Mechanical and leaching behaviour of slag-cement and lime-activated slag stabilised/solidified contaminated soil

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Abstract

Stabilisation/solidification (S/S) is an effective technique for reducing the leachability of contaminants in soils. Very few studies have investigated the use of ground granulated blast furnace slag (GGBS) for S/S treatment of contaminated soils, although it has been shown to be effective in ground improvement. This study sought to investigate the potential of GGBS activated by cement and lime for S/S treatment of a mixed contaminated soil. A sandy soil spiked with 3,000 mg/kg each of a cocktail of heavy metals (Cd, Ni, Zn, Cu and Pb) and 10,000 mg/kg of diesel was treated with binder blends of one part hydrated lime to four parts GGBS (lime-slag), and one part cement to nine parts GGBS (slag-cement). Three binder dosages, 5, 10 and 20% (m/m) were used and contaminated soil-cement samples were compacted to their optimum water contents. The effectiveness of the treatment was assessed using unconfined compressive strength (UCS), permeability and acid neutralisation capacity (ANC) test with determination of contaminant leachability at the different acid additions. UCS values of up to 800 kPa were recorded at 28 d. The lowest coefficient of permeability recorded was 5×10^{-9} m/s. With up to 20% binder dosage, the leachability of the contaminants was reduced to meet relevant environmental quality standards and landfill waste acceptance criteria. The pH-dependent leachability of the metals decreased over time. The results show that GGBS activated by cement and lime would be effective in reducing the leachability of contaminants in contaminated soils.

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Keywords: blast furnace slag; cement; mixed contamination; lime; pH-dependent leaching; stabilization/solidification.

1 **Introduction**

Soil contamination by organics and heavy metals from different chemical industries has received increased attention over the years. Stabilisation/solidification (S/S) basically involves the addition of cementitious binders to contaminated soils to cause physical encapsulation and fixation of contaminants within the binders. It is widely used for treatment of wastes and soils contaminated with heavy metals. With the use of additives like organo-clays and activated carbon, it has also been deployed for immobilisation of organic contaminants (LaGrega et al., 2001; Spence and Shi, 2005). Previous studies on contaminated soils have focused on Portland cement and blend of cement and other cementitious materials like pulverised fuel ash and lime (Conner and Hoeffner, 1998; Shi and Spence, 2004). However, there is need to promote sustainable reuse of industrial by-products like ground granulated blast furnace slag (GGBS) in contaminated land remediation.

GGBS is a by-product of the iron and steel industry. Molten slag is produced in the blast furnace where iron ore, limestone and coke are heated up to 1500°C. The molten slag is granulated by cooling it through high-pressure water jets. The granulated slag is dried and then ground to a very fine powder, which is GGBS (Higgins, 2005). GGBS has been utilised in many cement applications to provide enhanced durability, high resistance to chloride penetration and resistance to sulphate attack. It has also been used together with lime in ground improvement works where its incorporation into the blend is very effective in combating the expansion associated with the presence of sulphate or sulphide in the soil (Higgins, 2005). The use of GGBS has also enhanced the retention of many radionuclides in cementitious waste forms (Trussell and Spence, 1994). On its own, GGBS shows minimal hydration, therefore, it must be chemically activated by an alkaline medium to be useful for soil stabilisation. Portland cement and lime are among common activators listed in the literature (Nidzam and Kinuthia, 2010).

The use of large volumes of GGBS as cement replacement in concrete has attracted significant research attention due to its technical, economic and environmental benefits. The advantages of a well-proportioned mix of slag-cement include higher early and later strengths than Portland cement (CEMI) and better resistance in aggressive environments like immersion in water, acidic and sulphate solutions. It has been reported that heavy metals show much less interference with the hydration of slag-cement than with Portland cement. Further, the leachability of some contaminants (for e.g. As, Cr, Cu and Pb) from slag-cement stabilised hazardous and radioactive wastes is lower than that from Portland cement stabilised wastes (Shi and Jimenez, 2006). The strength of slag-cement depends on the mix proportion. The higher the replacement levels of GGBS in the mix, the lower the early strength. The optimum proportion of GGBS for maximum strength of slag-cement is between 50 - 60% of the total binder dosage (Khatib and Hibbert, 2005; Oner and Akyuz, 2007). Similarly, an optimum amount of lime is required for full hydration and pozzolanic reactions of lime-slag and for high strength, the amount of GGBS in the blend should be greater than the amount of lime. The optimum proportion for maximum strength is about one part lime and four parts GGBS (Higgins, 2005).

Very few studies have deployed both binder formulations for treatment of contaminated soils. The work of Akhter et al. (1990) documented positive effects on the use of both binder formulations in reducing the leachability of As, Cd, Cr and Pb, while Allan and Kukacka (1995) showed that slag-cement successfully stabilised Cr in toxicity characteristic leaching procedure (TCLP) tests. de Korte and Brouwers (2009) utilised a blend of lime and slag-cement and reported significant decrease in the leachability of low concentrations of Cd, Ni, Zn, Cu and Pb in monolithic leaching tests. The permeability of contaminated soils has also been found to decrease with increasing dosage of slag-cement (Allan and Kukacka, 1995). Previous studies dealt with leachability of contaminants within a 28 d period and a limited pH zone. However, cement reactions were found to continue beyond a 28 d curing time, which is a standardised curing period within the cement and concrete industries. Since hydration continues, there may be changes in release rates of contaminants from the treated material beyond this period and these must be considered when evaluating leaching data (Bone et al., 2004). Furthermore, the initial alkalinity of stabilised/solidified materials is neutralised over time by acidic influences in the environment. This would in turn affect metal leachability. For instance, in a co-disposed environment, the pH of landfill leachate typically lies between 5 and 8, depending on the age of the landfill (Halim et al., 2003). This informs the need for pH-dependent leaching behaviour of metals in slag-cement and lime-slag treated soils.

In our related study on the development of operating envelopes for lime-slag treatment of contaminated soil (Kogbara et al., unpublished), which involved different water contents, it was shown that compacting samples around the optimum moisture content (OMC) gives the best possible balance between acceptable mechanical (UCS and permeability) and leaching (Cd, Ni and petroleum hydrocarbons) properties. Hence, samples were compacted to the OMC in this study. The present study sought to compare the use of lime-slag and slag-cement for S/S treatment of a mixed contaminated soil. This paper considers the leachability of six contaminants, namely, Cd, Ni, Zn, Cu, Pb, and total petroleum hydrocarbons (TPH), which are among the regular contaminants found in soils. The contaminants are associated with carcinogenic, mutagenic, reproductive and teratogenic disorders, and they are known ecotoxins (Kabata-Pendias and Mukherjee 2007).

The effectiveness of the S/S treatment was evaluated in terms of compressive strength, permeability and pH-dependent leachability of the contaminants, and their variation over time. Some of the data presented in our related study on the lime-slag binder (Kogbara et al., unpublished) is duplicated here to facilitate comparison with slag-cement. As mentioned above, such information includes the UCS, permeability and leachability of Cd, Ni and TPH in OMC mixes of lime-slag stabilised soil. The objective of this study was to investigate the range of binder dosage that would lead to significant reduction in granular leachability of the contaminants.

2 **Materials and methods**

2.1 **Contaminated soil and binders**

A clayey silty sandy gravel comprising of 65% gravel, 29% sand, 2.8% silt and 3.2% clay was used. It was a real site soil contaminated with low levels of heavy metals and petroleum hydrocarbons, obtained from a Petrol station in Birmingham, UK. The natural water content of the soil was 12% and its pH was ~11.6. The unusual high pH of the soil was probably due to high calcium content (Hoyt and Neilsen, 1985) as preliminary leachability analysis indicated Ca, Na and Mg concentrations of 4,652, 30 and 64 mg/kg, respectively, at 2 meq/g HNO_3 addition. The soil had very low (0.22% m/m) organic carbon content. Soil particles < 20 mm was spiked in small batches of ~3kg with 3,000 mg/kg each of cadmium (using $Cd(NO_3)_2.4H_2O$), copper (using $CuSO_4.5H_2O$), lead (using $PbNO_3$), nickel (using $Ni(NO_3)_2.6H_2O$) and zinc (using $ZnCl_2$). The soil was also spiked with 10,000 mg/kg of diesel (from a local petrol station) in order to increase the concentration of contaminants to medium pollution levels found in soils.

Blends of CEMI (Lafarge, UK) and GGBS (UK Cementitious Slag makers Association, Surrey), and hydrated lime (Tarmac Buxton Lime and Cement, UK) and GGBS were used as binders. The binders comprised of 10% CEMI and 90% GGBS for slag-cement, and 20% hydrated lime and 80% GGBS for lime-slag. The mix proportions were chosen to be the same as those also used in parallel studies on S/S of metal filter cakes (Stegemann and Zhou, 2008) as part of the same ProCeSS (Process Envelopes for Cement-based Stabilisation/Solidification) project, whose screening and optimisation stage showed good leachability results for the blends, and with relevant literature. Thus, the slag-cement used contained higher proportion of GGBS in contrast to the optimum proportion for maximum strength previously mentioned since reduction in granular leachability is considered as the most important practical performance parameter from an industrial perspective. The physico-chemical properties of the constituents of the binders used, and the total concentrations of the contaminants recovered from the spiked contaminated soil are shown in Table 1.

2.2 **Stabilised/solidified product preparation**

The diesel was added to the soil first and thoroughly mixed, while the metallic compounds were dissolved in de-ionised water and then added to the mix. Further mixing was carried out until the mix appeared homogenous. The constituents of the binders were mixed together and de-ionised water added to form a paste. The binders were then added and mixed with the contaminated soil. The binder dosages used were 5, 10 and 20% (m/m).

The OMC of contaminated soil-binder mixtures was determined by standard Proctor compaction test (BSI, 1990), using a 2.5kg rammer. The compacted mix was then broken up and cast into cylindrical moulds, 50 mm diameter and 100 mm high. The S/S products were prepared at the maximum dry density (MDD) and OMC determined in the compaction test. The compaction parameters of the soil-binder mixtures are shown in Table 2. The moulded samples were demoulded after 3 d and cured at 95% relative humidity and 20°C until tested.

2.3 **Testing and analytical methods**

S/S products were tested for UCS, permeability and ANC with determination of contaminant leachability at different acid additions at some or all of 7, 28, 49 and 84 d. The testing programme started with low binder dosage (5%) with assessment of contaminant leachability, and the binder then increased until the leaching criteria were met. Hence, the performance parameters were not determined on 20% binder dosage mixes at all of the above curing ages.

The UCS was determined on triplicate samples, according to ASTM (2002), using a universal testing machine wherein the vertical load was applied axially at a constant strain rate of 1.143 mm/min until failure. The UCS was mainly conducted on samples without immersion, although 5 and 10% binder dosage mixes were tested after immersion. Water-saturated 49 d UCS data were obtained by curing samples as previously described for 42 d, and then immersing them in water for 7 d before UCS measurement. Permeability tests were carried out in flexible-wall permeameters (ASTM, 2003) using a confining pressure of 300 kPa and a constant flow rate, and the permeability calculated using Darcy's Law.

The ANC test was conducted on crushed UCS samples, according to Stegemann and Côté (1991) using 0, 1 and 2 meq/g HNO_3 acid additions. The pHs of the leachants were neutral, 1.10 and 0.85 for 0, 1 and 2 meq/g acid additions, respectively. The ANC without acid addition gives an estimate of the regulatory granular leaching test (BS EN12457-3). Both tests uses the same liquid:solid (L/S) ratio, but the former uses a smaller particle size and longer contact time than the latter resulting in higher leached concentrations. Crushed samples sieved to < 1.18 mm, were placed in 1 L glass bottles (due to the presence of diesel) with de-ionised water and 1 M HNO_3 to give a L/S ratio of 10:1 and the desired acid addition. The bottles were sealed and rotated end-over-end for 48-hours. The leachates were then allowed to settle and the pH determined. Leachates were filtered through 0.45 μm cellulose nitrate membrane filters (Whatman International Ltd.) for analysis of heavy metals using ICP-OES. While diesel in the water phase was directly extracted with hexane and the diesel extract in hexane analysed on the GC-FID following the procedure described by Vreysen and Maes (2005). The ANC test was also conducted on the untreated contaminated soil and the binders.

2.4 **Statistical analysis**

One and two-way ANOVA was used to test for differences in the performance of both binders due to the effects of binder dosage, curing age and acid addition. Significance was based on $\alpha = 0.05$.

3 **Results and discussion**

3.1 **UCS**

The UCS of slag-cement and lime-slag samples at different curing ages is shown in Fig. 1. The UCS of 20% dosage mixes was determined at only 7 and 28 days due to the reason given in section 2.3. The UCS values were quite low compared to values in the literature for uncontaminated soils. The contaminants used are known to cause deleterious effects on the UCS (Trussell and Spence, 1994). As expected, there were significant differences in UCS ($p < 0.001$) due to different binder dosages and curing ages in both binder systems. In spite of the high slag replacement level used in slag-cement, its strength over time was generally higher than that of lime-slag, with the exception of 20% dosage mixes. This corroborates the findings of Khatib and Hibbert (2005) on the potential of slag-cement for strength gain.

The 49 d UCS after immersion for 5 and 10% dosage mixes of slag-cement were 185 and 650 kPa, respectively. While those of lime-slag were 140 and 400 kPa for 5 and 10% dosage mixes, respectively. The values of the UCS after immersion for slag-cement are 14% lower and 37% higher than the UCS before immersion for 5 and 10% dosage mixes, respectively (see Fig. 1). Whereas, there was no appreciable difference between the UCS before and after immersion of lime-slag mixes. These results demonstrate that the stabilised materials have hardened chemically and were not susceptible to deleterious swelling reactions. They also support the influence of GGBS in improving resistance to aggressive environments noted in the literature.

3.2 **Permeability**

Fig. 2 shows the permeability of the mixes. The permeability of 5 and 10% dosage mixes was determined at 28 and 84 days, while that of 20% dosage mixes was determined at only 28 days in line with the objective of the testing programme noted in section 2.3. The permeability of the 5% dosage mix of slag-cement could not be determined due to breakage of the samples during testing. However, it was observed that higher moulding water content was required to enable determination of the permeability of 5% dosage mixes. The permeability results of slag-cement mixes corroborate the findings of Allan and Kukacka (1995). However, the permeability trend in lime-slag mixes was unclear. On one hand, there was significant increase ($p = 0.003$) in 28 d permeability with increasing binder dosage contrary to expectations that permeability would decrease with increasing binder dosage. On the other hand, 10% dosage mixes had a lower permeability than 5% dosage mixes at 84 d. A similar observation was reported by El-Rawi and Awad (1981) where the permeability of lime-stabilised sandy silty clay increased with increasing lime content. Hence, the presence of lime may be responsible for the observed permeability behaviour. Further work with more binder dosages is required to elucidate the effect of binder dosage on permeability of lime-slag. The permeability of 10 and 20% dosage slag-cement mixes was significantly lower (p = 0.01) than that of their lime-slag counterparts. The 84 d permeability of the mixes increased above the 28 d values. Similar increase in the permeability of cementitious systems due to the presence of contaminants has been reported (Trussell and Spence, 1994).

3.3 **ANC and leachability of contaminants**

The ANC tests on the binders showed that the pHs attained at 0, 1 and 2 meq/g HNO_3 addition were 12.60, 11.50 and 11.0, respectively for slag-cement and 12.94, 12.71 and 12.59, respectively, for lime-slag. Hence, the lime-slag formulation had a higher buffering capacity than the slag-cement. The leachability of all six contaminants in the S/S treated is shown in Fig. 3 - 8, for Cd, Ni, Zn, Cu, Pb and TPH, respectively. Each of the aforementioned figures contains four graphs numbered a – d, which are the leachability of the respective contaminants at 7, 28, 49 and 84 d, respectively. These are presented with the same vertical axis scale to show the leachability change over time. The leachability of 20% binder dosage mixes was determined at only 7 and 28 d due to the reason given in section 2.3. The amounts of contaminants leached from the contaminated soil before S/S treatment is also shown on the graphs for comparison purposes. It should be noted that leaching of the contaminated soil was done on the same day after spiking and leachability of contaminants measured thereafter. In other words, the data corresponding to the contaminated soil at the different curing ages in Fig. 3 - 8 are the same data as the leachability of the contaminated soil was not determined at the respective curing ages like the S/S treated soils. In the contaminant leachability versus pH graphs, each mix has three points, from left to right representing the leachate pH at 2, 1 and 0 meq/g acid additions. The solid lines on the metal leachability graphs are the theoretical pH-dependent solubility of the hydroxide a given metal (Spence and Shi, 2005).

The leachability of the metals in both binder systems demonstrated the well-known effect of the pH of the solution on metal solubility in the literature (Goumans et al., 1994; Spence and Shi, 2005). The effect of acid addition on leachate pH was more significant in slag-cement ($p < 0.001$) mixes than in lime-slag mixes ($p = 0.005$) due to their different buffering capacities. There were also significant differences in leachate pH due to differences in binder dosage ($p = 0.02$) in both soil-binder systems. Generally, leachability of all metals decreased with increasing pH up to about pH 11(±1), beyond which metal solubility increased with pH in line with the solubility of the metal hydroxides (Spence and Shi, 2005). Further, but for a few exceptions, metal leachability generally decreased with increase in binder dosage for both soil-binder systems. Slag-cement mixes generally leached out higher concentrations of the more mobile metals (Cd, Ni and Zn) than lime-slag mixes due to differences in leachate pH regime of both soil-binder systems (Fig. 3, 4 and 5).

The leached concentrations of the less soluble metals (Cu and Pb) were marginally lower in lime-slag mixes than in slag-cement mixes (Fig. 6 and 7). At 7 and 28 days, the pH regime of the 20% lime-slag dosage mix was such that it demonstrated the amphoteric behaviour of Cu and Pb leading to increased leached concentrations at high pH (11.5 - 12.5) (Fig. 6a, 6b, 7a and 7b). Thus, the leached concentrations were higher than the concentrations recorded in the corresponding slag-cement mix in the high pH region. There was no clear trend in TPH leachability between both soil-binder systems as slag-cement mixes recorded marginally lower leachability than lime-slag mixes at some curing ages and vice versa (Fig. 8).

It has been demonstrated 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. However, high metal solubility is sometimes observed in the presence of complexing agents or dissolved organic matter. The same observation can also be made when metals do not precipitate as their single-metal hydroxides but form other phases or other mixed hydroxides (Spence and Shi, 2005). The leached concentrations of Cd and Zn were higher than the theoretical solubility limits of Cd and Zn hydroxides in 5 and 10% dosage mixes of both binder systems (Fig. 3 and 5). However, with 20% dosage of both binders, the leached concentrations of both metals were lower than the theoretical solubility limits and they closely followed the hydroxide solubility profiles as pH varied. The influence of dissolved organic carbon (DOC) on the mobility of the metals is negligible as the soil contained very low organic matter and the contribution of diesel to DOC was found to be negligible. Thus, in the light of the above position of Spence and Shi (2005), it is implied that the metals may not have precipitated as their single-metal hydroxides in the lower binder (5 and 10%) dosage mixes. The leachability recorded in the 20% binder dosage mixes agrees with Halim et al. (2003) that with higher binder dosages, more $Cd(OH)_2$ precipitate may be incorporated or absorbed onto the calcium silicate hydrate (C-S-H) structure of the cementitious material thereby resulting in a lower Cd concentration. Overall, the behaviour of the mixes corroborates the findings of previous studies that Cd typically exists as its hydroxide in cementitious systems although it may also exist as cadmium carbonate (Halim et al., 2004), and in cement-based fixation processes, most of the Zn is precipitated as the hydroxide (Poon et al., 1985) depending on the formulation of the mixes.

The leachability of Ni in all mixes of both binder systems was well above the theoretical solubility limits of $Ni(OH)_2$ although that of the 20% lime-slag dosage mix was closer to the limits and more closely followed the hydroxide solubility profile in the high pH (11 – 12.5) region (Fig. 4a and 4b). It has been reported that at high pHs, chloro-complexes were negligible but carbonate complexes accounted for > 90% of soluble Ni (Christensen et al., 1996). This may probably account for the higher solubilities of Ni in the mixes.

The leachability of Cu more closely followed its hydroxide profile in both binder systems as pH varied. Hence, Cu leachability in the untreated soil was similar to that of treated soils especially at zero acid addition since the pH of the untreated soil fell in the region for minimum Cu solubility (Fig. 6). However, with acid addition, higher concentrations of Cu were leached out of the untreated soil than the treated soil. This is in agreement with Li et al. (2001) that $Cu(OH)_2$ could be the dominant species formed in cement hydration process, hence, it controls the leaching behaviour of Cu during leaching tests. The leachability of Pb followed that of its hydroxide especially as the leached concentrations of the metal were well below its hydroxide solubility limits (Fig. 7). Halim et al. (2003) made a similar observation and noted that this could be either due to the incorporation of Pb in the undissolved C-S-H matrix or the precipitation of Pb as Pb silicate compounds. The pH regime of the 20% lime-slag mix was such that it demonstrated the amphoteric behaviour of Pb as leachability at zero acid addition was higher than with acid addition and it was more pronounced at 28 d (Fig. 7a and 7b) but that was not the case with the corresponding slag-cement mix. There was no significant effect of binder dosage or pH on the leaching trend of TPH in both binder systems. However, 1 and 2 meq/g acid addition to the mixes was found to mobilise higher amounts of TPH than zero acid addition (Fig. 8), which agrees with Bone et al. (2004) that in many cases, the solubility of an organic contaminant depends on the pH of the environment in which it is present. TPH leachability in the treated soils was generally lower than in the untreated soil.

Generally, there was no clear trend in leachability of the contaminants between 7 and 28 d curing ages as in some cases, the leachability of contaminants in some mixes was higher at 7 d than at 28 d and vice versa. This was probably due to on-going hydration of the cementitious materials during that period. Such fluctuations in leachability may be due to slight differences in replicate samples used at different curing ages, as it was impossible to perfectly recreate conditions from one sample to the next. The 49-day leachability of the metals was also not significantly different from the 7 and 28-d values. However, at 84 d there was a drastic reduction in the leachability of the more mobile metals (Cd, Ni and Zn) below the 49-d values in 5 and 10% slag-cement dosage mixes, especially in the lower pH region (Fig. 3[a – d] to 5[a – d]). At 1 and 2 meq/g acid addition, the reduction was about an order of magnitude. Artemis et al (2010) made a similar observation for Zn in a 4-year old cement-stabilised soil compared to the historical stabilised soil. Similar reduction in concentration of the metals also occurred in lime-slag mixes, but it was less pronounced than in slag-cement mixes. There was no marked increase or decrease in the leachability of the less soluble metals (Cu and Pb) and TPH over time in both binder systems (Fig. 6[a – d] to 8[a – d]).

Furthermore, in contrast to the leaching behaviour at the standardised curing age of 28 d, Fig. 3, 4 and 5 shows that slag-cement mixes leached out lower concentrations of the more soluble metals than did their lime-slag counterparts at 84 d, in the lower pH (5.5 – 8.5) region. It has been reported that slag-cement exhibits superior mechanical performance over time since the pozzolanic reaction is slow and the formation of calcium hydroxide requires time (Oner and Akyuz, 2007). The findings of this study extend the same position to the leaching behaviour over time.

3.4 **Comparisons with regulatory limits**

There are no established regulatory limits for pH-dependent metal leachability as well as for TPH leachability. Thus, regulatory limits on metal leachability are based on samples without acid addition. The 28-day leachability data of the metals at zero acid addition is shown in Table 3 to facilitate easy comparison with regulatory limits. Table 4 shows the binder dosages of both soil-binder systems required to pass typical regulatory limits for compressive strength, permeability and leachability. The unit of the environmental quality standard (EQS) for Cd, Ni and Pb in inland surface waters is given in mg/l. Hence, for comparison, the leachability data in mg/kg should be divided by a factor of 10 – the L/S ratio used in the test – to get the corresponding values in mg/l. Generally, the range of binder dosage considered in this work would be adequate to meet most of the required regulatory limits. The exceptions are the UK Environment Agency UCS and permeability limits for landfill disposal and in-ground treatment, respectively. Higher binder dosages may also be required for the slag-cement formulation used to clearly pass the EQS for Cd and Ni in inland surface waters (Table 4). While, < 20% lime-slag dosage (Table 4) is required to pass the more stringent landfill waste acceptance criteria (WAC) (i.e. for the stable non-reactive hazardous waste and the inert waste landfills) for Pb as the pH regime attained with 20% lime-slag dosage falls in the region for increased Pb solubility. Hence, the binder is not suitable for treatment of similar Pb-laden contaminated soils destined for such landfills.

In certain cases, the 28-day leachability values of some mixes did not satisfy leaching criteria but the values at other curing ages did. For example, the 20% mix of slag-cement did not satisfy the EQS for Cd and Ni at 28 days but did so at 7 days (compare Fig. 3a, 3b, 4a and 4b, and Table 4). The same applies to the 10% lime-slag dosage mix for Cd for the stable non-reactive hazardous landfill WAC (compare Fig. 3a and 3b, and Table 4). This is indicative of the likelihood of such mixes also passing the leaching criteria considering the possibility for imperfections in samples at one or two testing times.

It should be noted that field scenario would involve soil with weathered contaminants as opposed to fresh contamination used here. Freshly contaminated soils are more likely to leach out higher concentrations of contaminants than would their weathered counterparts. Moreover, soils with weathered petroleum hydrocarbons are more likely to have higher UCS than soils with fresh hydrocarbon pollution. Hence, the results of these experiments provide a conservative estimate of the compressive strength, and a higher estimate of the leachability, that would be obtained in field situations.

4 **Conclusions**

This study has shown that GGBS activated by cement and lime could effectively reduce the leachability of the contaminants studied from contaminated soils. The strengths and weaknesses of the binder formulations used, with respect to the mechanical and leaching behaviour of the S/S treated soil, has also been shown. The results of the study suggest that with lower proportion of GGBS in slag-cement, the binder is likely to perform better than lime-slag over time in terms of mechanical behaviour since the proportion used here was based on screening and optimisation for leaching behaviour. Overall, slag-cement was observed to be more effective for Pb immobilisation than lime-slag as higher (20%) lime-slag dosage would increase Pb leachability above acceptable limits. The leaching behaviour observed over an 84-day period is promising for long-term behaviour of the treated soils.

This study sought to investigate the minimum binder dosage at which most leaching criteria would be satisfied. Generally, improved mechanical and leaching properties were observed with increasing binder dosage, except for the permeability and Pb leachability of lime-slag. Hence, the findings of the study imply that, depending on the types of contaminants present, with higher (> 20%) binder dosages, soils treated by the binders especially slag-cement could be put to beneficial uses, like redevelopment for housing purposes or as fill material in road construction.

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References

Akhter H, Butler LG, Branz S, Cartledge FK, Tittlebaum ME. Immobilization of As, Cd, Cr and Pb-containing soils by using cement or pozzolanic fixing agents. J Hazard Mater 1990; 24: 145–55.

Allan ML, Kukacka LE. Blast furnace slag-modified grouts for in situ stabilization of chromium-contaminated soil. Waste Manag 1995; 15: 193–202.

Al-Tabbaa A, Stegemann JA, editors. Stabilisation/solidification treatment and remediation. Proceedings of the International Conference, April. London: Taylor and Francis; 2005.

Artemis A, Hills CD, Carey PJ, Magnie M-C, Polettini A. Investigation of 4-year-old stabilised/solidified and accelerated carbonated contaminated soil. J Hazard Mater 2010; 181: 543–55.

ASTM Test Method D1633-00. Standard method for compressive strength of moulded soil–cement cylinders, 04.08(I): 161 – 164. West Conshohocken: American Society for Testing of Materials; 2002.

ASTM D 5084-03. Standard test methods for measurement of hydraulic conductivity of saturated porous materials using a flexible wall permeameter. West Conshohocken: American Society for Testing of Materials; 2003.

Bone BD, Barnard LH, Boardman DI, Carey PJ, Hills CD, Jones HM, et al. Review of scientific literature on the use of stabilisation/solidification for the treatment of contaminated soil, solid waste and sludges. Bristol: UK Environment Agency Science Report SC980003/SR2; 2004.

BS 1377: Part 4. Methods of test for soils for civil engineering purposes: Compaction-related tests. London: British Standards Institution; 1990.

Christensen TH, Lehmann N, Jackson T, Holm PE. Cadmium and nickel distribution coefficients for sandy aquifer materials. J Contam Hydrol 1996; 24: 75 – 84.

Conner JR, Hoeffner SL. A critical review of stabilization/solidification technology. Crit Rev Environ Sci Tech 1998; 28: 397-462.

de Korte ACJ, Brouwers HJH. Production of non-constructive concrete blocks using contaminated soil. Constr Build Mater 2009; 23: 3564–78.

El-Rawi MN, Awad AAA. Permeability of lime stabilized soils. J Trans Eng Div ASCE 1981; 107: 25–35.

Environment Agency. Guidance for waste destined for disposals in landfills, Version 2, Interpretation of the waste acceptance requirements of the landfill (England and Wales) regulations (as amended); 2006. <http://www.environment-agency.gov.uk/>. (accessed October 2010).

Förstner U. Environmental quality standards (EQS) applicable to sediment and/or biota. J Soils Sediments 2007; 7: 270.

Goumans JJJM, van der Sloot HA, Aalbers ThG, editors. WASCON: Environmental aspects of construction with waste materials. Amsterdam: Elsevier; 1994.

Halim CE, Amal R, Beydoun D, Scott DA, Low G. Evaluating the applicability of a modified toxicity leaching procedure (TCLP) for the classification of cementitious wastes containing lead and cadmium. J Hazard Mater 2003; B103: 125–40.

Halim CE, Amal R, Beydoun D, Scott DA, Low G. Implications of the structure of cementitious wastes containing Pb(II), Cd(II), As(V), and Cr(VI) on the leaching of metals. Cement Concrete Res 2004; 34: 1093 – 1102.

Higgins DD. Soil stabilisation with ground granulated blastfurnace slag, UK Cementitious Slag makers Association report. Available: http://www.ecocem.ie/downloads/Soil_Stabilisation.pdf?PHPSESSID=5ec729224273596073a6071e4f56075d; 2005. (accessed October 2010).

Hoyt PB, Neilsen GH. Effects of soil pH and associated cations on growth of apple trees planted in old orchard soil. Plant Soil 1985; 395 – 401.

Kabata-Pendias A, Mukherjee AB. Trace elements from soil to human. Berlin: Springer; 2007.

Khatib JM, Hibbert JJ. Selected engineering properties of concrete incorporating slag and metakaolin. Constr Build Mater 2005; 19: 460–72.

Kogbara RB, Yi Y, Al-Tabbaa A. Process envelopes for stabilisation/solidification of contaminated soil using lime-slag blend. Environ Sci Pollut R (submitted for publication).

LaGrega MD, Buckingham PL, Evans JC, Environmental resources management. Hazardous waste management. 2nd ed. New York: McGraw Hill; 2001.

Li XD, Poon CS, Sun H, Lo IMC, Kirk DW. Heavy metal speciation and leaching behaviours in cement based solidified/stabilized waste materials. J Hazard Mater 2001; A82: 215 – 30.

Nidzam RM, Kinuthia JM. Sustainable soil stabilisation with blastfurnace slag: a review. Proc Inst Civ Eng Constr Mater 2010; 163: 157–65.

Oner A, Akyuz S. An experimental study on optimum usage of GGBS for the compressive strength of concrete. Cement Concrete Comp 2007; 29: 505–14.

Poon CS, Peters CJ, Perry R. Mechanisms of metal stabilisation by cement based fixation processes. Sci Total Environ 1985; 41: 55 – 71.

Shi C, Jimenez F. Stabilization/solidification of hazardous and radioactive wastes with alkali-activated cements. J Hazard Mater 2006; B137: 1656–63.

Shi C, Spence R. Designing of cement-based formula for solidification/stabilisation of hazardous, radioactive, and mixed wastes. Crit Rev Environ Sci Tech 2004; 34: 391-417.

Spence RD, Shi C, editors. Stabilization and solidification of hazardous, radioactive and mixed wastes. Boca Raton, FL: CRC Press; 2005.

Stegemann JA, Zhou Q. Development of process envelopes for cement-based stabilisation/solidification of metal treatment filtercakes. In: Zamorano M, Popov V, Kungolos AG, Brebbia CA, Itoh H, editors. Waste management and the environment IV, WIT Transactions on Ecology and the Environment, Vol. 109. Southampton: WIT Press; 2008. p. 21 – 30.

Stegemann JA, Côté PL. A proposed protocol for evaluation of solidified wastes. Sci Total Environ 1996; 178: 103–110.

Stegemann JA, Côté PL. Investigation of test methods for solidified waste evaluation – cooperative program. Ottawa, Ontario: Environment Canada Report EPS 3/HA/8; 1991.

Trussell S, Spence RD. A review of solidification/stabilisation interferences. Waste Manag 1994; 14: 507–19.

Van der Sloot HA. Developments in evaluating environmental impact from utilisation of bulk inert wastes using laboratory leaching tests and field verification. Waste Manag 1996; 16: 65–81.

Vreysen S, Maes A. Remediation of a diesel contaminated, sandy-loam soil using low concentrated surfactant solutions. J Soils Sediments 2005; 5(4): 240 – 244.

Table 1. Physico-chemical properties of binder constituents and contaminated soil

Property / composition	Hydrated lime	GGBS	Portland cement	Contaminated soil
Bulk density (kg/m^3)	470 – 520	1,200	1,300 – 1,450	-
Specific gravity	2.30 – 2.40	2.90	3.15	2.50
Specific surface area (m^2/kg)	1,529	350	-	-
Colour	White	off-white	Grey	-
pH (1:5)	12.85	11.79	12.80	9.83
CaO (%)	-	40	63.6	-
$Ca(OH)_2$ (%)	96.9	-	-	-
SiO_2 (%)	-	35	13.9	-
MgO (%)	-	8	0.6	-
$Mg(OH)_2$ (%)	0.5	-	-	-
Al_2O_3 (%)	-	13	10.2	-
$CaCO_3$ (%)	1.4	-	-	-
$CaSO_4$ (%)	0.03	-	-	-
Fe_2O_3 (%)	-	-	2.7	-
K_2O (%)	-	-	0.9	-
TiO_2 (%)	-	-	0.1	-
SO_3 (%)	-	-	6.9	-
Cd (mg/kg)	-	-	-	3,467 ± 153
Ni (mg/kg)	-	-	-	3,567 ± 153
Zn (mg/kg)	-	-	-	4,233 ± 289
Cu (mg/kg)	-	-	-	3,167 ± 231
Pb (mg/kg)	-	-	-	3,733 ± 208
TPH (mg/kg)	-	-	-	6,312 ± 1,486

Table 2. Compaction parameters of soil-binder mixtures

Binder dosage (%)	Slag-cement		Lime-slag	
	OMC (%)	MDD (Mg/m^3)	OMC (%)	MDD (Mg/m^3)
5	16	1.78	18	1.74
10	17	1.78	15	1.77
20	15	1.84	14	1.87

Table 3. 28-day Concentrations of metals at zero acid addition for comparison with regulatory limits

	Cd (mg/kg)		Ni (mg/kg)		Zn (mg/kg)		Cu (mg/kg)		Pb (mg/kg)	
Binder dosage (%)	**Slag-cement**	**Lime-slag**	**Slag-cement**	**Lime-slag**	**Slag-cement**	**Lime-slag**	**Slag-cement**	**Lime-slag**	**Slag-cement**	**Lime-slag**
5	30.0	8.9	24.0	17.0	27.0	13	3.1	1.6	0.56	0.26
10	37.0	1.6	36.0	8.2	43.0	2.2	12.0	1.6	0.74	0.22
20	0.24	0.02	0.61	0.17	0.81	1.2	0.49	1.6	0.02	31

Table 4. Regulatory limits for mechanical and leaching behaviour

Performance criteria	UCS	Permeability	Cd	Ni	Zn	Cu	Pb	Binder dosage passing the limit	
								Slag-cement	Lime-slag
Environment Canada WTC: Proposed UCS before immersion for controlled utilisation[1] (kPa)	440	N/A	N/A	N/A	N/A	N/A	N/A	10%	between 10 and 20%
UK Environment Agency: 28 d UCS limit for disposal of S/S treated wastes in landfills[2] (kPa)	1,000	N/A	N/A	N/A	N/A	N/A	N/A	> 20%	> 20%
UK and USEPA permeability limit for in-ground treatment and landfill disposal, respectively[3] (m/s)	N/A	$< 10^{-9}$	N/A	N/A	N/A	N/A	N/A	> 20%	not clear, further work required
Environment Canada WTC: Proposed permeability limit for landfill disposal scenarios[2] (m/s)	N/A	$< 10^{-8}$	N/A	N/A	N/A	N/A	N/A	between 10 and 20%	not clear, further work required
Environmental Quality Standard for inland surface waters[4] (mg/l)	N/A	N/A	0.0045	0.02	N/A	N/A	7.2	20% *likely* for Cd and Ni, 5% for Pb	20% for Cd and Ni, 5% for Pb
Hazardous waste landfill WAC for granular leachability[2] (mg/kg)	N/A	N/A	5	40	200	100	50	20% for Cd, 5% for all other metals	10% for Cd 5% for all other metals
Stable non-reactive hazardous waste in non-hazardous landfill WAC (granular leaching)[2] (mg/kg)	N/A	N/A	1	10	50	50	10	20% for Cd and Ni 5% for Zn, Cu and Pb	10% *likely* for Cd, 10% for Ni, 5% for Zn and Cu, 5 – 10% but < 20% for Pb
Inert waste landfill WAC for granular leaching[2] (mg/kg)	N/A	N/A	0.04	0.4	4	2	0.5	Generally, 20% for all metals	20% for Cd and Ni, 10% for Zn, 5% for Cu, 5 – 10% but < 20% for Pb

[1] Stegemann and Côté (1996)
[2] Environment Agency (2006)
[3] Al-Tabbaa and Stegemann (2005)
[4] Förstner (2007)

WTC: Wastewater Technology Centre
WAC: Waste acceptance criteria
N/A: not applicable

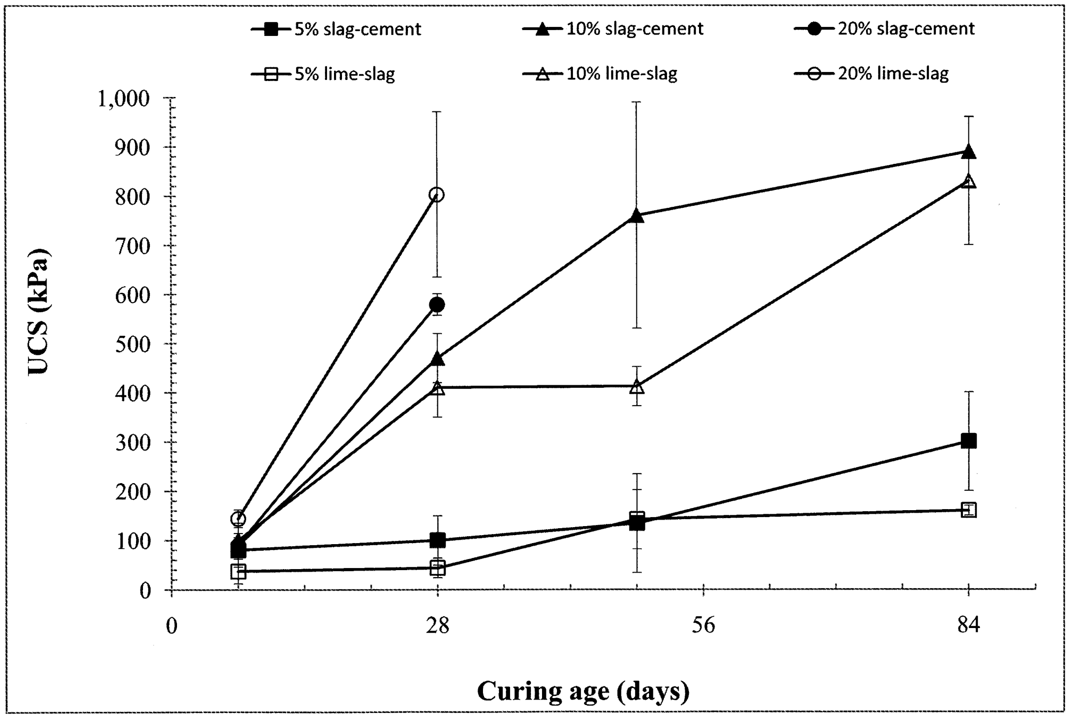


Figure 1. UCS of slag-cement and lime-slag mixes

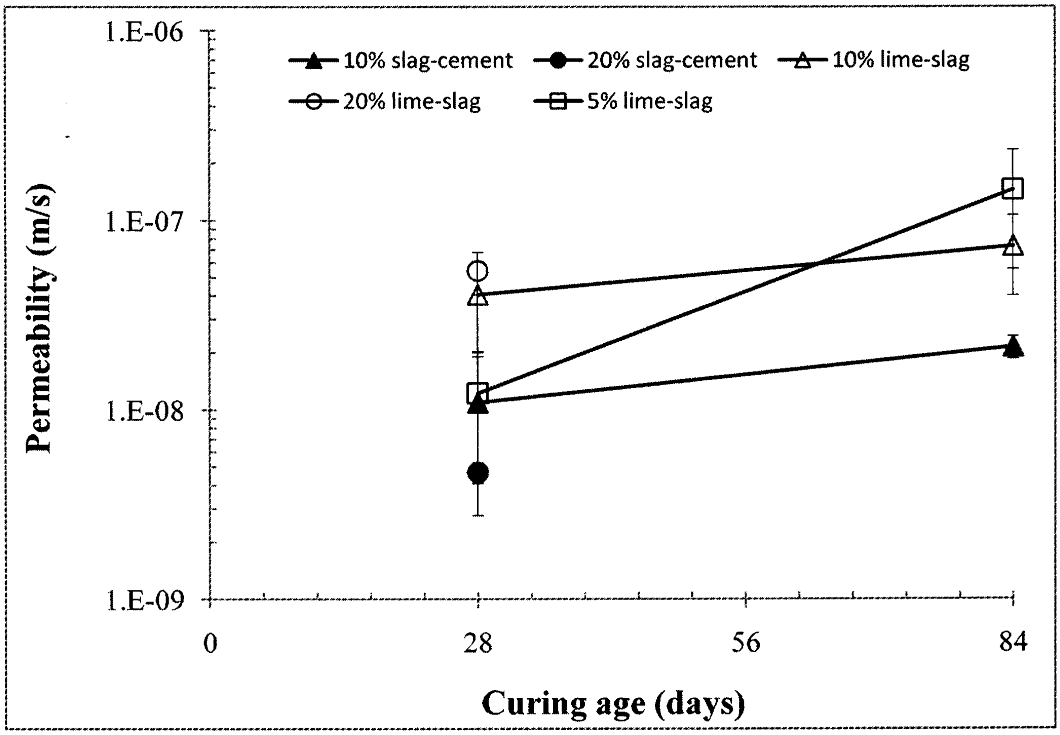


Figure 2. Permeability of slag-cement and lime-slag mixes

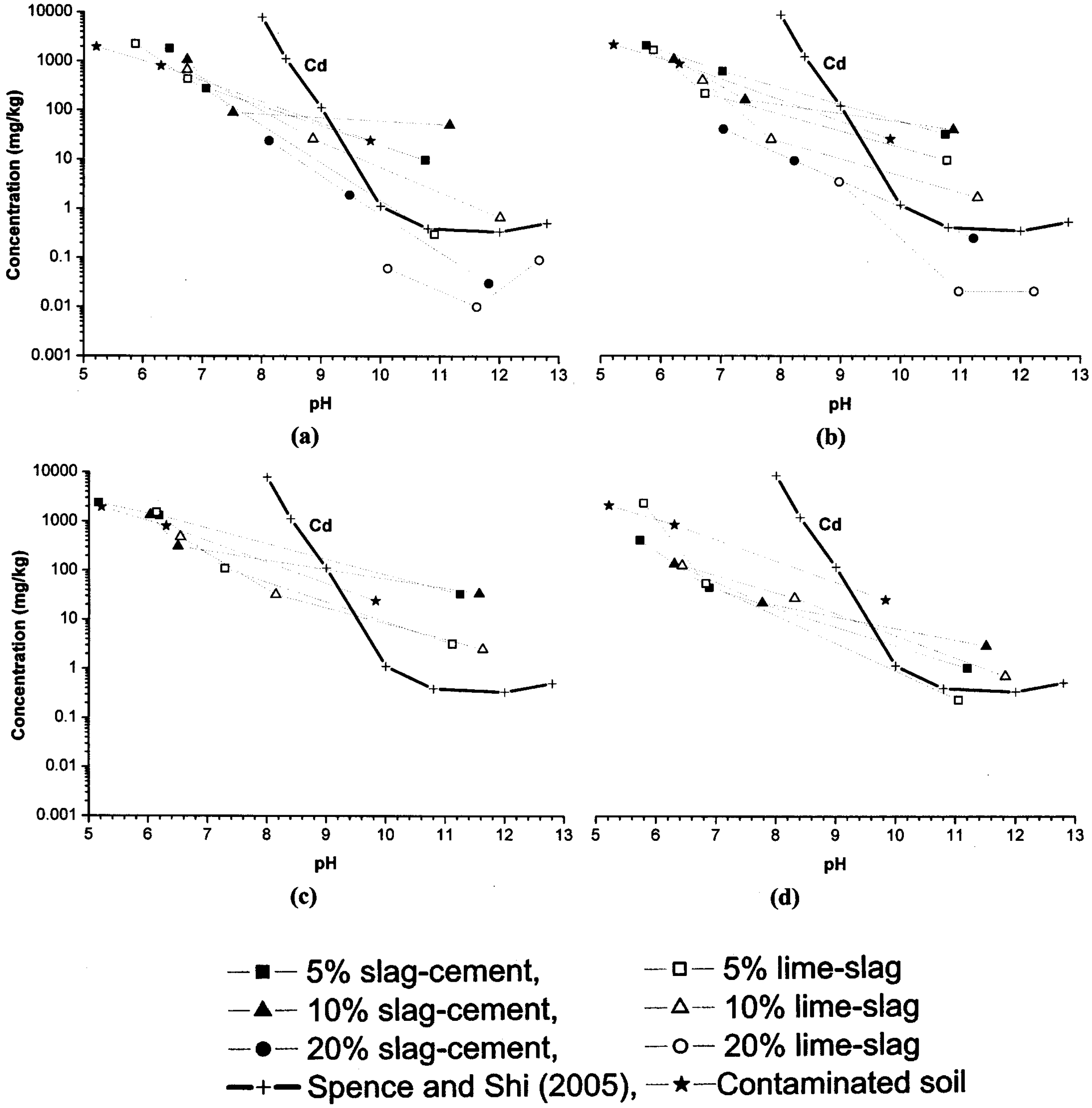


Figure 3. Leachability of Cd at (a) 7 d (b) 28 d (c) 49 d and (d) 84 d in slag-cement and lime-slag mixes

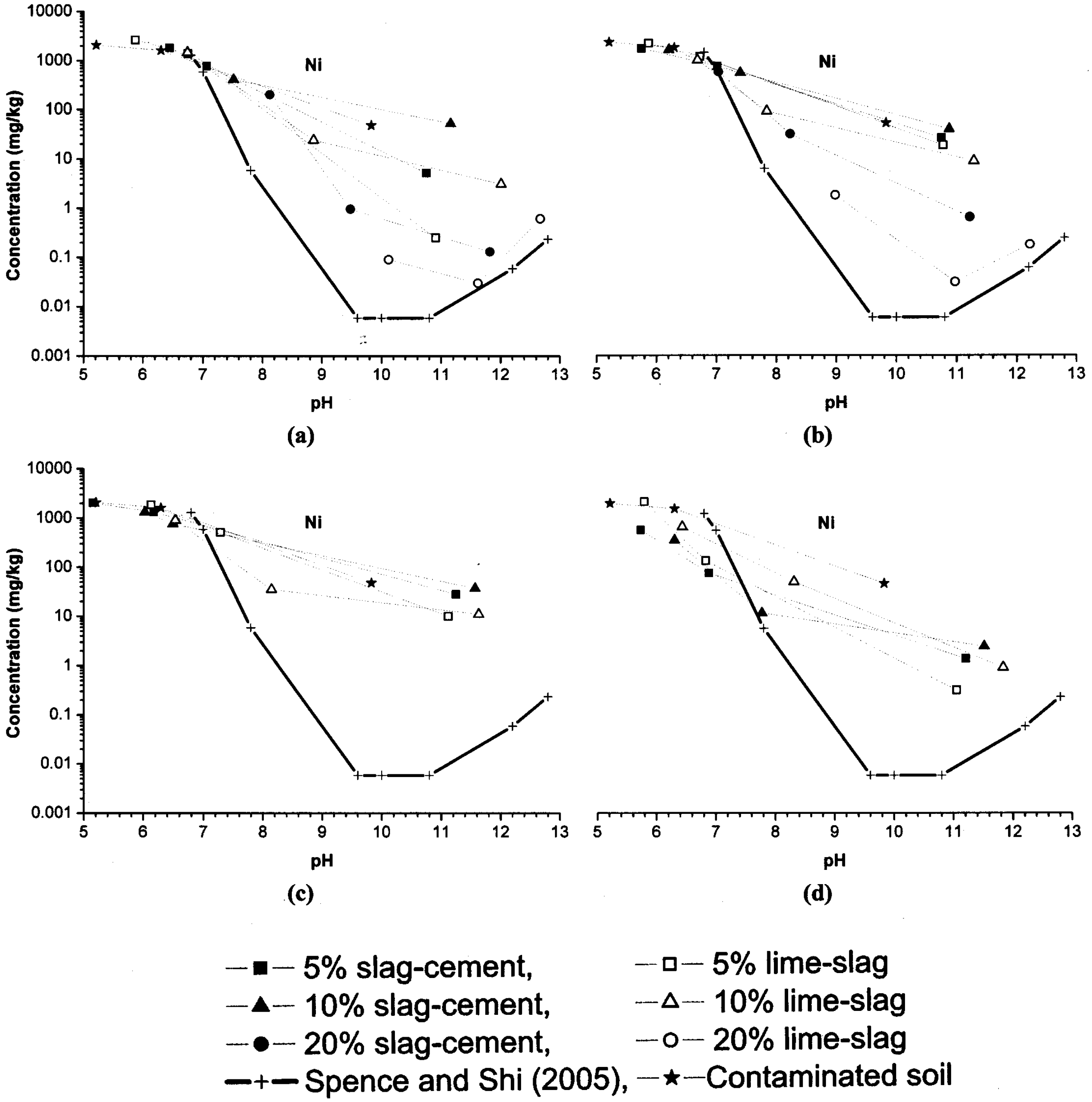


Figure 4. Leachability of Ni at (a) 7 d (b) 28 d (c) 49 d and (d) 84 d in slag-cement and lime-slag mixes

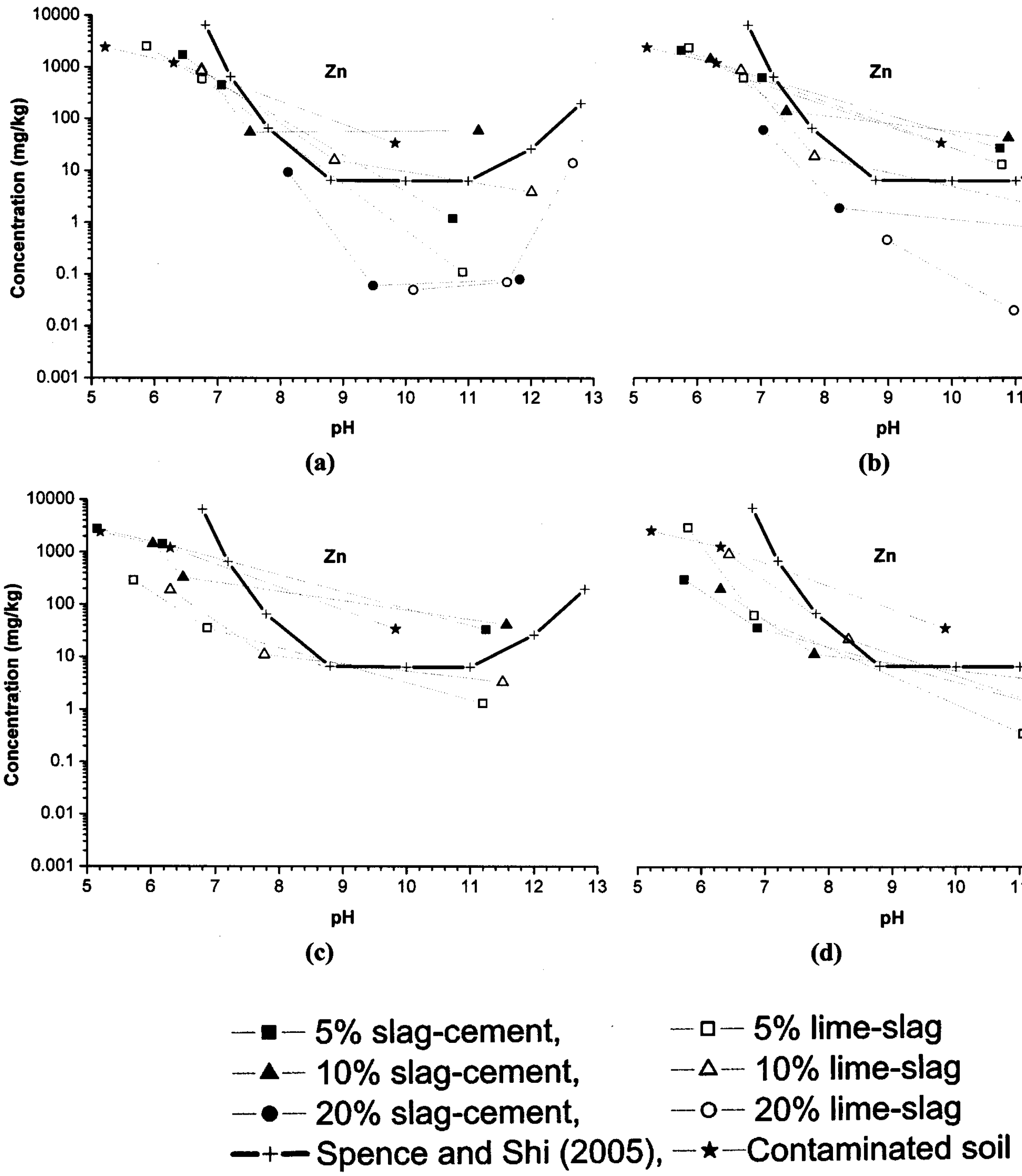

(a) (b) (c) (d)

Figure 5. Leachability of Zn at (a) 7 d (b) 28 d (c) 49 d and (d) 84 d in slag-cement and lime-slag mixes

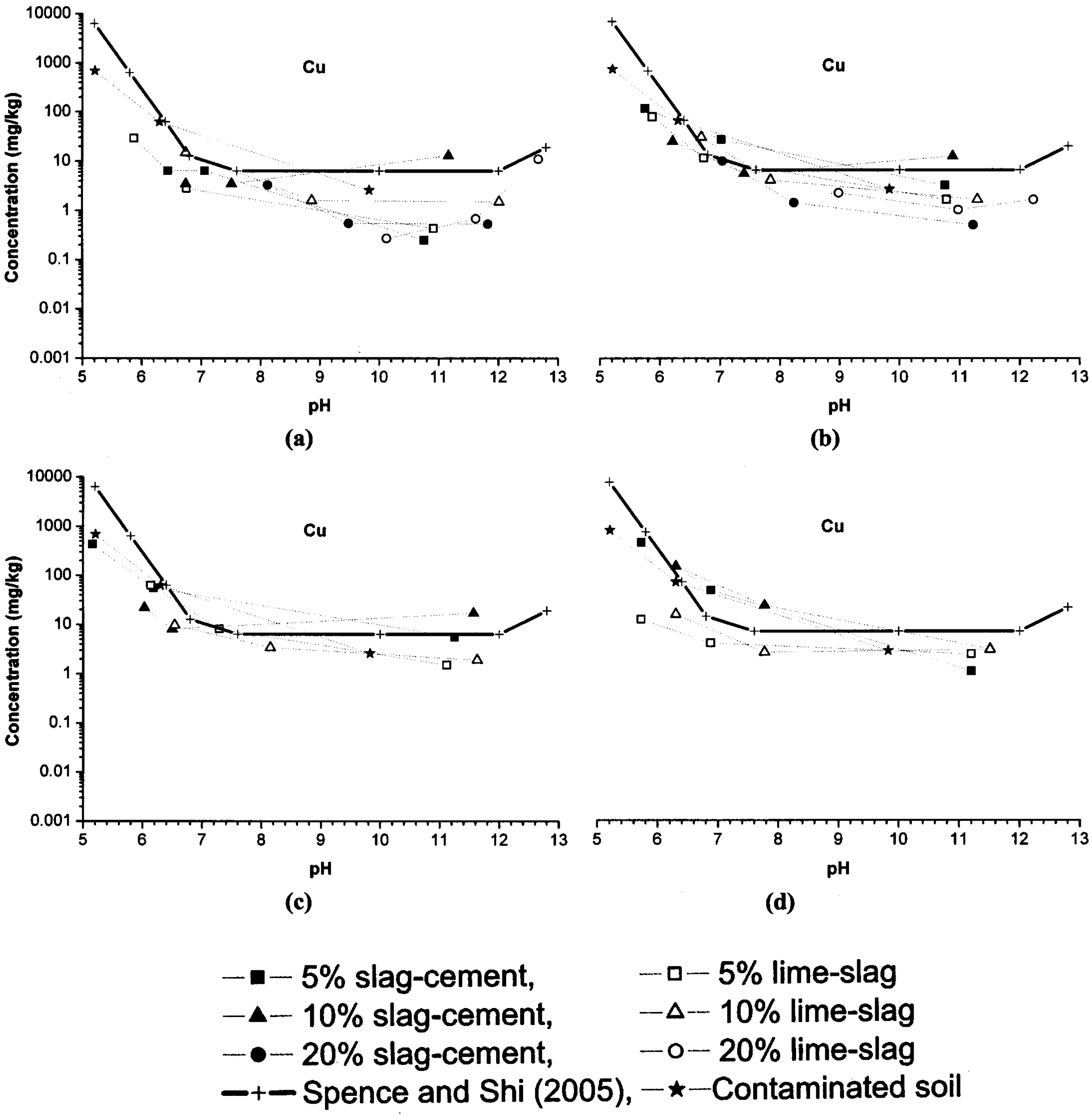
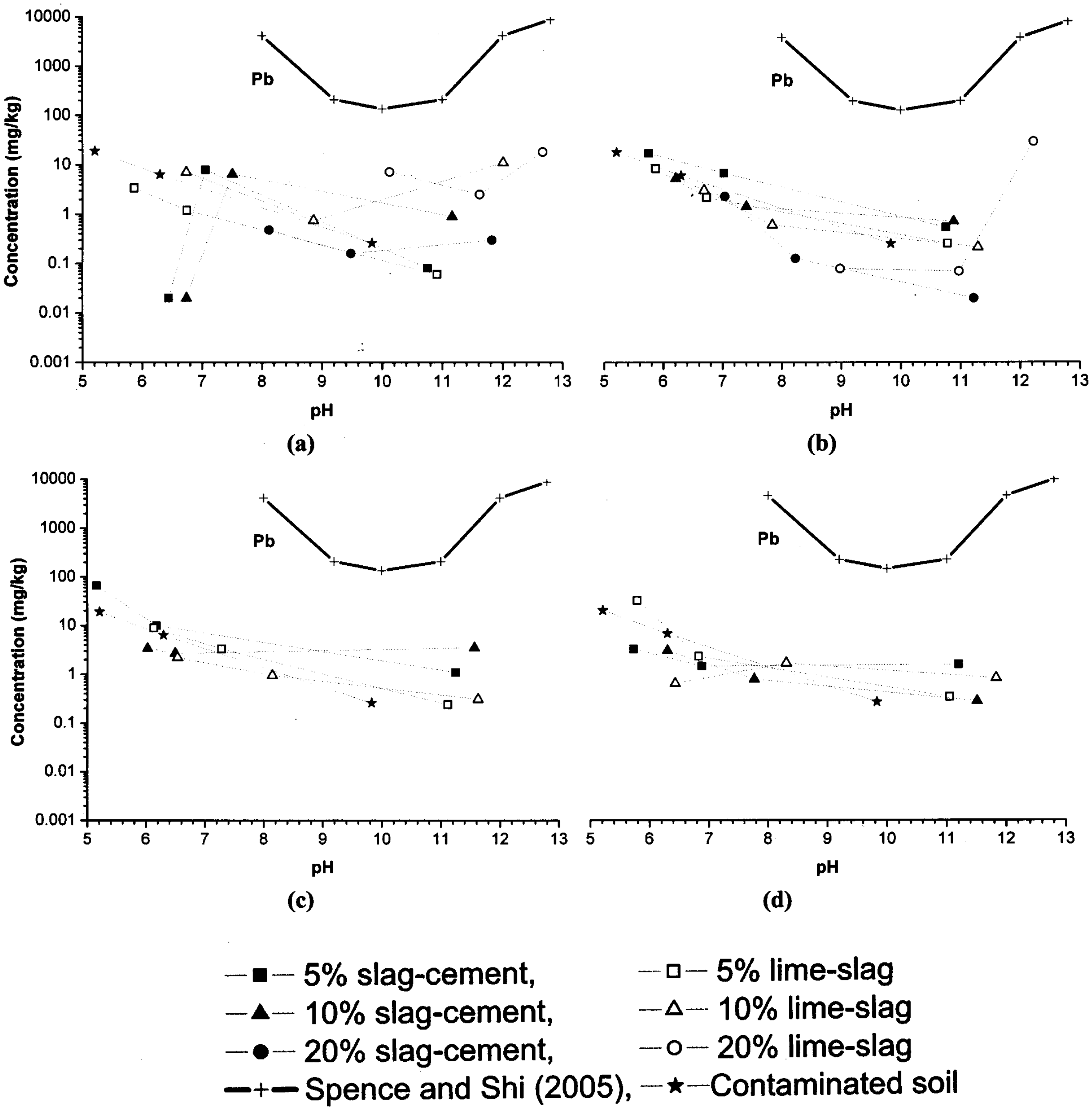


Figure 6. Leachability of Cu at (a) 7 d (b) 28 d (c) 49 d and (d) 84 d in slag-cement and lime-slag mixes



(a) (b) (c) (d)

Figure 7. Leachability of Pb at (a) 7 d (b) 28 d (c) 49 d and (d) 84 d in slag-cement and lime-slag mixes

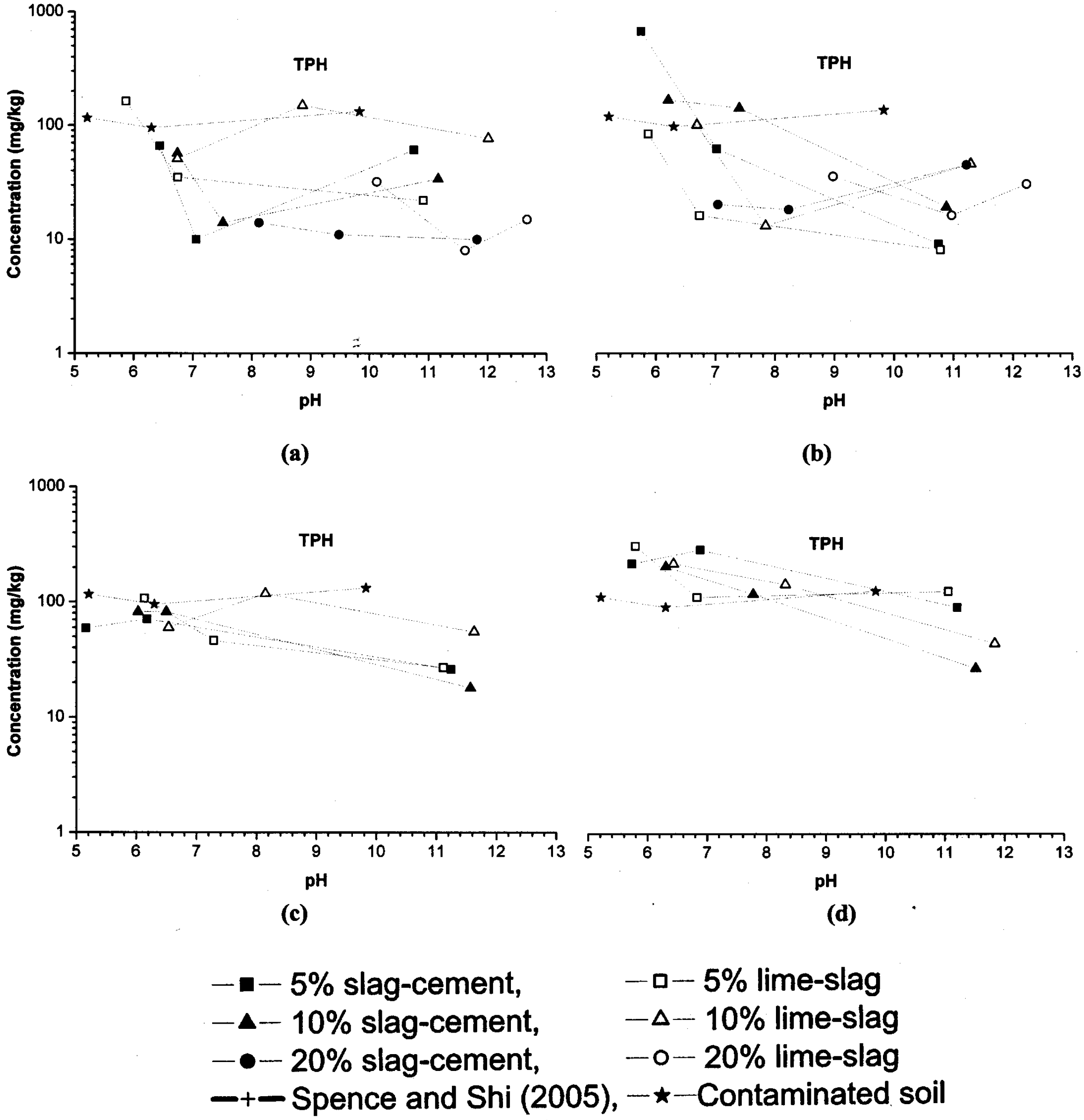


Figure 8. Leachability of TPH at (a) 7 d (b) 28 d (c) 49 d and (d) 84 d in slag-cement and lime-slag mixes