Process Envelopes for Stabilisation/Solidification of Contaminated Soil using Lime-Slag blend

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Abstract

Stabilisation/solidification (S/S) has emerged as an efficient and cost-effective technology for the treatment of contaminated soils. However, the performance of S/S treated soils is governed by several intercorrelated variables, which complicates the optimisation of the treatment process design. Therefore, it is desirable to develop process envelopes, which define the range of operating variables that result in acceptable performance. In this work, process envelopes were developed for S/S treatment of contaminated soil with a blend of hydrated lime (hlime) and ground granulated blast furnace slag (GGBS) as the binder (hlime:GGBS=1:4). A sand contaminated with a mixture of heavy metals and petroleum hydrocarbons was treated with 5, 10 and 20% binder dosages, at different water contents. The effectiveness of the treatment was assessed using unconfined compressive strength (UCS), permeability, acid neutralisation capacity (ANC) and contaminant leachability with pH, at set periods. The UCS values obtained after 28 days of treatment were up to ~800 kPa, which is quite low, and permeability was ~10^{-8} m/s, which is higher than might be required. However, these values might be acceptable in some scenarios. The binder significantly reduced the leachability of cadmium and nickel. With the 20% dosage, both metals met the waste acceptance criteria (WAC) for inert waste landfill and relevant environmental quality standards. The results show that greater than 20% dosage would be required to achieve a balance of acceptable mechanical and leaching properties. Overall, the process envelopes for different performance criteria depend on the end-use of the treated material.

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9 **Abstract**

10 *Purpose*

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12 the treatment of contaminated soils. However, the performance of S/S treated soils is

13 governed by several intercorrelated variables, which complicates the optimisation of the

14 treatment process design. Therefore, it is desirable to develop process envelopes, which

15 define the range of operating variables that result in acceptable performance.

16 *Methods*

17 In this work, process envelopes were developed for S/S treatment of contaminated soil with a

18 blend of hydrated lime (hlime) and ground granulated blast furnace slag (GGBS) as the

19 binder (hlime:GGBS=1:4). A sand contaminated with a mixture of heavy metals and

20 petroleum hydrocarbons was treated with 5, 10 and 20% binder dosages, at different water

21 contents. The effectiveness of the treatment was assessed using unconfined compressive

22 strength (UCS), permeability, acid neutralisation capacity (ANC) and contaminant

23 leachability with pH, at set periods.

24 *Results*

25 The UCS values obtained after 28 days of treatment were up to ~800 kPa, which is quite low,

26 and permeability was ~10^{-8} m/s, which is higher than might be required. However, these

27 values might be acceptable in some scenarios. The binder significantly reduced the

28 leachability of cadmium and nickel. With the 20% dosage, both metals met the waste

29 acceptance criteria (WAC) for inert waste landfill and relevant environmental quality

30 standards.

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33

1   *Conclusions*

2   The results show that greater than 20% dosage would be required to achieve a balance of

3   acceptable mechanical and leaching properties. Overall, the process envelopes for different

4   performance criteria depend on the end-use of the treated material.

5

6   **Keywords**: Acid neutralisation capacity, cadmium, blast furnace slag, nickel, leaching

7   behaviour, lime.

8

9   1. **Introduction**

10   Stabilisation/solidification (S/S) involves the addition of binders, mainly Portland cement-

11   based, to hazardous wastes to bring about chemical fixation, physical adsorption and physical

12   encapsulation of contaminants (Conner 1990). S/S has been widely used for the remediation

13   of contaminated sites, and with appropriate design, it is capable of improving the

14   geotechnical properties of treated soils to facilitate construction on the site. However, the

15   performance of S/S treated soils is governed by several variables including soil type and

16   properties, contaminant type, speciation and concentrations, curing environment, binder type

17   and dosage, to name a few. These factors complicate the optimisation of treatment process

18   design and as a result, it is important to develop process envelopes for generic S/S of

19   contaminated soils. A process envelope is defined as the range of operating variables that

20   result in acceptable performance, and hence describe the limits of applicability of S/S

21   treatment technology to the chosen waste type (Stegemann and Zhou 2008). The concept of

22   process envelopes is based on the premise that specific wastes generated by similar processes

23   will have similar properties in terms of their physical nature and composition and generic S/S

24   process envelopes developed using a few examples of a waste type will broadly apply to

25   other wastes of the same type (Stegemann and Zhou 2008).

26

27   Lime has been used extensively in remediation projects especially as lime-based S/S

28   processes are able to accommodate large quantities of organics as well as common inorganic

29   sludges (Conner and Hoeffner 1998). It is also used to activate pozzolans – materials that

30   react with it in the presence of water to produce a cementitious compound. Ground

31   granulated blast furnace slag (GGBS) is one of such materials (LaGrega et al. 2001). GGBS

32   is a by-product of the manufacturing of iron. It is used in many cement applications where it

33   provides enhanced durability, high resistance to chloride penetration and resistance to

sulphate attack as well as improved sustainability (Higgins 2005). GGBS has also been used in treatment of contaminated sediment and 4% dosage significantly reduced the leachability of low nickel and zinc concentrations (Barth et al. 2007). Hence, it is important to promote sustainable reuse of the industrial by-product in contaminated land remediation. Studies on lime-GGBS blends in the literature have mainly focused on the influence of GGBS on the strength and swelling potential of lime-stabilised clays due to the presence of sulphates. The strength level achieved would depend on the proportions of lime and GGBS in the blend. Overall, the optimum proportions of the blend for high strength and reduction in swelling require a GGBS amount about four times that of lime (Higgins 2005; Nidzam and Kinuthia 2010). There is a dearth of literature on the deployment of a blend of lime and GGBS for treatment of contaminated soils. Hence, this paper addresses S/S using lime-GGBS as binder.

The proportions of water and binder added to the waste mainly govern S/S product properties. Hence, these are primary independent operating variables. However, the effect of variation in water content on contaminant leachability is rare in the literature. Furthermore, previous studies dealt with leachability within a limited pH zone, whereas the initial alkalinity of S/S products is neutralised over time by acidic influences in the environment. For instance, carbonation by CO_2 uptake, and natural leachants such as rainwater or landfill leachate, whose pH is slightly acidic, will progressively lower the pH of stabilised materials over time. Thus, there is need for information on pH-dependent leaching behaviour of contaminants in a lime-GGBS treated soil. This study sought to fill in these gaps in the literature. In the light of the above, this work sought to generate data through laboratory tests and thus, develop correlations between variables that would lead to optimisation of the design process for S/S treatment of contaminated soil. The aim of the study was to develop process envelopes for S/S treatment employing a blend of hydrated lime (hlime) and GGBS as binder, with respect to handling, contaminant leachability, physical and chemical durability, and cost.

2 Materials and methods

2.1 Contaminated soil, binder and mix preparation

A real site soil contaminated with low levels of heavy metals and total petroleum hydrocarbons (TPH) obtained from a Petrol station in Birmingham, UK, was used. The soil was composed of ~65% gravel, ~29% sand, ~2.8% silt and ~3.2% clay, and is classified as a clayey silty sandy gravel. Its natural water content was ~12% and its pH was ~11.6, due to high

calcium content. The natural soil had very low (0.22% m/m) organic carbon content. The soil (sieved past 20 mm) was spiked in small batches of ~3kg with 3000 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 $ZnCl_2$), and 10,000 mg/kg of diesel (from a local petrol station) in order to increase its contaminant levels. Naturally contaminated soil is better to use, as opposed to spiking, which introduces contaminants in a form they normally are not entered into the soil. Moreover, there is the likelihood that with spiking, the partitioning between mineral and sorptive phases of the spike is not the same as that of the contaminant in the soil. However, the natural contaminant levels in the soil available were very low and below threshold limits for pollution. Further, the issue of heterogeneity of contaminants in the soil complicates analysis for comparisons of different mixes. Therefore, spiking was employed to bring about homogeneity and thus facilitate comparisons. The above contaminants were used since they are among the most common found at contaminated sites. A mixture of organics and heavy metals was used as many contaminated soils are characterised by the concomitant presence of both types of contaminants.

A blend of hlime (from Tarmac Buxton Lime and Cement, UK) and GGBS (from UK Cementitious Slag makers Association, Surrey, UK) in the ratio, hlime:GGBS = 1:4, was used as binder. The mix proportion was chosen for consistency with parallel studies on S/S of metal filter cakes (Stegemann and Zhou 2008) and with relevant literature. The physical and chemical properties of the hlime and GGBS used are shown in Table 1. The binder was applied in 5, 10 and 20% (m/m) dosages in paste form.

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. GGBS and hlime were mixed together and with de-ionised water forming a paste and then added and mixed with the contaminated soil.

Standard Proctor compaction test (BSI 1990), using a 2.5kg rammer, was carried out on the soil-binder mix at appropriately selected water content intervals. The compacted mix was then broken up after each stage and cast into cylindrical moulds, 50 mm diameter and 100 mm high, to the same compaction density for each water content. The moulded samples were demoulded after three days and cured at 95% relative humidity and 20°C until tested.

3 **Table 1. Physical and chemical properties of hlime and GGBS**

Property / composition	hlime	GGBS
Bulk density (kg/m^3)	470 – 520	1200
Specific gravity	2.3 – 2.4	2.9
Specific surface area (m^2/kg)	1529	350
Mean particle size (microns)	63 - 125	5 - 30
pH (1:5)	12.85	11.79
CaO (%)	-	40
Ca(OH)$_2$ (%)	96.9	-
SiO$_2$ (%)	-	35
MgO (%)	-	8
Mg(OH)$_2$ (%)	0.5	-
Al$_2$O$_3$ (%)	-	13
CaCO$_3$ (%)	1.4	-
CaSO$_4$ (%)	0.03	-

4

5

6 2.2 **Testing and analytical methods**

7 The tests conducted include unconfined compressive strength (UCS), permeability and acid

8 neutralisation capacity (ANC). The UCS was determined in triplicate samples, according to

9 ASTM (2002), using a universal testing machine wherein the vertical load was applied

10 axially at a constant strain rate of 1.143 mm/min until failure. The UCS was mainly

11 conducted in samples without immersion, although selected samples were tested after

12 immersion for comparison purposes. Permeability tests were carried out in flexible-wall

13 permeameters (ASTM 2003) using a confining pressure of 300 kPa and a constant flow rate,

14 and the permeability calculated using Darcy's Law.

15

16 The ANC of samples, using sub-samples of the crushed UCS samples, was determined

17 according to Stegemann and Côté (1991) using 0, 1 and 2 meq/g HNO$_3$ acid additions. The

18 ANC without acid addition gives a conservative estimate of the regulatory granular leaching

19 test (BS EN12457-3) as the same liquid:solid (L/S) ratio is used, but the former uses a

20 smaller particle size and longer contact time than the latter resulting in higher leached

21 concentrations. Crushed samples dried at 60 °C and sieved to < 1.18 mm, were placed in 1 L

22 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. Thereafter, the leachates were allowed to settle, the pH determined and then filtered through 0.45 μm cellulose nitrate membrane filters (Whatman International Ltd.) and aliquots taken for contaminant analysis using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) for heavy metals and Gas Chromatography-Flame Ionisation Detector (GC-FID) for TPH. Determination of TPH content of the filtered leachate for possible contribution to dissolved organic carbon (DOC) showed negligible concentration of the contaminant. Hence, leachates used for the TPH results reported here were not filtered. Diesel in the water phase was directly extracted with hexane and the diesel extract in hexane analysed on the GC-FID. Details of the procedure involved are described in the work of Vreysen and Maes (2005). The ANC test was also conducted on the untreated contaminated soil and the binder alone.

Testing was generally conducted at some or all of 7, 28, 49 and 84 days with some testing only performed on optimum compaction mixes. The testing programme was used on starting with low binder (5%) mixes with assessment of contaminant leachability and the binder then increased until the leaching criteria were met. Hence, fewer tests were performed on 20% binder dosage mixes.

2.3 **Statistics and 3D plotting**

One and two-way analysis of variance (ANOVA), was used for data analysis to test for differences in performance parameters due to the effects of water content, binder dosage and age. Statistical significance was defined as $P < 0.05$. Spearman's rank correlation was used to examine the relationship between selected performance parameters.

Three-dimensional graphs were plotted from experimental results to enhance data visualisation and representation of the relationship between the main variables that govern S/S product properties, in order to describe process envelopes. The graphs were produced using Origin 8.1 software (OriginLab Corporation, Northampton, USA) and the kriging correlation, which best fit the data points among the options provided by the software package, was used to produce response surfaces.

1   3 **Results and discussion**

2   The presentation of results for the performance parameters at different ages has water:solids

3   (w/s) ratio as a major variable. The w/s ratios in the graphs represent the initial water contents

4   at which the samples were prepared and not the water contents of the samples determined at

5   different testing times. It should be noted that the calculation of the w/s ratio does not include

6   the liquid content due to diesel. Hence, the optimum w/s ratio and the OMC are used

7   interchangeably in this paper. Where applicable, OMC mixes are indicated on the graphs by

8   larger marker sizes.

9

10   3.1 **Compaction behaviour and UCS**

11   The dry density-moisture content relationship of the hlime-GGBS-treated contaminated soil

12   is shown in Figure 1(a) together with that of the untreated soil. The figure shows that the

13   optimum water content decreases and dry density increases as binder content increases

14   consistent with trends reported by others (Akinmurusu 1991; Wild et al. 1996).

15

16   Figure 1 (b) shows the 7 and 28-day UCS results of the S/S soil mixes clearly showing that

17   the mixes had low strength of less than 100 kPa at 5% binder dosage and less than 500 kPa at

18   10% binder dosage. Figure 2 shows the UCS developments over time. Higgins (2005)

19   reported a 7-day UCS of 2,000 kPa, for uncontaminated silty/clayey sand stabilised with 10%

20   binder dosage of the same proportion of lime-GGBS used here, which attained 6,000 kPa at

21   90 days. It is likely that the relatively lower values here are due to the presence of

22   contaminants as it is well known that the presence of contaminants, especially hydrocarbons,

23   leads to detrimental effects on UCS of stabilised soils (Shi and Spense 2004; Paria and Yuet

24   2006). With 10% binder dosage, the highest UCS values at 7 and 28 days were obtained at

25   the OMC+2, but with 5% dosage there was very little increase in UCS with increasing water

26   content. There was significant increase in UCS between 7 and 28 days with 10% binder

27   dosage (p<0.001), but 5% binder dosage did not cause any significant increase (p=0.41) in

28   UCS.

29

30   Comparing the closest water contents on both sides of the OMC for 10% binder dosage, the

31   UCS trend differs from that of stabilised uncontaminated soil reported by Piratheepan et al

32   (2010). In their study, UCS was highest at the OMC and there was relatively smaller

33   difference in UCS on the dry side of OMC than the wet side, hence they suggested a

preference for the dry side of the OMC rather than the wet side, during field application. However, the results of this work suggest that the wet side of OMC may give a higher UCS for contaminated soil than the dry side. Comparing Figures 1a and 1b, the compaction behaviour shows that the dry and bulk density on the wet side of OMC was slightly higher than that on the dry side, thus the density-moisture content relationship during compaction would determine the water content range that would give a higher UCS. There was significant difference in 28-day UCS due to differences in water content at the 0.1% probability level. There was also significant difference in UCS with binder dosage at 7 ($p < 0.01$) and 28 ($p < 0.001$) days.

The 49-day UCS after immersion for 5 and 10% dosage mixes is shown in Figure 2. The UCS before and after immersion at 49 days are about the same value which shows that the stabilised material has hardened chemically and is not susceptible to deleterious swelling reactions. It also supports the influence of GGBS in reducing swelling reported in the literature (Higgins 2005; Nidzam and Kinuthia 2010). The 5 and 10% binder dosage mixes exhibited significantly different patterns ($p < 0.001$) of strength gain with time (Figure 2).

The UCS of the treated soil is mainly controlled by the binder dosage and water content, and it increases with curing age. Thus, all the UCS results in terms of the aforementioned parameters were combined together to produce a 3-D plot representing a simple process envelope for UCS of the S/S treated soil (Figure 3).

1

2   (a)

3

4

5   (b)

6
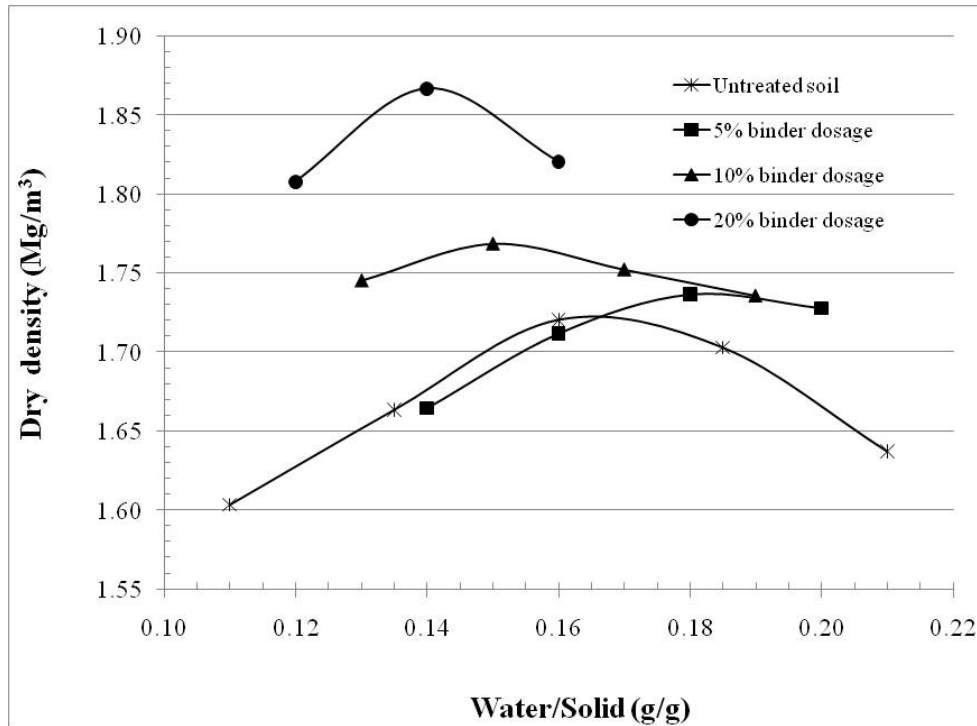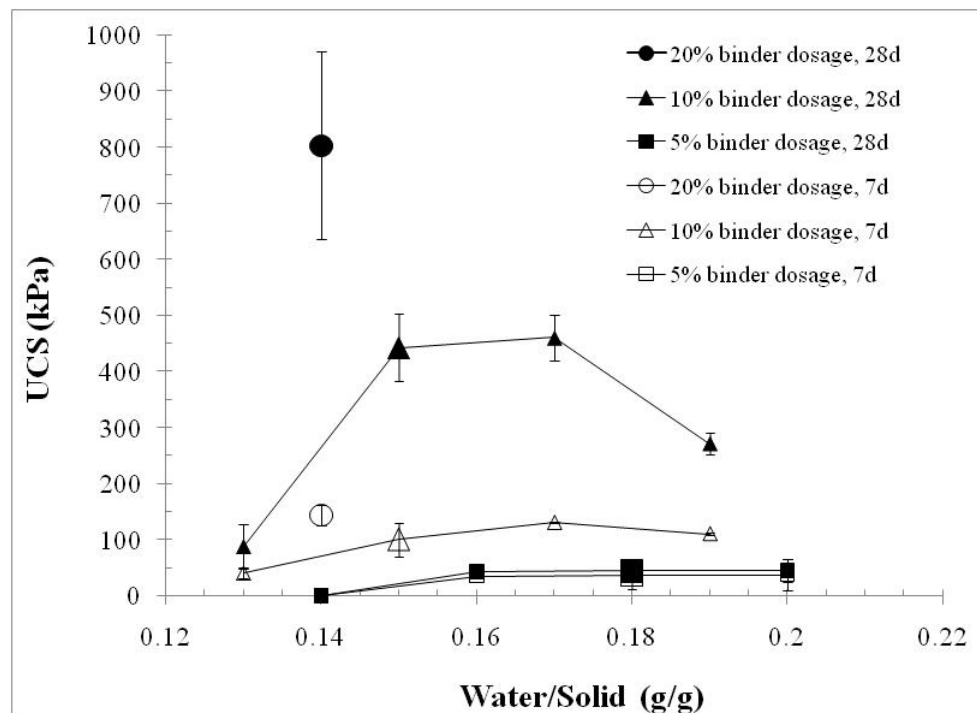
7   Figure 1. (a) Compaction behaviour and (b) 28-day UCS of the S/S mixes
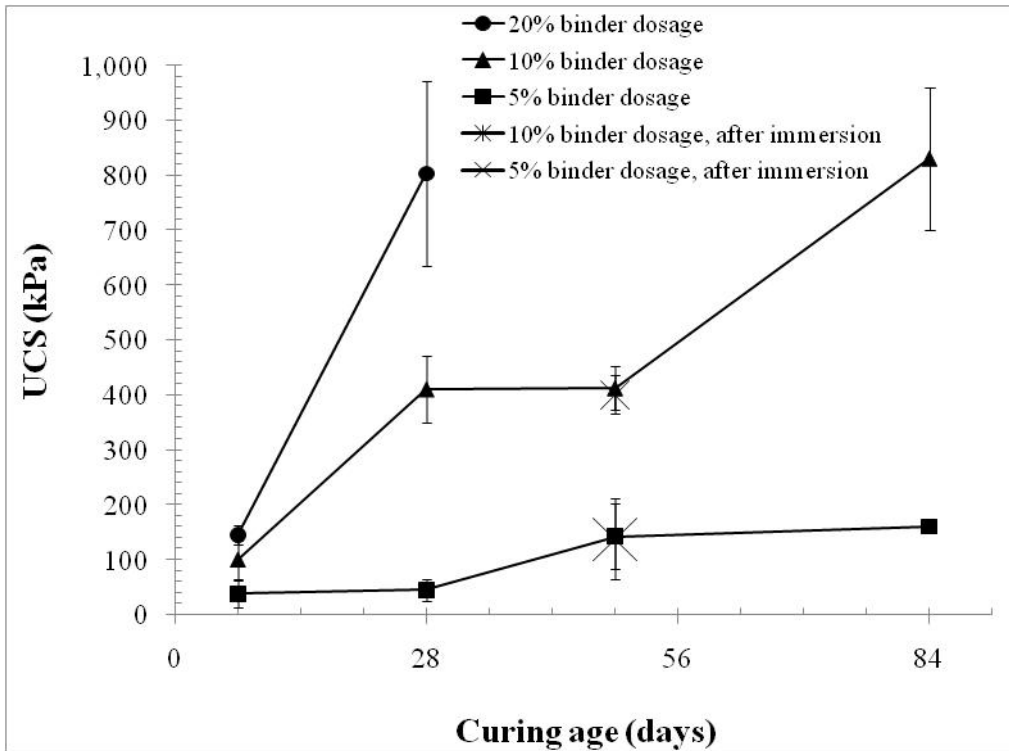
Figure 2. Variation of UCS with time in optimum w/s mixes
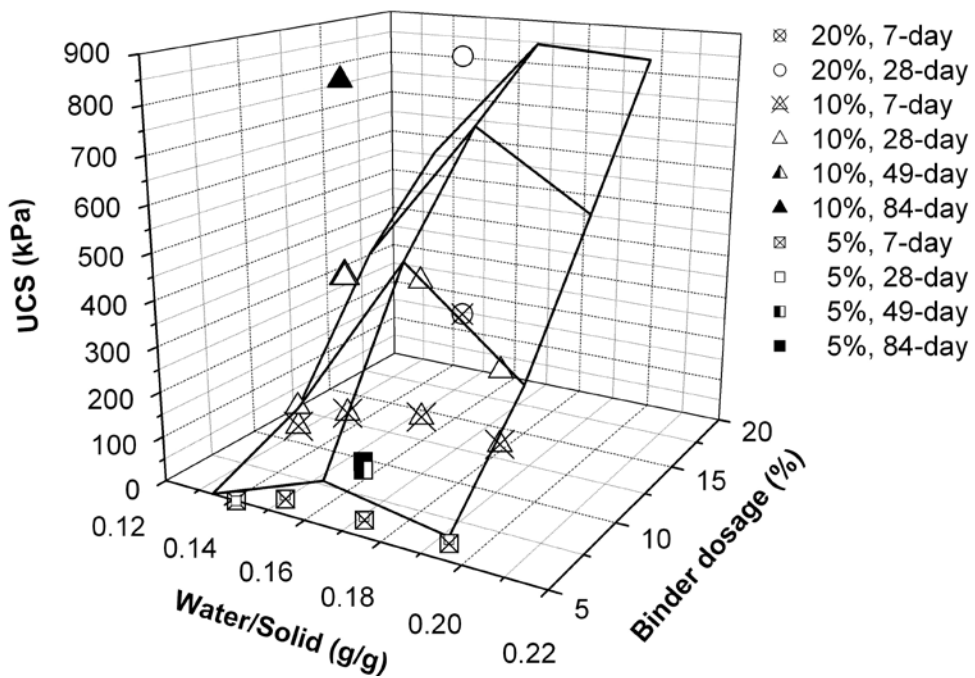
Figure 3. Process envelope for UCS of hlime-GGBS-treated contaminated soil

3.2 **Permeability**

The 28 and 84-day permeability of the mixes is shown in Figure 4. The permeability of 5% dosage mixes, with the exception of the OMC, could not be determined, as the samples were not strong enough for the test to be carried out on them. Differences in water content led to different ($p < 0.001$) permeability values of 10% dosage mixes, and the values were between 2×10^{-8} and 5×10^{-8} m/s. The 28-day permeability of the OMC mixes increased with increasing binder dosage. It was expected that permeability would decrease with increasing binder dosage as observed in previous works on uncontaminated soils. Nevertheless, El-Rawi and Awad (1981) reported a similar situation where the permeability of lime-stabilised sandy silty clay increased with increasing lime content. Strictly speaking, the effect of increased binder dosage on permeability is not clear, since different water contents were not used for 20% binder dosage. It is likely that lower permeability would be obtained at water contents to the wet of the OMC. El-Rawi and Awad (1981) observed that with lime-stabilised sand, there existed a moulding water content at which the permeability reached a minimum, and samples compacted on the wet side of OMC gave lower permeability values than those on the dry side. Thus, further work with more binder dosages and water contents would be required to clarify the effect of binder dosage on permeability of lime-GGBS-stabilised contaminated sand.

The permeability of OMC mixes of 5 and 10% dosage also increased with curing age, contrary to the findings on uncontaminated soil stabilised by lime or lime-GGBS where permeability decreased with curing age (El-Rawi and Awad 1981; Higgins 2005). Moreover, at 84 days the permeability of the OMC mix of 5% binder dosage increased by an order of magnitude and was higher than that of 10% binder dosage which increased from 4×10^{-8} to 7×10^{-8} m/s (Figure 4).
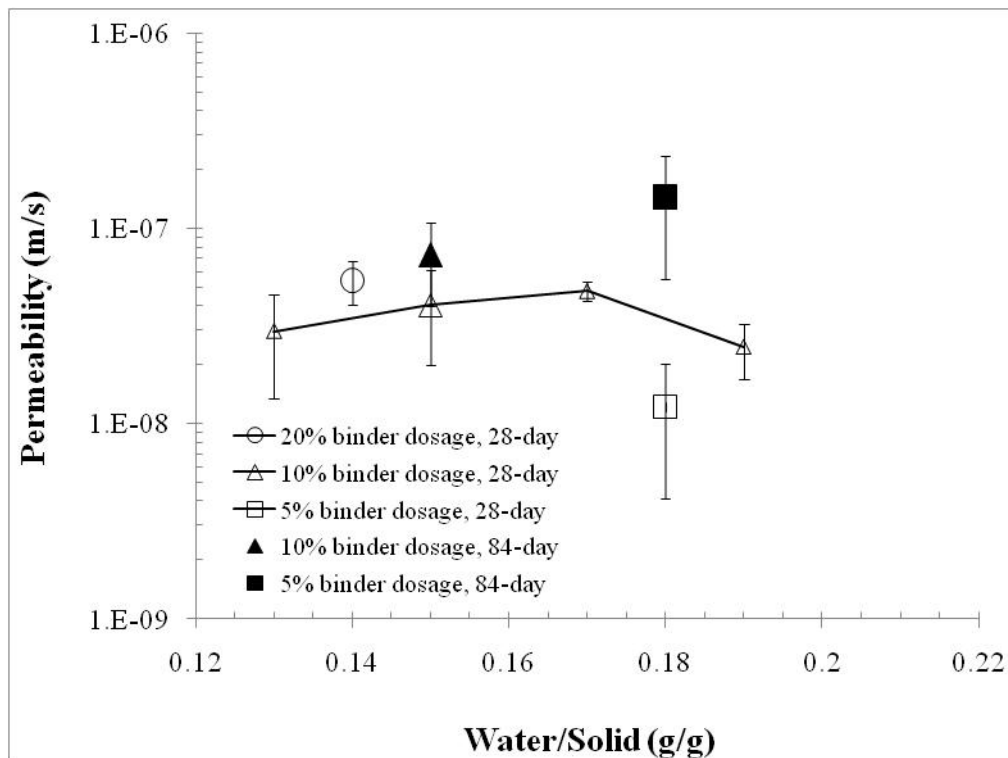
Figure 4. Permeability of hlime-GGBS-treated contaminated soil

3.3 **ANC and leachability of contaminants**

This paper considers the leaching behaviour of three of the spiked contaminants, namely, Cd, Ni and TPH. The leaching behaviour of the other contaminants would be dealt with in a subsequent paper since the paper would be too long to address all the contaminants.

The 3-point ANC of hlime-GGBS binder formulation showed that the pH at 0, 1 and 2 meq/g HNO_3 addition were 12.94, 12.71 and 12.59, respectively, which demonstrates the high buffering capacity of the binder. The pHs attained by the untreated contaminated soil at the three acid additions is shown in subsequent graphs together with metal leachability at those pHs. Contaminant leachability was determined on only three of the four water contents of 5 and 10% binder dosages: the OMC and the next water content on the dry and wet side of OMC. In the graphs of metal concentrations with pH, each mix has three points, from left to right representing the leachate pH at 2, 1 and 0 meq/g acid additions. The solid and dash lines are two theoretical solubility profiles of the metal: the former is the solubility of the metal hydroxide (Spense and Shi 2005) and the latter is the solubility of the metal in an equilibrium solution containing all five metallic compounds used in the study (Liska, unpublished).

The leachability of Cd and Ni at 28 days of treatment is shown in Figures 5 and 6. The effect of pH on metal solubility is well known and Figures 5 and 6 clearly show that the leachability of Cd and Ni was greatly influenced by the leachate pH. Small changes in pH led to marked differences in leachability. On the other hand, particulate and dissolved organic matter plays a key role in the potential for either mobilisation or sorption of contaminants in matrices that contain organic matter (Van der Sloot 2003). The soluble fraction of organic matter (DOC) enhances the total concentration of soluble metals like the ones considered here. However, the soil used in this work had a very low level of organic matter. The main contribution to organic carbon was from the diesel spiked as diesel contains about 50% carbon content (Environmental Protection Service 1984). Nevertheless, as mentioned in section 2.2, the contribution of the diesel to DOC was negligible; therefore, DOC was not measured in the experiments. Thus, there was inconsiderable influence of organic matter in the leaching patterns observed here. The leachate pH was found to be a primary factor influencing the leachability of metals as it governs the solubility of the metal hydroxides. Halim et al (2003) reported a similar observation.

Cadmium concentration decreased with increasing pH, due to precipitation as insoluble $Cd(OH)_2$ at high pH. This is justified by the mixes (especially the 20% dosage mix) closely following the solubility profile of Spense and Shi (2005) (Figure 5). It has been shown that Cd typically exists as its hydroxide in cementitious systems, although it may also exist as cadmium carbonate (Christensen et al. 1996; Halim et al. 2004). The solubility product constants (K_{sp}) of $Cd(OH)_2$ and $CdCO_3$ are 2.5×10^{-14} and 5.2×10^{-12} m/s, respectively. Hence, the former is less soluble in water than the latter. It was observed that around pH 11, which falls within the region for minimum solubility of $Cd(OH)_2$, the leachability of Cd was different in mixes with different binder dosages. In fact, Cd solubility decreased with increasing binder dosage in that pH zone. The solubility of Cd in 5 and 10% dosage mixes was higher than the estimated solubility of the metal at pH 11, while that of 20% dosage mixes was lower than the estimated values (Figure 5). 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 estimated solubility limits when metals precipitate as their single-metal hydroxide (Spense and Shi 2005). Thus, the higher solubility values of the 5 and 10% dosage mixes may be due to the metal not precipitating as its single metal

hydroxide but rather forming other more soluble phases or mixed hydroxides. The increase in Cd release in the higher pH range with the formation of Cd-carbonato complex has been reported (Christensen et al. 1996). This possibly accounts for the higher solubilities observed. However, with a higher binder dosage (20%), 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 (Halim et al. 2003).

The concentrations of Ni leached out was higher than the estimated values of its hydroxide (Spense and Shi 2005) in all cases, suggesting the presence of more soluble phases other than the metal hydroxide. The same applies to the profile of Liska (unpublished) at zero acid addition, but with acid addition it was lower and the leaching trend closely followed the solubility profile (Figure 6). Nickel is known to precipitate as $Ni(OH)_2$ at high pH (Chirenje et al. 2002), which is reflected in the 20% dosage mix following the profile of Spense and Shi (2005) rather than that of Liska (unpublished) at pHs 11 – 12. However, Christensen et al (1996) observed that at high pHs, chloro-complexes were negligible but carbonate complexes accounted for > 90% of soluble Ni. Since $NiCO_3$ ($K_{sp} = 6.6 \times 10^{-9}$) is more soluble than $Ni(OH)_2$ ($K_{sp} = 2.0 \times 10^{-15}$), this may well be responsible for the higher solubilities of Ni in the mixes.

At zero acid addition, there was no marked difference between the leachability of Cd and Ni in the untreated soil, and 5 and 10% dosage mixes, although OMC mixes were marginally better (Figures 5 and 6). This is because the untreated soil had high Ca content, which had a binding effect on the metals. However, change in pH with acid addition led to destruction of the structure of the cementitious material resulting in the release of Ca. This in turn led to the release of higher quantities of the metals within the pH zone 5.5 – 8. It is interesting to note that although the solubility profiles show that Cd solubility at pH 11.5 is several orders of magnitude lower than at pH 8, there was little difference in leachability of 10% dosage mixes (with 0 and 1 meq/g acid addition) at both pH zones (Figure 5b). Cadmium solubility in both sets of mixes was up to two orders of magnitude higher or lower than the estimated values. This suggests the influence of some other controlling factor on Cd leachability in addition to pH. There was evidence of chemical immobilisation of the metals at about pH 6.5, where the leachability of the treated soil (especially the 10% dosage wettest mix) was much less than that of the untreated soil at the same pH (Figures 5b and 6b).

The leachability of TPH from the mixes is shown in Figure 7. There was a marked reduction in leachable TPH in the treated soil (except for the driest mix of 5% dosage), compared to the untreated soil, at alkaline pH (9 – 12). However, as shown in Figure 7, TPH leachability was not governed by pH, although the contaminant was apparently mobilised in acidic solution. The results also corroborate the observations of Schifano et al (2005) that TPH reduction was independent of binder dosage.

The mobilisation of Cd and enhancement of the total concentration of soluble metals due to induced mobilisation of DOC in the pH range, pH > 9, reported by Van der Sloot (2003), was not observed in this work. This is because the effect of organic matter on the leaching behaviour of the contaminants studied was inconsiderable. This is further supported by the TPH results, which shows that there was no clear relationship between leachable TPH and the concentrations of the metals. The mobilisation of the metals above the estimated solubility limits in some mixes at alkaline pH did not correspond to an increase in TPH leachability in the mixes (compare Figures 5, 6 and 7).

Generally, OMC mixes were marginally better in reducing the leachability of the metals, but not TPH, at zero acid addition. With acid addition, OMC-2 mixes were marginally better. Nevertheless, two-way ANOVA without replication showed that there was no significant difference in leachability of the contaminants ($p > 0.12$ for all contaminants) due to the effect of water content in both 5 and 10% dosage mixes. However, as expected, different pH values arising from the different acid additions led to significant differences in leachability of the metals in 5 and 10% dosage mixes, but there was no significant difference ($p > 0.50$ for Cd and Ni) in 20% dosage mixes. This shows that $\geq 20\%$ dosage would be required in an environment with strong acidic influences. There was significant difference in 28-day pH of OMC mixes of the different binder dosages ($p = 0.02$) at different acid additions ($p = 0.005$). Moreover, the differences in leachability of all three contaminants at different curing ages were not statistically significant ($p > 0.33$ in all cases). Thus, binder dosage and pH due to different acid additions are the main variables that cause differences in metal leachability. Consequently, data from all binder-water content combinations at different ages have been used to produce 3-D plots representing simple process envelopes for Cd and Ni leachability in lime-GGBS treated soil (Figure 8). Interestingly, the process envelopes for both metals are

similar. The process envelope for TPH is not shown as there was no significant effect of the operating variables (binder dosage and pH condition) on TPH leachability. TPH data was only shown with the purpose of linking the diesel addition to the leaching behaviour of the metals.

3.4 **Performance thresholds for mechanical and leaching behaviour**

Performance thresholds are required to define process envelopes and they are usually end-use driven. Typical performance criteria for the mechanical and leaching properties used in this work are shown in Table 2. The United States Environmental Protection Agency (USEPA) standard for immersed UCS at 28 days can be achieved with 10% binder dosage since the UCS before and after immersion at 49 days were about the same value (> 350 kPa) with the 28 day UCS before immersion (Figure 2). However, greater than 20% dosage would be required to meet the UK standard for landfill disposal (Table 2). The permeability results obtained were higher than the performance thresholds, although it appears that the OMC mix of 5% dosage was around the higher limit for disposal scenarios (10^{-8} m/s) in Canada. However, the acceptable limits of operating variables are not clear since the effect of binder dosage on permeability in this study is unclear.

There are no established performance thresholds for metal leachability with pH. Thus, performance thresholds here are based on the samples with zero acid addition. There are also no established criteria for TPH leachability. The data in Figures 5, 6 and 8 compare with the Environmental Quality Standards (EQS) by dividing them by a factor of 10 – the L/S ratio used in the leaching test. The OMC mix of 20% dosage passed all leaching criteria for Cd and Ni. The 28-day leachability values of the OMC mix of 5% dosage were higher than the WAC of hazardous waste landfill for Cd, and that of stable non-reactive hazardous waste in non-hazardous landfill for Ni. However, values lower than the limits were obtained at 7, 49 and 84 days (data not shown, but incorporated in Figures 8a and 8b), which is indicative of the OMC mix of 5% dosage also passing the WAC for both disposal scenarios considering the possibility for imperfections in the 28-day samples (Table 2).

It should be noted that although there are currently no regulations for metal leachability at different pH conditions, it may be envisaged that progressive carbonation will lower the pH of the treated material over time to ultimately about pH 8 (Van Gerven et al. 2006). In the

light of this, it may be deduced from the 28-day pH dependent leaching data of the metals (Figures 5b and 6b) that the leachability of the 20% dosage mix may not satisfy the more stringent leaching criteria like the EQS and inert waste landfill WAC over a long time. However, the data shows that there was decrease in leachability of the metals with increasing binder dosage even in acidic solution. Thus, the results suggest that with a higher binder dosage (> 20%); the leaching criteria could still be met over a long time.

3.5 **Correlations between performance parameters**

It can be deduced from Figure 1a that the bulk density increased with increasing water content for 5 and 10% dosage mixes. The OMC occurred at the third and second wettest point for 5 and 10% binder dosage, respectively, but the UCS was highest at the fourth and third wettest points for 5 and 10% dosage, respectively. It stands to reason therefore that UCS was highest at the OMC+2, that is the next successive water content to the OMC at which an increase in bulk density causes a slight decrease rather than an increase in dry density.

The permeability trend of 10% dosage mixes was strangely similar to that of the UCS, with a direct proportionality rather than the inverse relationship observed in previous studies. The permeability increased with increasing w/s ratio, had the highest value at OMC+2 and declined at the wettest mix, although the decrease at the wettest mix did not follow the same pattern as did the UCS. However, the correlation between 28 and 84-day UCS and permeability for 10% dosage mixes was not significant (r=0.9; p=0.07). Generally, there was reduction in leachability of Cd and Ni with increase in UCS among binder dosages but differences in UCS within a given binder dosage due to differences in water content had no significant effect on leachability.
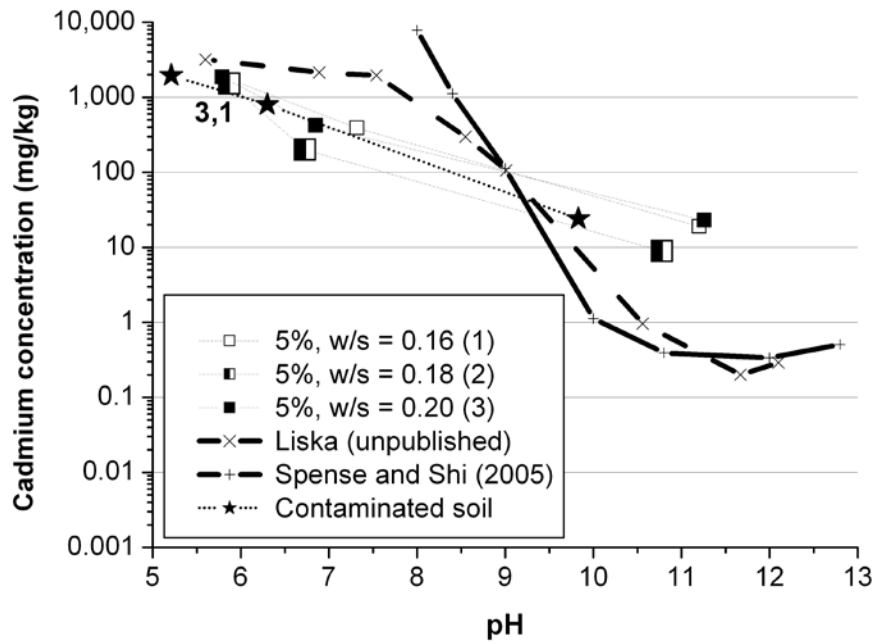
(a)

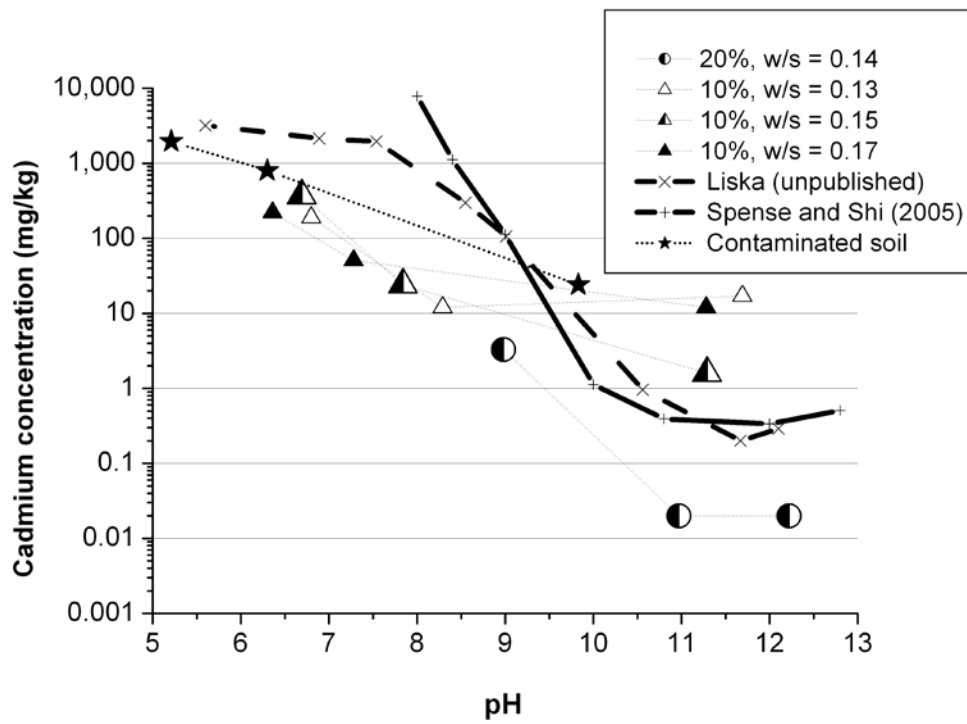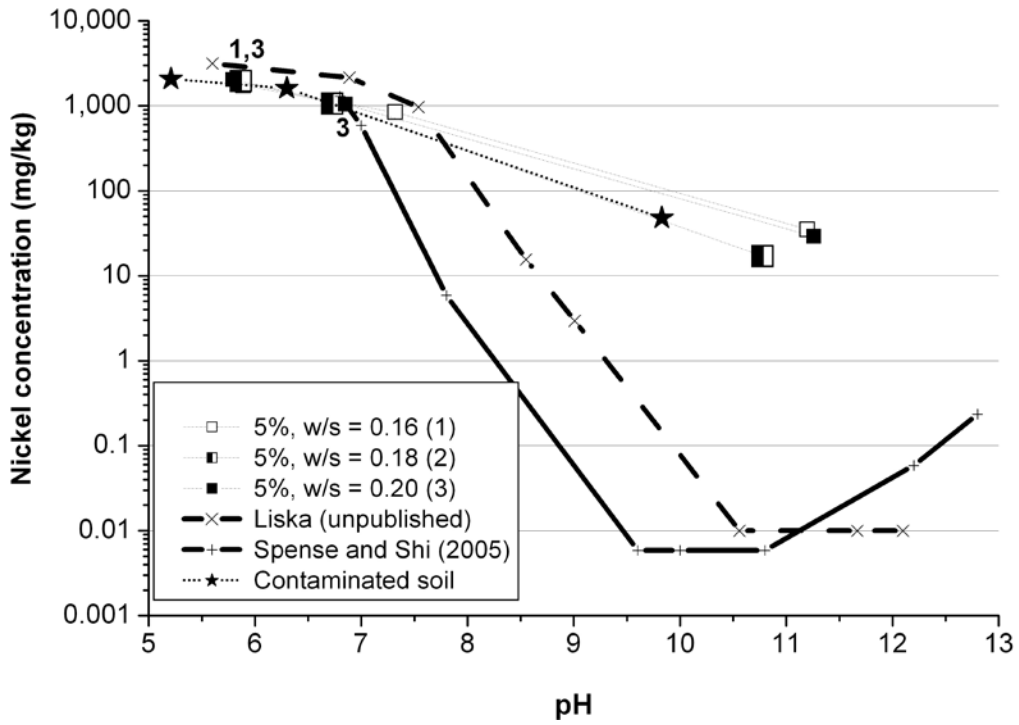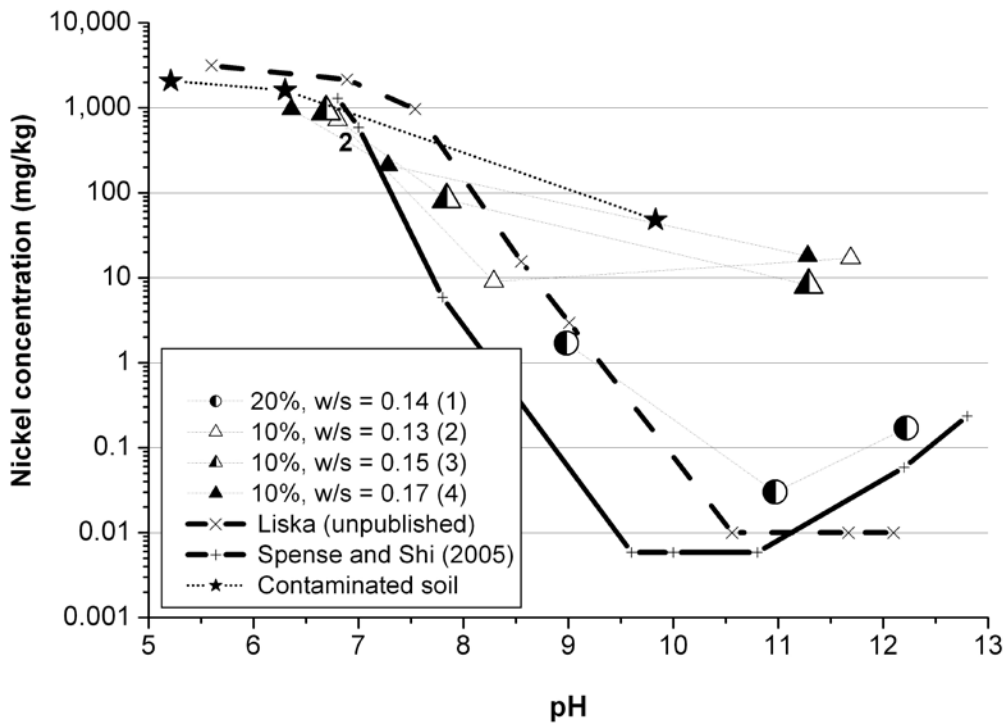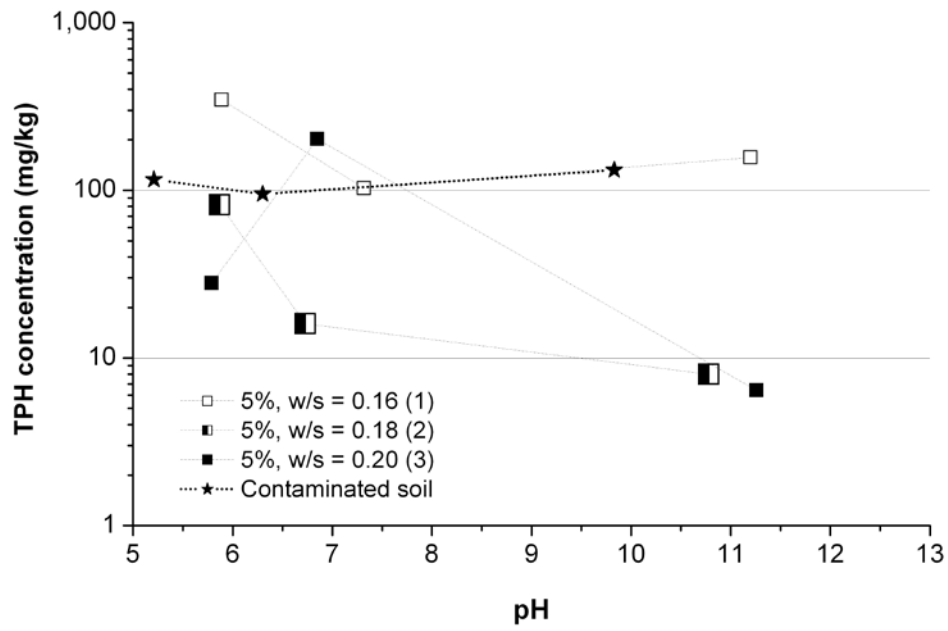

(b)

Figure 5. 28-day Cd leachability in (a) 5% (b) 10 and 20% dosage hlime-GGBS mixes

1
2   (a)
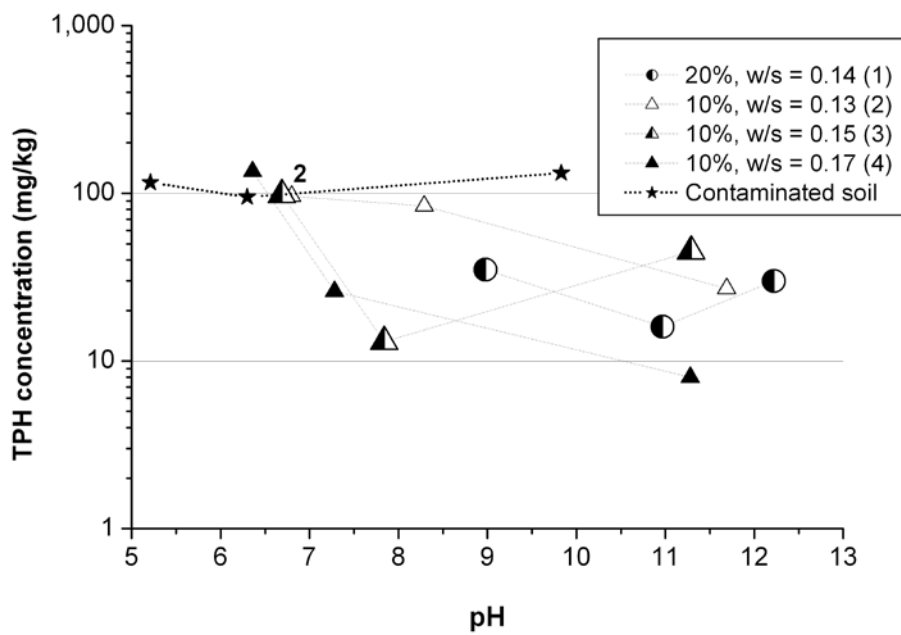3

4
5   (b)
6
7   **Figure 6. 28-day Ni leachability in (a) 5% (b) 10 and 20% dosage hlime-GGBS mixes**
8

(a)

(b)

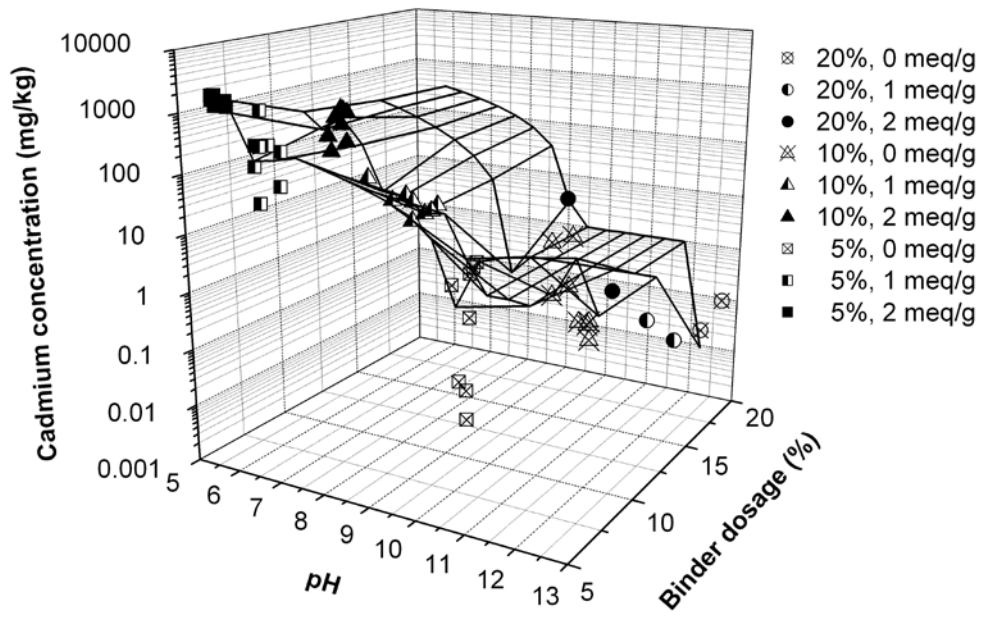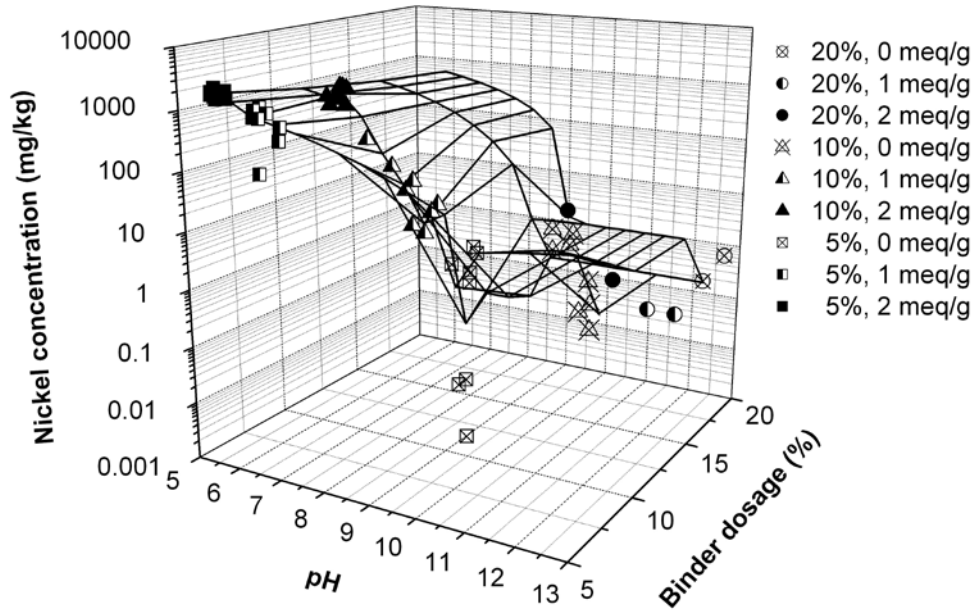**Figure 7. 28-day TPH leachability in (a) 5% (b) 10 and 20% dosage hlime-GGBS mixes**

(a)

(b)

Figure 8. Process envelope for (a) Cd (b) Ni leachability in hlime-GGBS-treated soil

1 **Table 2. Performance thresholds for mechanical and leaching behaviour**

Performance criteria	UCS	Permeability	Cd	Ni	Limits of operating variables acceptable
USEPA immersed UCS limit at 28 days to support overburden and equipment (kPa)[1]	350	-	-	-	≥ 10% binder dosage, w/s from OMC to OMC+2
UK Environment Agency 28 day UCS limit for disposal in landfill (kPa)[2]	1,000	-	-	-	> 20% binder dosage required
Typical limit for in-ground treatment in the UK[1] (m/s)	-	$< 10^{-9}$	-	-	None
USEPA limit for landfill disposal[3] (m/s)	-	$< 10^{-9}$	-	-	None
Canadian limit for disposal scenarios[1] (m/s)	-	$< 10^{-8}$	-	-	Not clear
Environmental Quality Standard for inland surface waters[4] (mg/l)	-	-	0.0045	0.02	20% binder dosage
Hazardous waste landfill WAC[2] (mg/kg)	-	-	5	40	≥10% dosage, but 5% likely for Cd, ≥5% dosage for Ni
Stable non-reactive hazardous waste in non-hazardous landfill WAC[2] (mg/kg)	-	-	1	10	OMC of 5 – 10% dosage likely, 20% dosage certain
Inert waste landfill WAC[2] (mg/kg)	-	-	0.04	0.4	20% binder dosage

2 [1]Al-Tabbaa and Stegemann (2005) [2]Environment Agency (2006) [3]USEPA (1986) [4]Förstner (2007)

3

4

5 4.0 **Conclusions**

6 The results of this study have demonstrated the effectiveness of lime-slag blend in reducing
7 the leachability of Cd and Ni in a mixed contaminated soil. The presence of hydrocarbons did
8 not have any deleterious effect on leachability of the metals as the binder also showed the
9 potential to reduce TPH leachability to some extent. Within the workable range of water
10 content, there was no significant effect of water content on leachability of the contaminants,
11 although in some cases, OMC and OMC-2 mixes performed marginally better. The study
12 showed that samples compacted at the next successive water content to the OMC (i.e.
13 OMC+2) achieved higher strength than those compacted at the OMC. Nevertheless, since
14 reduction in granular leachability is the most practical performance parameter from an
15 industrial perspective, the results suggest that compacting samples to the OMC gives the best
16 possible balance between acceptable mechanical and leaching properties.

Mechanical properties were largely governed by water and binder proportions, while heavy metal leachability was mainly controlled by pH and binder dosage. With 20% binder dosage, both metals met the WAC for inert waste landfill and relevant environmental quality standards, at 28 days. The implication of the pH-dependent leaching data questioned the capacity of the binder to satisfy the more stringent leaching criteria over a long time with 20% dosage. Nevertheless, the leaching behaviour of the metals suggests that long-term leaching concerns could be addressed with a higher (> 20%) binder dosage. The leaching behaviour of Cd and Ni were used to illustrate the immobilisation capacity of the binder because apart from Zn, both metals are the most mobile, and toxic, of the metals studied. All the same, the results of the other metals, which would be presented in a future paper, generally demonstrate the effectiveness of the binder. Therefore, the results of this study suggest that greater than 20% dosage would be required to achieve a balance of acceptable mechanical and leaching properties. This implies that with higher binder dosages, hlime-GGBS-treated contaminated soil could potentially be directed towards beneficial uses, for e.g. road construction, without environmental consequences. Overall, the process envelopes for the different performance criteria depend on the end-use of the treated material.

Acknowledgement

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