaline pH region. All the same, TPH leachability in the treated soils was apparently influenced by increasing acidity as higher amounts was generally leached out at 1 and 2 meq/g acid addition than at zero acid addition. Bone et al. (2004) reported that in many cases, the solubility of an organic contaminant depends on the pH of the environment in which it is present. Although the exact mechanism for the apparent influence of pH on TPH leachability was not investigated, it is thought that increasing nitric acid concentration in aqueous solution tends to solubilise more hydrocarbon molecules. Hanson and Ismail (1975) reported a similar observation.

2.3 Monolithic leaching test

The pH and conductivity measurements during the test (results not shown) indicated that the binder matrix did not dissolve. Hence, the determination of the leaching mechanisms and the quantification of the leaching of components were meaningful. The cumulative measured and derived leaching of the metals is shown in Fig. 3. The data are for representative leachate samples from the entire leachant volume; hence, there is no margin of error associated with the individual points. The concentrations of metals leached out throughout the 64-day period were very low (Fig. 3). The low leachability of metals from the monoliths is probably due to the high alkalinity of the soil-binder system. The leachate concentrations were a little lower than those of Voglar and Leštan (2010), who used a higher binder dosage, although the concentrations of some metals were far greater than the concentrations used here. The leaching behaviour of amphoteric metals like Cu and Pb, whose concentrations were higher than those of the other metals (Fig. 3a and b), suggests the influence of pH on the leachate concentrations of the metals. It was even more pronounced in Pb, where higher concentrations were leached out from the 10% binder dosage OMC mix than the 5% dosage OMC mix. Soluble Pb and Cu hydroxide complexes can be formed at pH > 12 thus increasing Pb and Cu mobility. Voglar and Leštan (2010) reported a similar observation.

Table 1 shows the slopes and standard deviations determined in the increments described by NEN 7345 (Environment Agency, 2004) for determination of the leaching mechanisms involved. The slopes of the total increment (2–7) for the mixes were all < 0.35, with the exception of Cu release from the 5% dosage mix (Table 1). This indicates that the predominant mechanism of release was surface wash-off of contaminants otherwise physically encapsulated within the cementitious matrix.

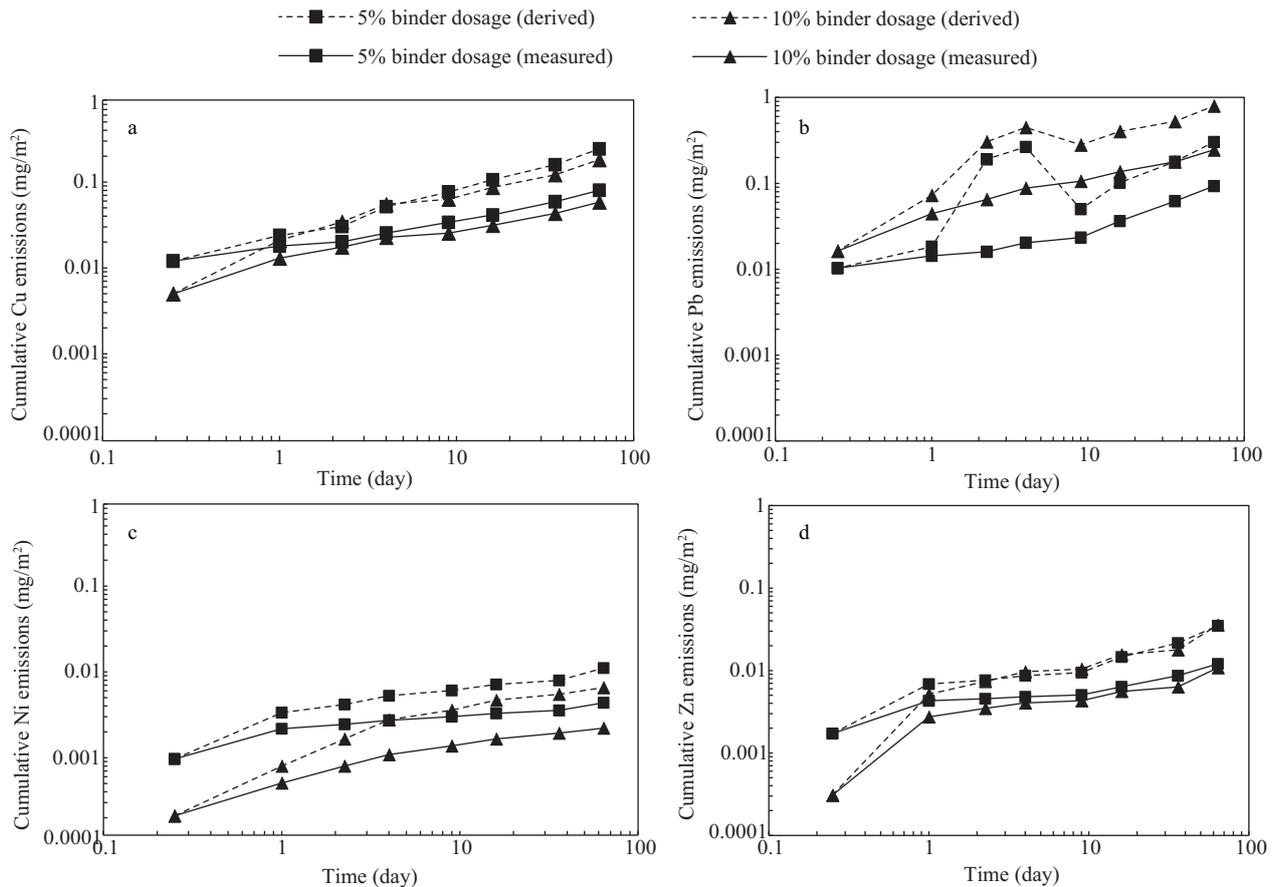


Fig. 3 Cumulative measured and derived leaching in cement-treated mixed contaminated soil of Cu (a), Pb (b), Ni (c), and Zn (d).

Voglar and Leštan (2010) reported the same observation. Nevertheless, Cu release from the 5% dosage mix was largely a diffusion-controlled process with a slope approximately 0.5. Moreover, the slopes in Table 1 also show that in increment 5–8, there was evidence of diffusion-controlled release of Ni in 5% dosage mixes. The same was observed for Pb in 10% dosage mixes in increment 1–4. Furthermore, the slopes of some increments indicate the possibility of dissolution of the components, which appears contrary to the finding that the test piece did not dissolve. This, however, need not be the case. It is concluded that viewed from the leaching mechanism of the matrix, the dissolution of the components has no permanent character, and it is possible that dissolution was

only occurring from the outer layer of the test piece (NEN 7375: Environment Agency, 2004).

2.4 Comparisons with performance thresholds

The typical performance thresholds for hydraulic conductivity and leachability of contaminants are summarised in Table 2. There are no established performance thresholds for ANC and contaminant leachability at specific pH values. Thus, performance thresholds for leachability of contaminants in Table 2 are based on the criteria for leachability at zero acid addition. Similarly, there are no established performance thresholds for porosity and TPH leachability; hence, they are not included in Table 2. More-

Table 1 Determination of the leaching mechanisms involved in CEM I mixes during the monolithic leaching test

Increment* a-b	Mix detail	Cu		Pb		Ni		Zn		Significance of slopes (rc) of increments		
		rc	Sd _{rc}	rc	Sd _{rc}	rc	Sd _{rc}	rc	Sd _{rc}	≤ 0.35	0.35 < rc ≤ 0.65	> 0.65
2-7	5% dosage	0.49	0.17	0.70	0.28	-0.20	0.15	0.26	0.48	Surface wash-off	Diffusion	Dissolution
	10% dosage	0.19	0.21	0.21	0.13	0.10	0.10	-0.12	0.33			
5-8	5% dosage	0.63	0.05	1.20	0.23	0.54	0.24	1.30	0.26	Depletion	Diffusion	Dissolution
	10% dosage	0.95	0.12	0.70	0.13	0.07	0.08	1.22	0.43			
4-7	5% dosage	0.41	0.06	0.82	0.32	-0.09	0.08	1.02	0.31	Depletion	Diffusion	Dissolution
	10% dosage	0.35	0.28	0.21	0.18	-0.09	0.08	0.20	0.40			
3-6	5% dosage	0.70	0.18	0.90	0.33	0.07	0.08	0.77	0.33	Depletion	Diffusion	Dissolution
	10% dosage	0.08	0.25	0.20	0.18	0.07	0.08	0.17	0.41			
2-5	5% dosage	0.46	0.24	0.20	0.26	-0.41	0.17	-0.78	0.30	Depletion	Diffusion	Dissolution
	10% dosage	-0.23	0.17	0.03	0.13	0.20	0.11	-0.78	0.12			
1-4	5% dosage	0.07	0.26	0.06	0.27	0.01	0.25	-0.30	0.40	Surface wash-off	Diffusion	Delayed diffusion or dissolution
	10% dosage	0.48	0.13	0.60	0.10	0.65	0.05	0.70	0.44			

rc: slope of the relevant increment; Sd_{rc}: standard deviation of the slope of the relevant increment. Criteria for diffusion controlled leaching in increment a-b: CF_{a-b} ≥ 1.5, Sd_{rc} ≤ 0.5, 0.35 < rc ≤ 0.65 CF_{a-b}: concentration factor in increment a-b, it was > 1.5 in all cases, hence it is not shown here.

* These are data points on Fig. 3.

Table 2 Performance thresholds for hydraulic conductivity and leachability of contaminants

Performance criteria	Hydraulic conductivity	Cu	Pb	Ni	Zn	Acceptable limits of operating variables
UK and USEPA hydraulic conductivity limit for in-ground treatment and landfill disposal, respectively ¹ (m/sec)	$< 10^{-9}$	N/A	N/A	N/A	N/A	None: higher binder dosages may be required to satisfy this threshold
Environment Canada WTC: Proposed hydraulic conductivity limit for landfill disposal scenarios ² (m/sec)	$< 10^{-8}$	N/A	N/A	N/A	N/A	$\geq 10\%$ binder dosage, water/solid around OMC. 5% dosage would satisfy if samples are moulded at the OMC
Environmental Quality Standard (EQS) for inland surface waters ³ (mg/kg)*	N/A	N/A	72	0.2	N/A	$\geq 5\%$ binder dosage, water/solid around OMC for Pb and Ni
Hazardous waste landfill WAC for granular leachability ⁴ (mg/kg)	N/A	100	50	40	200	$\geq 5\%$ binder dosage adequate for all metals, water/solid around OMC
Stable non-reactive hazardous waste in non-hazardous landfill WAC (granular leaching) ⁴ (mg/kg)	N/A	50	10	10	50	5% binder dosage adequate for all. With $> 5\%$ dosage, Pb exceeds limit due to the pH attained
Inert waste landfill WAC for granular leaching ⁴ (mg/kg)	N/A	2	0.5	0.4	4	$\geq 5\%$ binder dosage adequate for Cu, Ni and Zn; none for Pb due to pH attained
Monolithic WAC ⁴ (mg/m ²) for: hazardous waste	N/A	60	20	15	100	$\geq 5\%$ binder dosage adequate for all metals, water/solid around OMC
Non-reactive hazardous waste	N/A	45	6	6	30	OMC

¹Al-Tabbaa and Stegemann, 2005; ²Stegemann and Côté, 1996; ³Förstner, 2007; ⁴Environment Agency, 2006.

WTC : Wastewater Technology Centre; WAC: Waste Acceptance Criteria; N/A: not applicable.

* EQS is usually quoted in mg/L but is converted here for direct comparison purposes.

over, the results showed that there was no significant effect of binder dosage or water content on TPH leachability.

None of the mixes satisfied the 10^{-9} m/sec hydraulic conductivity threshold, higher binder dosages are required to satisfy that criteria. However, the 10^{-8} m/sec criterion of the Environment Canada WTC was satisfied with $\geq 10\%$ binder dosage (Table 2). Most of the waste acceptance criteria (WAC) for the different landfill disposal scenarios were met with 5% binder dosage. It was previously reported (Kogbara et al., 2010) that higher binder dosages would be required for the treated contaminated soil to pass the thresholds for the environmental quality standard (EQS) and the inert landfill WAC for Cd. The binder also had problems with meeting the stable non-reactive hazardous waste in non-hazardous landfill WAC for Pb as the pH attained at $> 5\%$ dosage falls within the zone for increase in Pb leachability. The same applies to the inert waste landfill WAC where only the driest mix of 5% dosage, which had improper binder hydration, met the leaching criteria. Hence, treatment with CEM I is unlikely to pass the said limit for Pb. Nevertheless, these observations might be unique to the soil considered due to its naturally high alkaline pH. The leaching behaviour might be different in non-calcerous soils with lower pH stabilised by the binder.

Furthermore, as noted earlier, there are no regulatory limits for metal leachability under different pH conditions. Nevertheless, the pH-dependent leachability data, coupled with the leaching trend observed with increasing binder dosage suggests that with a higher binder dosage ($> 20\%$); leaching criteria could still be met over a long time when acidic influences in the environment ultimately lowers the pH of the treated material to about pH 8 (Van Gerwen et al., 2006).

3 Conclusions

This work has shown the utility of CEM I for S/S treatment of soil contaminated with a mixture of organics and heavy metals. Scenarios where the binder would be effective and areas that present problems have been highlighted. The chemical immobilisation potentials of the binder for different metals have been shown and insights into the chemical durability of the S/S matrix provided. Generally, comparison of the results with those in the literature suggest that metal speciation in the mixed contamination scenario studied was similar to that obtained when only individual metals are present. In other words, the presence of other contaminants did not have much influence on the leaching behaviour of individual metals.

There was no significant effect of water content on contaminant leachability within the water content range for workability of the soil-cement mix. Naturally, the acceptable binder dosage limit for granular leachability is the threshold at which leaching criteria for all metals in the treated soil are satisfied. In the light of this, about 20% binder dosage is required to satisfy the most stringent leaching criteria, viz, the EQS for inland surface waters and the inert waste landfill WAC. However, the presence of Pb brings about problems as low binder dosage may satisfy certain leaching criteria but higher dosage may not, especially where the pH attained by higher binder dosages corresponds to the zone for increased Pb leachability. Thus, the binder may not be suitable for similar soils with high concentrations of Pb destined for the stable non-reactive hazardous and inert waste landfills. Overall, the results showed that compacting samples around the OMC leads to the best mechanical and leaching performance of

the treated soils. Furthermore, although only one contaminant concentration was considered in this work and heavy metal leachability also varies with its initial concentration in soil; it is thought that the findings of the research would serve as baseline for future in-depth studies in the area including validation for other concentrations.

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References

- Akhter H, Butler L G, Branz S, Cartledge F K, Tittlebaum M E, 1990. Immobilization of As, Cd, Cr and Pb-containing soils by using cement or pozzolanic fixing agents. *Journal of Hazardous Materials*, 24(2-3): 145–155.
- Al-Rawas A, Hassan H F, Taha R, Hago A, Al-Shandoudi B, Al-Suleimani Y, 2005. Stabilization of oil-contaminated soils using cement and cement by-pass dust. *Management of Environmental Quality: An International Journal*, 16(6): 670–680.
- Al-Tabbaa A, Evans C W, 2000. Pilot in situ auger mixing treatment of a contaminated site. Part 3. Time-related performance. *Proceedings of the Institution of Civil Engineers, Geotechnical Engineering*, 143: 103–114.
- Al-Tabbaa A, Stegemann J A, 2005. Stabilisation/solidification treatment and remediation. In: Proceedings of the International Conference. April, Taylor and Francis, London.
- ASTM D1633-00, 2000. Standard Test Method for Compressive Strength of Molded Soil-Cement Cylinders. American Society for Testing of Materials, West Conshohocken.
- Bone B D, Barnard L H, Boardman D I, Carey P J, Hills C D, Jones H M et al., 2004. Review of scientific literature on the use of stabilisation/solidification for the treatment of contaminated soil, solid waste and sludges. UK Environment Agency Science Report SC980003/SR2, Bristol.
- British Standards Institution (BSI). BS EN 12457: Part 2, 2002. Characterisation of waste. Leaching. Compliance test for leaching of granular waste materials and sludges. One stage batch test at a liquid to solid ratio of 10 L/kg for materials with particle size below 4 mm (without or with size reduction). BSI, London.
- Christensen T H, Lehmann N, Jackson T, Holm P E, 1996. Cadmium and nickel distribution coefficients for sandy aquifer materials. *Journal of Contaminant Hydrology*, 24(1): 75–84.
- Conner J R, 1997. Guide to Improving the Effectiveness of Cement-Based Stabilization/Solidification. Report No. PCA EB 211, Portland Cement Association, Skokie, IL.
- Environment Agency, 2006. Guidance for waste destined for disposal in landfills, Version 2, interpretation of the waste acceptance requirements of the landfill (England and Wales) regulations (as amended). Available: <http://www.environment-agency.gov.uk/> (accessed May 2011).
- Environment Agency, 2004. NEN 7375: Leaching characteristics of moulded or monolithic building and waste materials – Determination of leaching of inorganic components with diffusion test – ‘The Tank Test’, Version 1.0, Environment Agency, Bristol, USA.
- Förstner U, 2007. Environmental quality standards (EQS) applicable to sediment and/or biota. *Journal of Soils and Sediments*, 7(4): 270.
- Glasser F P, 1997. Fundamental aspects of cement solidification and stabilisation. *Journal of Hazardous Materials*, 52(2-3): 151–170.
- Halim C E, Amal R, Beydoun D, Scott J A, Low G, 2003. Evaluating the applicability of a modified toxicity leaching procedure (TCLP) for the classification of cementitious wastes containing lead and cadmium. *Journal of Hazardous Materials*, 103(1-2): 125–140.
- Hanson C, Ismail H A M, 1975. Solubility and distribution data for benzene and toluene between aqueous and organic phases. *Journal of Applied Chemistry and Biotechnology*, 25(5): 319–325.
- Heathcote K, 1991. Compressive strength of cement stabilized pressed earth blocks. *Building Research and Information*, 19(2): 101–105.
- Kogbara R B, Al-Tabbaa A, 2011. Mechanical and leaching behaviour of slag-cement and lime-activated slag stabilised/solidified contaminated soil. *Science of the Total Environment*, 409(11): 2325–2335.
- Kogbara R B, Yi Y, Al-Tabbaa A, Stegemann J A, 2010. Process envelopes for stabilised/solidified contaminated soils: Initiation work. In: Proceedings of the 5th International Conference on Environmental Science & Technology (Sorrial G A, Hong J, eds.). Houston, Texas, July, American Science Press. Vol. 2: 90–96.
- Kogbara R B, Yi Y, Al-Tabbaa A, 2011. Process envelopes for stabilisation/solidification of contaminated soil using lime-slag blend. *Environmental Science and Pollution Research*, 18(8): 1286–1296.
- Kogbara R B, 2011. Process envelopes for and biodegradation within stabilised/solidified contaminated soils. PhD thesis, Cambridge University, UK.
- LaGrega M D, Buckingham P L, Evans J C, 2001. Environmental resources management. In: Hazardous Waste Management (2nd ed.). McGraw Hill, New York.
- Li X D, Poon C S, Sun H, Lo I M C, Kirk D W, 2001. Heavy metal speciation and leaching behaviours in cement based solidified/stabilized waste materials. *Journal of Hazardous Materials*, 82(3): 215–230.
- Lin S L, Cross W H, Chian E S K, Lai J S, Giabbai M, Hung C H, 1996. Stabilisation and solidification of lead in contaminated soils. *Journal of Hazardous Materials*, 48(1-3): 95–110.
- Moon D H, Lee J R, Grubb D G, Park J H, 2010. An assessment of Portland cement, cement kiln dust and Class C fly ash for the immobilization of Zn in contaminated soils. *Environmental Earth Sciences*, 61(8): 1745–1750.
- Poon C S, Peters C J, Perry R, 1985. Mechanisms of metal stabilization by cement based fixation processes. *Science of the Total Environment*, 41(1): 55–71.
- Reddy B V V, Kumar P P, 2010. Cement stabilised rammed earth. Part A: compaction characteristics and physical properties of compacted cement stabilised soils. *Materials and Structures*, 44(3): 681–693.
- Sanchez F, Barna R, Garrabrants A, Kosson D S, Moszkowicz P, 2000. Environmental assessment of a cement-based solidified soil contaminated with lead. *Chemical Engineering Science*, 55(1): 113–128.

- Spence R D, Shi C, 2005. Stabilization and Solidification of Hazardous, Radioactive and Mixed Wastes. CRC Press, Boca Raton, FL.
- Stegemann J A, Côté P L, 1991. Investigation of Test Methods for Solidified Waste Evaluation-Cooperative Program. Ottawa, Ontario: Environment Canada Report EPS 3/HA/8.
- Stegemann J A, Côté P L, 1996. A proposed protocol for evaluation of solidified wastes. *Science of the Total Environment*, 178(1-3): 103–110.
- Stegemann J A, 2005. Interactions between wastes and binders. In: Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes (Spence R D, Shi C, eds.). CRC Press, Boca Raton, FL. 151–176.
- Trussell S, Spence R D, 1994. A review of solidification/stabilisation interferences. *Waste Management*, 14(6): 507–519.
- USEPA (United States Environmental Protection Agency), 1986. Test methods for evaluating solid waste: physical/chemical methods. In: USEPA Office of Solid Waste and Emergency Response (OSWER) Publication No. SW-846, 3rd ed. Washington DC.
- van der Sloot H A, 2003. Horizontal standardization and harmonization of leaching test methods for waste, secondary raw materials, construction materials and (contaminated) soil. WASCON 2003, San Sebastian, Spain.
- van der Sloot H A, Comans R N J, Meeussen J C L, Dijkstra J J, 2003. Leaching methods for soil, sludge and treated biowaste. ECN Environmental Risk Assessment, Draft version 2. Available: http://www.ecn.nl/docs/society/horizontal/hor_desk_23_leaching2.pdf.
- Van Gerven T, Cornelis G, Vandoren E, Vandecasteele C, Garrabrants A C, Sanchez F et al., 2006. Effects of progressive carbonation on heavy metal leaching from cement-bound waste. *AIChE Journal*, 52(2): 826–837.
- Vítková M, Ettler V, Šebek O, Mihaljevi M, Grygar T, Rohovec J, 2009. The pH-dependent leaching of inorganic contaminants from secondary lead smelter fly ash. *Journal of Hazardous Materials*, 167(1-3): 427–433.
- Voglar G E, Leštan D, 2010. Solidification/stabilisation of metals contaminated industrial soil from former Zn smelter in Celje, Slovenia, using cement as a hydraulic binder. *Journal of Hazardous Materials*, 178(1-3): 926–933.
- Vreysen S, Maes, A, 2005. Remediation of a diesel contaminated, sandy-loam soil using low concentrated surfactant solutions. *Journal of Soils and Sediments*, 5(4): 240–244.
- Yılmaz O, Çokça O, Ünlü K, 2003. Comparison of two leaching tests to assess the effectiveness of cement-based hazardous waste solidification/stabilization. *Turkish Journal of Engineering and Environmental Science*, 27: 201–212.
- Yoon S, Abu-Farsakh M, 2009. Laboratory investigation on the strength characteristics of cement-sand as base material. *KSCE Journal of Civil Engineering*, 13(1): 15–22.