Utilisation of magnesium phosphate cements to facilitate biodegradation within a stabilised/solidified contaminated soil

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Stabilisation/solidification (S/S) of heavy metals and a parallel biodegradation of an organic contaminant using Magnesium phosphate cements (MPC) was investigated under laboratory conditions. The study was aimed at improving the robustness of S/S technology by encouraging biodegradation in order to bring about some form of contaminant attenuation over time. A silty sand soil, amended with compost was spiked with an organic contaminant, 2-chlorobenzoic acid (2CBA), and two heavy metal compounds, lead nitrate and zinc chloride. Two formulations of the MPC grouts based on different proportions of the cement constituents, with paste pH of approximately 6.5 and 10, were utilised for S/S treatment. The study involved treating the organic contaminant present in the soil with and without the heavy metals by employing the low and high pH MPC grout mixes, and using 10 and 25% compost content. Microbial activity was monitored using dehydrogenase assay, whilst the tests pertaining to the performance criteria such as contaminant concentration, unconfined compressive strength, elastic stiffness, permeability and batch leaching tests were evaluated at set periods. Contaminant recovery analysis after 140 days indicated a similar reduction in 2CBA concentration to approximately 56% in the different grout mixes. The cement constituents exhibited stimulatory and inhibitory effects on soil dehydrogenase activity. Heavy metal leachability as well as the engineering behaviour of the treated soils conformed to acceptable standards. The results of the investigations show considerable promise for the application of MPC in contaminated land remediation.

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Stabilisation/solidification (S/S) of heavy metals and a parallel biodegradation of an organic contaminant using Magnesium phosphate cements (MPC) was investigated under laboratory conditions. The study was aimed at improving the robustness of S/S technology by encouraging biodegradation in order to bring about some form of contaminant attenuation over time. A silty sand soil, amended with compost was spiked with an organic contaminant, 2-chlorobenzoic acid (2CBA), and two heavy metal compounds, lead nitrate and zinc chloride. Two formulations of the MPC grouts based on different proportions of the cement constituents, with paste pH of approximately 6.5 and 10, were utilised for S/S treatment. The study involved treating the organic contaminant present in the soil with and without the heavy metals by employing the low and high pH MPC grout mixes, and using 10 and 25% compost content. Microbial activity was monitored using dehydrogenase assay, whilst the tests pertaining to the performance criteria such as contaminant concentration, unconfined compressive strength, elastic stiffness, permeability and batch leaching tests were evaluated at set periods. Contaminant recovery analysis after 140 days indicated a similar reduction in 2CBA concentration to approximately 56% in the different grout mixes. The cement constituents exhibited stimulatory and inhibitory effects on soil dehydrogenase activity. Heavy metal leachability as well as the engineering behaviour of the treated soils conformed to acceptable standards. The results of the investigations show considerable promise for the application of MPC in contaminated land remediation.

Keywords: Stabilisation/solidification, Biodegradation, Soil contamination, Magnesium Phosphate Cement, Land reclamation.

1. Introduction

Many contaminated soils are characterised by the concomitant presence of both organics and heavy metals, which limits the deployment of a single remedial technology to achieve a successful cleanup of contaminated sites, since most treatment technologies are contaminant group specific. Hence, developing a remediation technology, which could robustly deal with a wide range of contamination, is not only desirable but also more sustainable.

Stabilisation/Solidification (S/S), which usually employs the addition of cementitious binders, mainly Portland cement (PC) based, has emerged as an efficient and cost-effective method for the treatment of a wide range of heavy metals in both hazardous wastes and contaminated soils, and has gained wide international acceptance (Al-Tabbaa and Stegemann 2005). Its effectiveness for the immobilisation of organic compounds has however been less successful due to interference of organics with setting and hydration processes of the cement. The mechanisms of conventional S/S treatment include chemical fixation and physical encapsulation of contaminants thereby reducing the potential for pollutant transfer into the environment (Al-Tabbaa and Stegemann 2005). S/S treatment therefore reduces the migration of contaminants, both organics and heavy metals, rather than their elimination.

Biodegradation, which generally entails the transformation and degradation of organic compounds through metabolic processes of microorganisms, is the most effective remediation technique for organic contamination to date. Therefore, it would be desirable to facilitate the biodegradation of organic contaminants within a S/S treated contaminated soil to bring about some form of contaminant attenuation over time. However, the characteristic high pH of PC (around 12-13) along with its low porosity impede microbial survival. Moreover, it has been documented that the PC industry contributes to around 5% of global anthropogenic CO_2 emissions; one of the major green house gases contributing to climate change (Worrell et al. 2001; van Oss and Padovani 2003). Hence, the application of a binder with a relatively lower pH, which could also address the sustainability issue with regard to CO_2 emissions, was considered in this work.

Magnesium phosphate cements (MPCs) are formed at room temperature by rapid acid-base reaction between dead burned magnesia and an acid phosphate source. Different variants of MPCs can be formed depending on the acid phosphate. For example, using ammonium

phosphate ($NH_4H_2PO_4$) would lead to magnesium ammonium phosphate cement, while use of potassium phosphate (KH_2PO_4) would lead to magnesium potassium phosphate cement. The main reaction product of conventional magnesium ammonium phosphate cement employing $NH_4H_2PO_4$ is struvite ($MgNH_4PO_4.6H_2O$) (Abdelrazig et al. 1989). The reaction of MgO with KH_2PO_4 yields magnesium potassium phosphate hexahydrate or K-struvite ($MgKPO_4.6H_2O$) (Wagh 2004). MPCs have found application in structural repair works, refractory materials, borehole sealants in oil drilling and completion works, recycling of benign wastes like coal ashes and mineral waste for use as construction products, and in-drum S/S of radioactive and hazardous wastes (Rao et al. 2000). Such cements have been credited with certain technical advantages beneficial to S/S treatment including reduced leachability, higher propensity for binding with waste inclusion, higher resistance to sulphate attack, lower permeability, higher early-age and long-term strengths and higher durability (Abdelrazig et al. 1989).

An added advantage of MPC is its potential to form mixes with different pH ranges, depending on the magnesia (i.e. basic component) and phosphate (i.e. acidic component) contents. This suits environmental applications like biodegradation wherein certain range of pH (5.5 – 8.5) is desired. One potential concern with such low pHs is that heavy metals are likely to leach out as the solubility of a number of metal speciations increase. However, it has been reported that MPCs immobilise heavy metals converting them to phosphates, which are relatively insoluble at the aforementioned pH range (Wagh 2004). This work utilised previously developed MPC mixes (Iyengar and Al-Tabbaa 2007; Iyengar 2008: PhD thesis, Cambridge University) at two extremes of the paste pH range, approximately 6.5 and 10, based on different proportions of the component materials i.e. dead burned magnesia and triple super phosphate (TSP). The ability of these mixes to bring about significant reduction in the leached concentrations of heavy metals from S/S treated contaminated soils has been reported (Iyengar and Al-Tabbaa 2008).

There is a paucity of literature on facilitation of biodegradation within stabilised/solidified waste systems, which were considered in the context of different applications and scenarios. The earliest studies in similar direction focussed on microbial influenced degradation of stabilised/solidified wastes disposed of in landfills (Knight et al. 2002; Sophia et al. 2007). However, these studies highlighted the possible effects on stabilised/solidified waste forms

through microbial action, which may be a problem if microbial growth is encouraged. The possibility of facilitating biodegradation within stabilised/solidified soil systems using a range of additives to PC-based as well as alternative grout systems in the form of Magnesium Oxide Cement and MPC have been investigated (Al-Tabbaa et al. 2007; Harbottle and Al-Tabbaa 2006; Harbottle and Al-Tabbaa 2008). The findings of these studies highlighted the importance of compost addition in encouraging the growth and survival of microbial life within soil-grout systems. However, these studies were limited to organic contaminants; but mixed contamination, which presents a much more complex scenario and is the characteristic of most contaminated soils, was not considered. Furthermore, the engineering behaviour of the S/S treated soil, which is likely to be affected by the incorporation of a biodegradative mechanism, was not evaluated in previous studies.

In this work, 2-Chlorobenzoic acid (2CBA) was used as organic contaminant, and lead nitrate and zinc chloride as metallic contaminants. Chlorobenzoates (CBs) are present in the environment because of the widespread use of herbicides deriving from compounds such as 2,3,6-TCB, dicamba and others; as dead-end products in the degradation of polychlorobiphenyls (PCBs) (Baggi and Zangrossi 1999) and as metabolites of chlorotuolenes (Lehning et al. 1997). 2CBA is the main CB that originates from PCB (Harkness et al. 1993). It was chosen because of its relatively low toxicity and relative ease of degradation (Harbottle and Al-Tabbaa 2008).

Lead and zinc were chosen as typical heavy metal contaminants. Soil pollution due to these metals is from a wide range of industrial and other processes including mining activities, metal processing, electronic industries, various chemical industries, including solvent applications, medical and dental applications, etc (Landner and Reuther 2004; Kabata-Pendias and Mukherjee 2007). The principal factors influencing potential risks of heavy metals are their solubility (or mobility), environmental bioavailability (adsorbed dose), and their toxicological bioavailability (effective dose). Metal mobility and bioavailability are mainly governed by abiotic factors, such as pH, redox conditions, and soil contents of organic matter and clay minerals (Ragnvaldsson et al. 2007).

Specific remediation techniques for soils contaminated by the above-mentioned contaminants include cover systems, in-ground barriers, stabilisation/solidification, soil vapour extraction,

air sparging, in situ soil flushing, bioremediation and soil washing. Although some of these techniques are potentially applicable, their application to the remediation of a specific contaminated site is dependent on a number of factors. Those factors considered of particular importance are the clean-up target, technical feasibility relative to the particular site, soil and contaminant characteristics, long-term monitoring arrangements for slow remedial techniques or for immobilisation and containment techniques, validation of the remediation, health and safety aspects, regulator and public acceptance and cost (Pearl 2000). The present study focuses on the combination of stabilisation/solidification and bioremediation.

The objective of this study was to investigate the feasibility of facilitating organic contaminant degradation and heavy metal immobilisation within a S/S treated soil without compromising the structural integrity of the treated material.

2. Materials and methods

2.1 Model contaminated soil

A model contaminated silty sand providing a simplified simulation of contamination conditions was prepared using Fraction-D Leighton Buzzard sand (D_{50} ~150-300 μm, David Ball Ltd., UK) and silt (silica flour, D_{50}< 150 μm, David Ball Ltd, UK). Eco-compost (sieved past 2 mm; Scotsdales Ltd., Cambridge, UK), with oven dried moisture content of 100%, was added as organic matter to provide a microbial inoculum as well as a source of nutrients. As the experiments involved different treatment options, three variants of the same soil type with similar composition were used. The sand-silt ratios used were 3, 3.5 and 4 due to difference in compost content, since the effects of compost addition and abiotic contaminant loss were investigated:

- The soil in majority of the mixes was composed of 70% sand, 20% silt and 10% compost.
- One of the mixes had increased compost content and its soil was composed of 60% sand, 15% silt and 25% compost.
- Two mixes were used as abiotic controls, the soil was composed of 75% sand and 25% silt.

In all cases, the soil was prepared with a moisture content of 15%, which includes the moisture content of the compost added. The soils were contaminated with 3000 mg/kg of

each of the three contaminants, 2CBA, lead nitrate and zinc chloride. This resulted in theoretical concentrations of around 1877 and 1439 mg/kg for lead and zinc respectively.

2.2 Binder materials

Two MPC mixes were used, one at the lower pH end (pH ~6.5) and the other at the higher pH end (pH ~10), based on two different combinations of TSP (supplied by RS Minerals, UK) and dead burned magnesia (MgO, Richard Baker Harrison, UK). TSP is a common fertiliser, it is predominantly calcium dihydrogen phosphate, and contains some gypsum (Iyengar and Al-Tabbaa 2008). Dead burned magnesia is composed of 82.6% by weight MgO, 7.5% SiO_2, 5.6% CaO, 3.4% Al_2O_3 and 0.9% Fe_2O_3. The cement constituents were mixed in the ratio, TSP:MgO = 8:1 for the lower pH end, and TSP:MgO = 1:2 for the higher pH end. De-ionised water was used to produce the wet grout in which the cement:water ratio was 2:1. This water content was chosen to ensure a moist environment for microorganisms and was based on related S/S work (Iyengar 2008, PhD thesis, Cambridge University).

2.3 Preparation of stabilised/solidified soil systems

In preparing the model-contaminated soil, the dry soil components (which include the compost) were mixed in a pre-dried and clean rotary drum mixer for several minutes until a consistent mix was achieved. 2CBA was then added in dry powdered form and the soil mixed for several minutes. The metallic compounds were dissolved in de-ionised water and then added to the mix. However, not all mixes included the metallic contaminants. Further mixing was carried out until the mix appeared homogenous. The soil was then incubated at room temperature (i.e. 20 ± 2 °C) for 5 hours. Thereafter, soil samples were taken for initial measurements of contaminant concentration and dehydrogenase activity, prior to cement grout addition. The soil was then mixed with the cement grout in the rotary drum mixer at a dry soil: grout ratio of 2:1. A set of S/S treated uncontaminated soil mixes were used as control samples for engineering behaviour and their preparation followed the same procedure described above except that there was no contaminant addition. Similarly, S/S treated soil containing all three contaminants, prepared in the same way described above but without compost addition, were used as abiotic controls. However, the soil used in the abiotic controls was sterilised in an autoclave at 121 °C, twice, before addition of the contaminants and cement grout. Soil containing compost, autoclaved as above, was initially used for abiotic controls but after S/S

treatment, there was evidence of microbial activity in mixes treated with the higher pH cement formulation. Hence, they were discontinued and soil without compost was used.

Soil-cement mixes were produced by carefully casting the mix materials into cylindrical moulds, 50 mm diameter with length 100 mm, while ensuring a uniform and homogenous mass devoid of air bubbles. The average mass of each cylindrical sample containing the soil-cement grout was approximately 440 g. The moulded samples were stored in curing tanks at room temperature of 20 ± 2 °C for 3 days after which they were demoulded and incubated at 32 ± 4 °C and $95 \pm 3\%$ relative humidity in order to encourage biodegradation. The samples were loosely covered with plastic film to prevent excessive moisture loss.

2.4 Experimental design

Nine treatment options were employed as detailed in Table 1. Each soil-cement mix had three replicate samples for each time point of analysis. In addition, the standard mixes on which permeability testing was conducted had extra duplicate samples for each of three time points of analysis. Analysis of all the S/S treated samples was conducted at 0, 14, 28, 84, and 140 days, unless specified otherwise. The ideas behind the different treatments are as follows:
- Mixes 1 and 2: Standard mixes (mixed contamination scenario)
- Mixes 3 and 4: Effect of the absence of heavy metals, in comparison to mixes 1 and 2
- Mix 5: Effect of increasing the compost content in comparison to mix 2
- Mixes 6 and 7: Uncontaminated controls (for engineering behaviour)
- Mixes 8 and 9: Abiotic controls in comparison to mixes 1 and 2

2.5 Sampling

Generally, the unconfined compressive strength (UCS) of the cylindrical samples was first determined before they were destructively sampled for other tests. Destructive sampling involved crushing the S/S material in a mortar with pestle subsequent to which granular or powdered samples were taken. As a result, samples at different time points were not taken from the same S/S monolith. Separate monolithic cylindrical samples were used for permeability tests.

Table 1. Components for each of the nine mixes (% by weight)

Mix description	Soil				Cement			Contaminants		
	Sand	Silt	Compost	Water	TSP	MgO	Water	2CBA	$Pb(NO_3)_2$	$ZnCl_2$
1: Soil with 10% compost containing organic and metallic contaminants, treated with TSP:MgO = 8:1 grout	37.65	10.76	5.38	5.38	23.91	2.99	13.45	0.16	0.16	0.16
2: Soil with 10% compost containing organic and metallic contaminants, treated with TSP:MgO =1:2 grout	37.65	10.76	5.38	5.38	8.97	17.93	13.45	0.16	0.16	0.16
3: Soil with 10% compost containing only organic contaminant, treated with TSP:MgO = 8:1 grout	37.68	10.77	5.38	5.38	23.93	2.99	13.46	0.16	-	-
4: Soil with 10% compost containing only organic contaminant, treated with TSP:MgO = 1:2 grout	37.68	10.77	5.38	5.38	8.97	17.95	13.46	0.16	-	-
5: Soil with 25% compost containing organic and metallic contaminants, treated with TSP:MgO = 1:2 grout	32.28	8.07	13.45	5.38	8.97	17.93	13.45	0.16	0.16	0.16
6: Soil with 10% compost without contaminants, stabilised/solidified with TSP:MgO = 8:1 grout	37.84	10.81	5.41	5.41	24.03	3.00	13.51	-	-	-
7: Soil with 10% compost without contaminants, stabilised/solidified with TSP:MgO = 1:2 grout	37.84	10.81	5.41	5.41	9.01	18.02	13.51	-	-	-
8: Autoclaved soil without compost containing organic and metallic contaminants, treated with TSP:MgO = 8:1 grout	40.34	13.45	-	5.38	23.91	2.99	13.45	0.16	0.16	0.16
9: Autoclaved soil without compost containing organic and metallic contaminants, treated with TSP:MgO = 1:2 grout	40.34	13.45	-	5.38	8.97	17.93	13.45	0.16	0.16	0.16

2.6 Testing and analytical methods

The following tests were carried out on the standard treatment mixes: microbial enzyme activity, organic contaminant extraction, batch leaching, pH of soil-cement grout, moisture content, unconfined compressive strength (UCS), elastic stiffness and permeability. Some of the above tests focussed on the behaviour of the contaminant(s) while others assessed the effect of biodegradation on the performance of the stabilised/solidified material over time.

Microbial enzyme activity was determined using the TTC dehydrogenase assay following the combined methods of Cassida et al. (1964) and Harbottle and Al-Tabbaa (2008). This was necessary in order to suit the peculiar circumstances of this study as the high concentration of contaminants used caused suppression of microbial activity. Six grams of soil or crushed soil-cement was placed in a 16×150 mm test tube with 3.5 ml of 0.75% 2,3,5-Triphenyltetrazolium chloride (TTC) solution containing 50 mM Trizma hydrochloride. The resulting slurry was vortexed, and the test tube stoppered and incubated for 24 hours at 37 °C. This was followed by ethanol extraction and determination of the amount of 2,3,5-triphenyltetrazolium formazan (TPF—a water-insoluble red dye) produced using a UV/VIS Spectrophotometer at a wavelength of 485 nm. The choice of dehydrogenase assay in this study was due to the test been indicative of the total metabolic activity of soil microorganisms and its successful deployment as a measure of soil biological activity in several works.

Organic contaminant analysis was done using the sulphuric acid/ethanol extraction previously described by Harbottle and Al-Tabbaa (2008). The moisture content was recorded as the mass of water divided by the oven-dry (105 °C) mass of soil/grout sample. The pH of soil-cement grout was determined by dipping the electrode into a 1:5 soil-cement:water (de-ionised water) suspension that has been stirred and allowed to settle for at least 2 hours (ISO 10390, 2005). Batch leaching followed BS EN 12457 (BSI 2002). 100g of crushed soil-cement sample with particle size < 4 mm was agitated in a litre of water at a pH of 5.6 on a rotating table for 24 hours. Thereafter, the leachate was analysed for lead and zinc using an atomic absorption spectrophotometer.

The UCS of the soil-cement samples was determined according to ASTM test method D1633 (2000) using a universal testing machine in which the vertical load was applied axially at a

constant strain rate of 1.143 mm/min until failure. The maximum pressure was calculated from the maximum force and the cross-sectional area of the sample, and reported as the UCS in kPa. Elastic stiffness was calculated in terms of the secant modulus (E_{50}) (i.e. modulus at stress level equal to 50% of unconfined compressive strength) using the stress-strain curve derived from the UCS test. Permeability tests were carried out on the samples in duplicate using flexible-wall permeameters (ASTM 2003). Confining pressure of 300 kPa was applied. The volume of water passed through a saturated monolithic specimen under pressure in a given period was measured, and the permeability calculated using Darcy's Law.

2.7 Statistical analysis

One-way and two-way analysis of variance (ANOVA) was used for data analysis to test for differences in the performance properties above due to age of testing and differences in cement formulation, compost content, type of contaminants present or the absence of contaminants, and the presence of microbes. Significance was based on $\alpha = 0.05$.

3. Results and discussion

The presentation of the results for organic contaminant analysis and microbial enzyme activity are based on unit mass of oven dry soil, not unit mass of soil-cement sample. This is because the mass of dry soil in the soil-cement mix remained constant throughout the experiment as opposed to that of the soil-cement mix, which changed due to setting and hydration reactions of the cement. The values of measured properties presented in the figures are the mean values; the standard deviation is shown by the error bars. Where applicable, the 'day 0' values on the graphs represent data obtained for contaminated soil-only samples prior to grout addition. In describing the mixes, for brevity the abbreviations, P, M and C are used to refer to triple super phosphate, dead burned magnesia and compost, respectively.
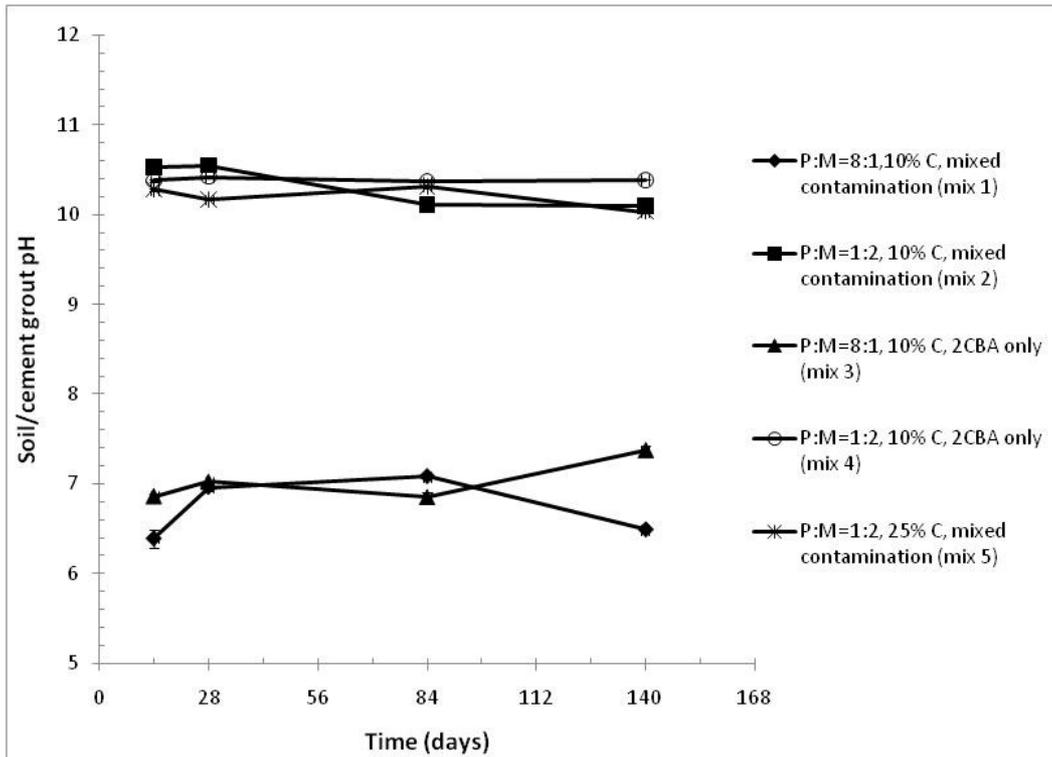
3.1 pH of soil-cement grout

Measures were made of soil-cement grout pH in order to confirm that there was no change in the parameter with time; hence, it does not affect contaminant behaviour over time. The pH of the contaminated soil before treatment was 4.54 due to the acidity of the organic contaminant. Figure 1 shows that with both grout systems, the variation in pH was consistently around 6.5 and 10 for the lower pH and higher pH mixes respectively. With both grout systems, there was significant difference in pH over time due to differences in compost

content and type of contaminant(s) present, at the 0.1% level. However, the variation in pH was consistently around the aforementioned values; hence, the variability was unlikely to affect contaminant behaviour. The consistence of the pH stems from the fact that after S/S treatment, the behaviour of the resulting monolith is governed by the grout characteristics.
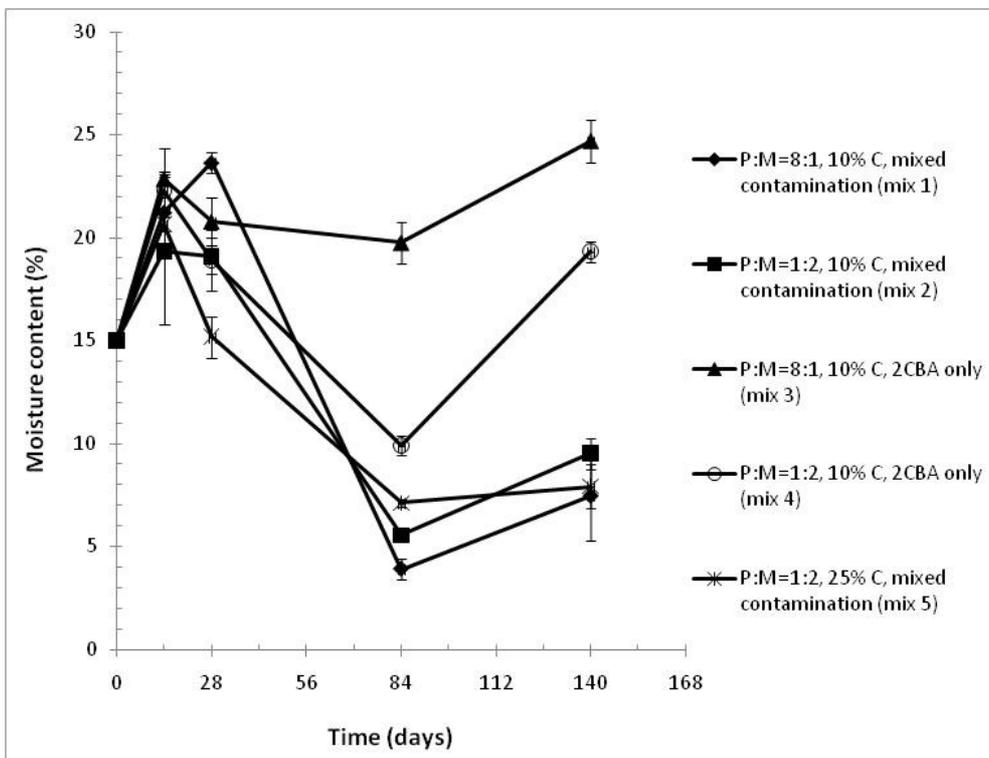
3.2 Moisture content

Moisture content was monitored in order to assess the effects of fluctuations in the parameter on microbial activity. It has been reported that soil microbial biomass and activity declined with decreasing water content (Van Gestel et al. 1993). The water content clearly increased at 14 days from its 0-day value of the untreated soil due to grout addition (Figure 2). Thereafter it decreased over time due to evaporation (caused by drying in the curing conditions) and possibly because of the cement hydration reactions (Harbottle and Al-Tabbaa 2008). There was significant moisture loss with increase in sample age ($p < 0.1\%$), but there was no significant difference between the moisture content of both cement formulations. The dip in moisture content at 84 days in the soil-cement systems is mainly due to fluctuations in temperature and relative humidity in the incubator in which the samples were stored. As analytical samples were taken from different soil-cement systems at each sampling point, fluctuations in the aforementioned properties of the incubator is bound to affect the results obtained at the various time points. Moreover, amidst the high relative humidity of the incubator there were still problems with maintaining steady moisture content in the soil-grout systems. The differences in moisture content of the samples cannot be directly linked to any treatment, as these were mainly response of the mixes to fluctuations in environmental conditions, which is likely to have been affected by factors such as position within the incubator and time of sample preparation/storage.

P: triple super phosphate, M: dead burned magnesia, C: compost, 2CBA: 2-chlorobenzoic acid

Figure 1. pH of soil-cement grout

P: triple super phosphate, M: dead burned magnesia, C: compost, 2CBA: 2-chlorobenzoic acid

Figure 2. Moisture content of S/S treated contaminated soils

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3.3 Organic contaminant analysis

Table 2 shows 2CBA recovery from the mixes over time. At 28 days, it appeared that mixes 1 and 2 (with mixed contamination) indicated higher contaminant loss than the mixes with only organic contamination and higher compost content. However, from 84 to 140 days of treatment, contaminant loss in the mixes with 10% compost content (mixes 1, 2, 3 and 4) were similar. After 140 days, there was a reduction in 2CBA concentration to ~56.5% and ~56.3% of the initial amount within the lower and higher pH mixes with mixed contamination (mixes 1 and 2), respectively. Contaminant reduction in samples without heavy metals was down to approximately 56.5% of the initial value for both cement formulations. Hence, both binders were as effective in contaminant degradation. The contaminant concentrations observed in mix 2 with 10% compost were significantly lower ($p = 0.002$) than those in mix 5 with 25% compost. A similar observation was made by Harbottle (2006) (unpublished results) wherein 10% compost addition to soil was found to cause better contaminant attenuation than 20% compost addition. There was no statistically significant difference in contaminant concentration ($p = 0.74$) between the two cement formulations, but the contaminant concentrations recorded over time were significantly different at the 1% level.

The abiotic controls (mixes 8 and 9) were monitored for 84 days, unlike the other mixes, which were monitored for 140 days. Hence, comparison between the abiotic controls and the standard mixes (i.e. mix 1 and mix 8, and mix 2 and mix 9) is done at 84 days. There was a large decrease in 2CBA concentration in the abiotic controls between 0 and 14 days compared to the standard mixes. However, at 28 days, 2CBA concentration was marginally lower in the abiotic mixes than the standard mixes. The large difference in contaminant concentration in both sets of mixes at the initial stage may be due to differences in hydration process of the cement formulations since they had different composition. The standard mixes contained compost but the abiotic mixes did not. After 84 days, there was a reduction in 2CBA concentration to 75.9% and 75.4% of the initial value in the lower and higher pH mixes of the abiotic controls, respectively. In the standard mixes, 2CBA concentration was reduced to 56.7% and 57.3% for the lower and higher pH mixes respectively, at 84 days. There was significant difference ($p = 0.04$) between the standard mix and the abiotic control of the higher pH cement formulation. However, in the lower pH mixes, there was no significant difference ($p = 0.576$) between the standard mix and the abiotic control, but there was significant interaction ($p = 0.001$) between age and biological activity. In both cement formulations, contaminant reduction with time was significant at the 0.1% level.

Table 2. Organic contaminant concentration for the mixes

Mix description	Time (days)				
	0	14	28	84	140
	Contaminant concentration (mg 2CBA/kg dry soil)				
1: P:M=8:1, 10% C, mixed contamination	3000	2890 ± 110	2474 ± 189	1701 ± 289	1694 ± 326
2: P:M=1:2, 10% C, mixed contamination	3000	2683 ± 193	2552 ± 272	1719 ± 35	1688 ± 144
3: P:M=8:1, 10% C, 2CBA only	3000	2976 ± 20	2920 ± 42	1715 ± 129	1694 ± 84
4: P:M=1:2, 10% C, 2CBA only	3000	2992 ± 157	2982 ± 53	1718 ± 185	1695 ± 170
5: P:M=1:2, 25% C, mixed contamination	3000	2906 ± 79	2805 ± 91	1956 ± 171	1950 ± 188
8: P:M=8:1, No C, mixed contamination (abiotic)	3000	2504 ± 97	2419 ± 105	2278 ± 126	-
9: P:M=1:2, No C, mixed contamination (abiotic)	3000	2702 ± 55	2522 ± 62	2262 ± 122	-

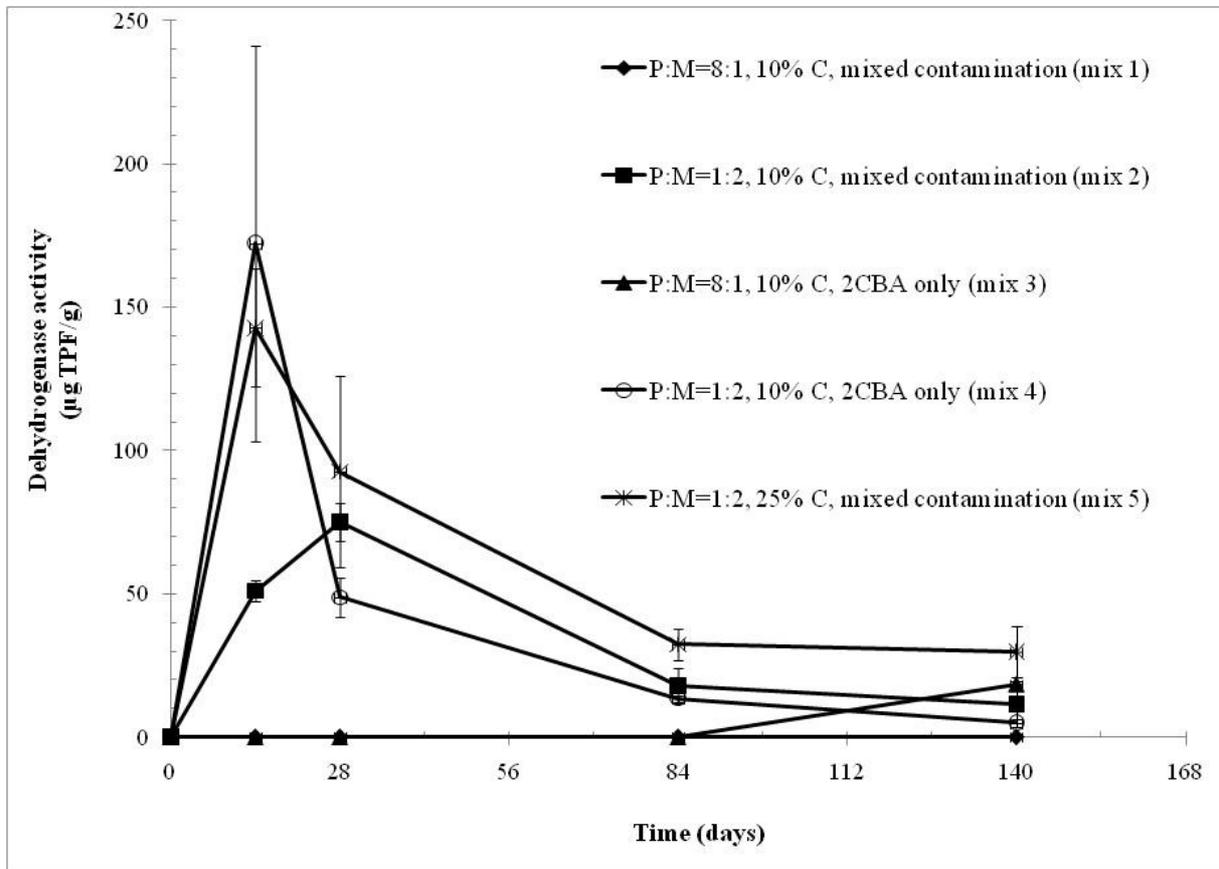P: triple super phosphate, M: dead burned magnesia, C: compost, 2CBA: 2-chlorobenzoic acid

3.4 Microbial enzyme activity

The day 0 points (i.e. the contaminated soils immediately prior to S/S treatment) in Figure 3 indicate that in the aftermath of soil contamination by the organic contaminant with or without the presence of heavy metals and with both compost contents, there was no evidence of dehydrogenase activity in the soil. However, the model soil composition with 10% compost content had a mean dehydrogenase activity of 29.9 μg TPF/g before contamination. With 25% compost content, the uncontaminated model soil had a mean dehydrogenase activity of 52.3 μg TPF/g (see Table 3, section 1). Details of further investigations on dehydrogenase activity, which explains the reason for lack of microbial activity in the day 0 samples, are shown in Table 3, section 2. It was observed that at mixed contamination levels of 93.75 and 187.5 mg/kg, dehydrogenase activity was higher than that in uncontaminated soil, but was reduced at 750 mg/kg and inhibited at 1500 mg/kg and above. Harbottle and Al-Tabbaa (2006) used soil contaminated with 500 mg/kg of the organic contaminant, and there was considerable amount of dehydrogenase activity. These show that the absence of dehydrogenase activity in the contaminated soils prior to S/S treatment was due to the high level of contamination. A similar observation in which dehydrogenase activity was stimulated at low levels of mixed contamination and inhibited at higher levels was reported by Gong et al. (1996). It has been documented that the maximum level microbes can tolerate for each of

both metals used in this study is about 1000 mg/kg (Ruthven and Cairns 1973; Stuczynski et al. 2003).

Figure 3. Dehydrogenase activity for S/S contaminated soils

The test result at 14 days after grout addition indicated the presence of microbial activity in soil-cement systems with the greater magnesia content (P:M=1:2, pH ~10), mixes 2, 4 and 5; but surprisingly there was no evidence of microbial activity in soil-cement systems with greater phosphate content (P:M=8:1), mixes 1 and 3. It was thought that the lower pH mixes whose pH (~6.5) falls within the optimum pH range favourable for microbial activity (5.5 to 8.5) would enhance microbial activity more than the higher pH mixes (Harbottle and Al-Tabbaa 2006). The resuscitation of microbial activity after the addition of the higher pH cement is likely due to the stimulatory effect of the cement as it helps to bind the contaminants in an unavailable form thus creating less toxic conditions. It is likely that the organic contaminant was trapped in pores within the solid matrix thereby reducing its toxicity to microbes, especially for mix 4 with 2CBA only. In the course of the experiments, it was

observed that TSP was responsible for the suppression of dehydrogenase activity in the lower pH mixes. The lower pH mixes did not indicate any trace of dehydrogenase activity up to when sampling was done at 84 days. However, it was observed that 140-day samples of mix 3 (P:M=8:1, 2CBA only, pH~6.5) had evidence of dehydrogenase activity. The exact mechanism responsible for this is poorly understood but it is likely that the interaction of age and absence of heavy metals may have had some effect on such anomalous behaviour. It is suspected that dehydrogenase activity in mix 1 (P:M=8:1, mixed contamination, pH~6.5) may have recovered over time like mix 3 but for its rapid moisture loss and slight decrease in pH (see Figures 1 and 2). Figure 3 also shows that for samples treated with the higher pH grout, compared to 10% compost content, 25% compost content led to comparatively increased microbial activity. In all samples treated with the higher pH grout, considerable amounts of dehydrogenase activity were sustained for over 28 days, thereafter the activity decreased with time. There was significant difference in dehydrogenase activity between mixes with 10% and 25% compost content at the 0.1% level. The difference between dehydrogenase activities observed in the higher pH mixes with and without heavy metals was not statistically significant ($p = 0.06$). However, the dehydrogenase activities recorded at different sample ages were significantly different at 0.1% level.

Further investigations into the absence of dehydrogenase activity in the lower pH mixes, which ought to encourage biological activity revealed two interesting findings. Dead burned magnesia was found to interfere with the test result by inducing a similar colour change (pink colouration) associated with TPF production, which is brought about by the action of dehydrogenase enzymes in the assay. Thus, it apparently stimulates dehydrogenase activity. It was also observed that TSP apparently inhibits soil dehydrogenase activity. The results of the tests are shown in Table 3, section 3. The abiotic dehydrogenase activity due to magnesia content was quantified to be about 21.1 µg TPF/g. Cement constituents (MgO and TSP) only, in the ratio P:M=1:2 (pH ~10), had an increased amount of about 27.5 µg TPF/g, while the cement formulation with pH ~ 6.5 (P:M=8:1) had an activity of 21.4 µg TPF/g. Tests on the abiotic control with higher magnesia content showed a similar amount of the abiotic dehydrogenase activity, which appeared to fade with time (Table 3, section 5). These results suggest that the presence of dead burned magnesia or perhaps some impurities/compounds within it stimulates soil dehydrogenase activity, though there are indications that the main reaction product of the cementitious system, Ca-Struvite (Iyengar 2008: PhD thesis,

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Cambridge University), further enhances the stimulation. A list of substances that could cause a similar stimulation of soil dehydrogenase activity has been identified in the literature (Weaver et al. 1994) but magnesium was not listed. The work of Takahashi and Weiner (1980) which reported the stimulation of catalytic activity of horse liver aldehyde dehydrogenase by magnesium ions is probably the only related case in the literature. However, the steady state assay used in the said work did not involve soil. The results of this study also show that the influence of pH noted by Mahmoud and Ghaly (2004), whereby high pH environments ($9.5 \leq pH \leq 13$) can lead to non-enzymatic production of TPF in the TTC dehydrogenase assay, does not seem to be responsible for the aforementioned abiotic dehydrogenase activity. This is because both cement mixes, with pH 10 and 6.5, indicated the non-enzymatic TPF production; hence, the abiotic dehydrogenase activity is due to the effect of magnesia not pH. The results further indicate that the dehydrogenase activity observed in the higher pH soil-cement mixes has a biotic and an abiotic component.

The investigations suggested that TSP apparently inhibits soil dehydrogenase activity, which explains the absence of dehydrogenase activity in the lower pH soil-cement mixes. TSP was found to inhibit dehydrogenase activity in pristine compost even at 2.5% TSP content in compost-TSP mixture (Table 3, section 3). In the light of the above, it is interesting to note that although the percentage of TSP in soil-cement samples with the higher pH was ~ 9%, and that in the combination of only TSP and MgO (P:M=8:1), was 88.9%, dehydrogenase activity was still observed in these mixtures. It is likely that this is due to the relative amounts of magnesia and TSP in the said mixtures, as reaction between TSP and sufficient amount of magnesia removes the inhibitory effect of TSP. Moreover, the results in section 3 of Table 3 show that the abiotic dehydrogenase activity was reduced when TSP was in greater amount than magnesia. This is probably one of the first studies reporting inhibition of dehydrogenase activity by TSP. It is in the literature that added phosphates stimulated soil dehydrogenase activity, and although substances that seemed to inhibit the activity have been identified, TSP is not listed (Weaver et al. 1994). A different phosphate source, potassium dihydrogen phosphate (KH_2PO_4), was employed in a similar study (Harbottle and Al-Tabbaa 2008) but no such inhibition was observed. However, the percentage of KH_2PO_4 was about 10% in the said work, which is similar to the amount of TSP in the higher pH soil-cement mixes that indicated dehydrogenase activity in this study. Furthermore, a few studies have reported

1 reduction of soil microbial activity, as measured by other indices of soil biological activity, in

2 the presence of phosphates (Kelly and Henderson 1978; Thirukkumaran and Parkinson 2000).

3 **Table 3. Details of other Dehydrogenase activity tests**

Section	Treatment kind		Dehydrogenase activity (μg TPF/g)
1	Uncontaminated model soil with 10% compost content		29.9 ± 12.3
	Uncontaminated model soil with 25% compost content		52.3 ± 1.15
2	Model soil with 10% compost content and different levels of mixed contamination, using the same amount of each of the three contaminants (2CBA, lead nitrate and zinc chloride) at the following contaminant levels:	0 mg/kg	29.9 ± 12.3
		93.75 mg/kg	63.4 ± 9.0
		187.5 mg/kg	47.7 ± 10.3
		750 mg/kg	25.0 ± 6.6
		1500 mg/kg	0.0
		2250 mg/kg	0.0
	Compost only, with 3000 mg/kg mixed contamination		0.0
3	Triple Super Phosphate (P) only		0.0
	Dead burned magnesia (M) only		21.1 ± 0.5 (**abiotic**)
	Grout constituents only, P:M = 8:1 (pH~6.5)		21.4 ± 0.0 (**abiotic**)
	Grout constituents only, P:M = 1:2 (pH~10)		27.5 ± 0.2 (**abiotic**)
	Uncontaminated soil with 10% compost content treated with P:M = 8:1 grout, mix 6 (after 1and 5 days)		0.0
	Uncontaminated soil with 10% compost content treated with P:M = 1:2 grout, mix 7 (after 5 days)		28.4 ± 2.7
	Compost plus different amounts of P, P being: 2.5%, 5%, 10%, 20% and 30% of the mixture, without any contamination		0.0
4	Mix 8, P:M=8:1, no compost, mixed contamination (abiotic control) (at 0, 14, 28 and 84 days)		0.0
5	Mix 9, P:M=1:2, no compost, mixed contamination (abiotic control)	0-day	0.0
		14-day	21.1 ± 0.0
		28-day	7.3 ± 0.5
		84-day	5.2 ± 0.5

4 Results represent mean ± standard deviation of three replicates

5 P: triple super phosphate, M: dead burned magnesia, 2CBA: 2-chlorobenzoic acid

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7 **3.5 Batch leaching**

8 Batch leaching was carried out on the standard treatment mixes only (mixes 1 and 2). The

9 results are shown in Table 4. As expected, S/S treatment significantly reduced the

10 leachability of lead and zinc in the soils. The leachate concentrations of both metals in soil-

11 cement samples treated with the two different grout mixes were well below the inert landfill

waste acceptance criteria (WAC) specified in the EU Landfill Directive (European Commission 1999) at all sampling times. A comparison of the leachate concentration of zinc in both grout systems indicates that the higher pH system achieved a slightly better immobilisation of the contaminant than the lower pH system over time. It is common knowledge that metal solubility usually increases with decreasing pH and this seems to have been more pronounced in the grout systems, with zinc than lead. There was significant difference (p = 0.002) in the leached concentrations of lead over time in both cement formulations. The difference in the leached concentrations of zinc over time between both cement formulations was significant at the 0.1% level.

Table 4. Batch leaching results for Lead and Zinc recovery

Mix description	Time (days)			Time (days)		
	28	84	140	28	84	140
	Lead leachate concentration (mg/kg)			Zinc leachate concentration (mg/kg)		
1: P:M=8:1, 10% C, mixed contamination	0.005 ± 0.0005	0.002 ± 0.0001	0.0095 ± 0.0002	0.815 ± 0.045	0.833 ± 0.056	0.94 ± 0.036
2: P:M=1:2, 10% C, mixed contamination	0.0075 ± 0.0008	0.018 ± 0.003	0.0045 ± 0.0006	0.34 ± 0.0006	0.1 ± 0.021	0.1 ± 0.014

Maximum concentrations of lead and zinc expected are 1325 and 1016 mg/kg respectively

Waste acceptance criteria for inert landfills for lead and zinc are 0.5 and 4 mg/kg respectively

P: triple super phosphate, M: dead burned magnesia, C: compost

3.6 Linkage between dehydrogenase activity and concentration of contaminants

The results in Table 2 and Figure 3 show that loss of the organic contaminant in mix 5 (25% compost content) was lower than that in mix 2 (10% compost content), although the dehydrogenase assay showed that 25% compost content led to increased microbial activity than 10% compost content. As mentioned earlier, this has been previously observed (Harbottle 2006, unpublished results) but the exact mechanism responsible for the behaviour is not clearly understood. Furthermore, loss of the organic contaminant in the lower pH mixes in which dehydrogenase activity was inhibited was similar to that observed in the higher pH mixes with evidence of microbial activity. Moreover, there was contaminant reduction in abiotic controls too, and the contaminant concentrations recorded at the initial stage was lower than those obtained in the standard mixes. However, the attenuation recorded in the

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standard mixes at 84 days was significantly lower than that in the abiotic controls. In the higher pH cement, the difference was significant at the 1% level; in the lower pH cement, it was significant at the 5% level. Figure 3 shows that by 84 days, dehydrogenase activity in the higher pH mixes had significantly declined such that data obtained at 140 days were only slightly lower. This is corroborated by the results in Table 2 in which contaminant concentrations at 84 and 140 days followed a similar trend. Dehydrogenase activity was also observed for the first time in a set of soil-cement samples treated with the lower pH cement (mix 3) at 140 days, when 44% of the organic was lost. These observations question the influence of microbes in the contaminant reduction recorded, as well as the suitability of dehydrogenase assay for evaluating microbial activity in the cementitious system. It also suggests the likelihood of abiotic sources of contaminant loss. It is thought that contaminant loss is due to the combined effect of biodegradation and other abiotic factors like chemical fixation of the contaminant by interaction between the cement's hydration product(s) and the contaminant, especially as volatilisation is ruled out since 2CBA is non-volatile. The potential for direct immobilisation of organic contaminants by S/S treatment processes, albeit with low efficiency, has been reported (Paria and Yuet 2006).

The results of the batch leaching test suggest that the effect of heavy metals on biological activity in the treated soils is ruled out, especially as leachability of the metals was significantly reduced and also considering the fact that some of the treated soils indicated biological activity.

3.7 Engineering properties

The results of UCS, elastic stiffness and permeability are presented in Figures 4, 5 and 6 respectively. These tests sought to evaluate the effect of grout mix, mixed contamination and increased compost content on the measured properties. Hence, only results of the standard mixes (mixes 1 and 2), the mix with 25% compost content (mix 5) and those of the uncontaminated control mixes for engineering behaviour (mix 6 and 7) are shown.

There was a marked difference ($p < 0.001$) in the UCS of soil-cement systems treated with both cement formulations. Figure 4 shows that the higher pH grout system (mixes 2, 5, and 7) had UCS values of at least 2000 kPa after 28 days of treatment while the UCS of the lower pH grout system (mixes 1 and 6) was about 200 kPa. There was an appreciable increase in the UCS of the former over time while that of the latter was fairly constant. MPCs are primarily

formed by acid-base reactions initially and subsequent strength development may be caused by some condensation as well as hydration reactions. In the lower pH soil-cement samples, there was considerable unreacted TSP that does not therefore contribute to strength development. Visual inspection showed that samples with higher phosphate content appeared more porous than those with higher magnesia content. Crystals of unreacted TSP were noticeable on the surface of aged samples of the higher phosphate formulation. This is probably responsible for the low UCS values obtained. Compressive strength is known to decrease with increase in porosity (Pandey and Sharma 2000). With the lower pH grout (P:M=8:1), there was no significant effect of the presence of contaminants ($p = 0.22$) or age ($p = 0.14$) on strength development. There was significant response of UCS of the higher pH grout (P:M=1:2) to the presence of contaminants ($p < 0.001$) as it favoured strength development over time (Figure 4). It has been reported that in certain instances, increased concentrations of heavy metal contaminants like lead in the range of 1000 mg/kg to 2000 mg/kg led to a stronger structure (van Jarsveld and van Deventer 1999). It was assumed that the chemical nature of the immobilised ion contributed to the formation of specific phases during synthesis leading to a stronger structure. It is interesting to note that increased compost content did not impair strength development but rather it appears to have favoured it. The 28-day UCS of mix 5 (with 25% compost) was about twice (4218 kPa) the value obtained for mixes 2 and 7 with 10% compost (about 2000 kPa). However, over time, 10% compost content proved to be better. The UCS of the higher pH mixes is well above acceptable standards; for example, the UK Environment Agency (2006) requires a minimum UCS of 1 MPa at 28 days. However, this was favoured by the high curing temperature as there is a tendency for UCS to increase as a function of temperature since temperature affects hydration rate, and coarsens the matrix structure (Kim et al 2002).
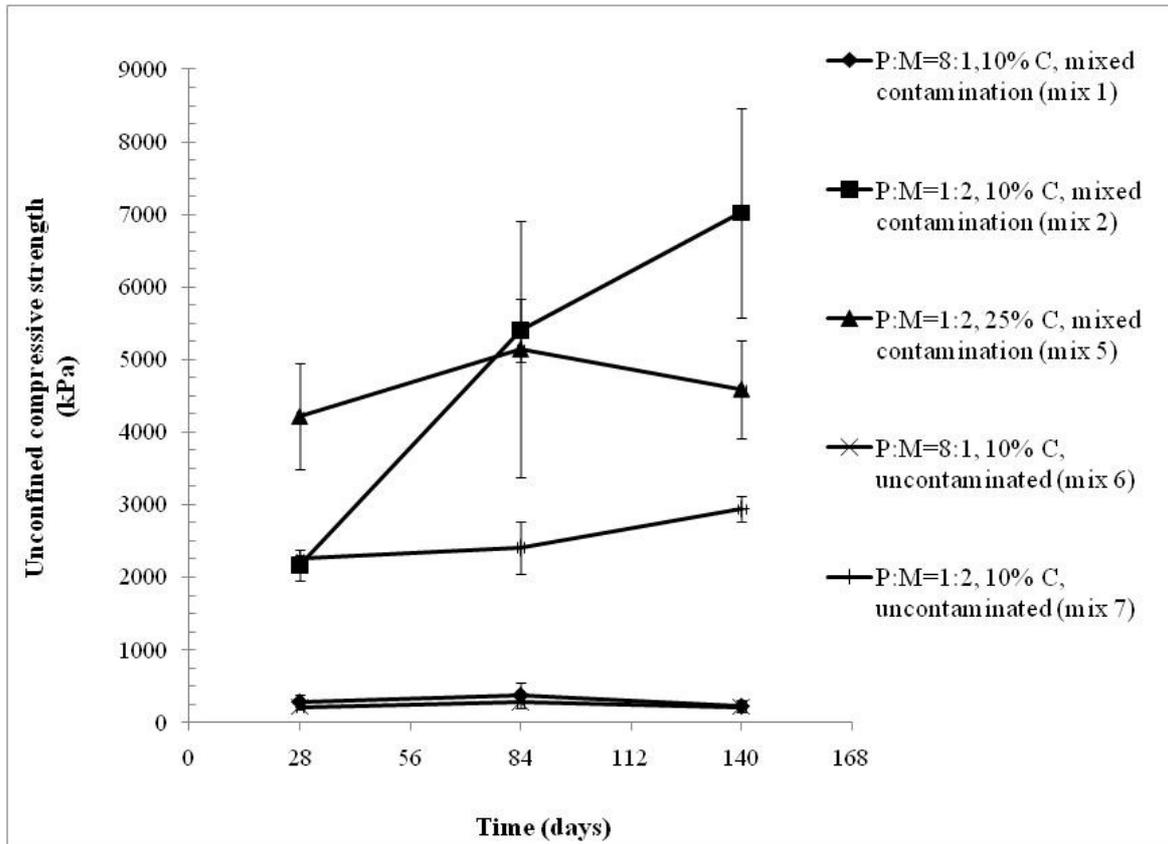
Figure 4. Unconfined Compressive Strength for the mixes

The variation of stiffness with time (see Figure 5) in the cement-treated soils was similar to that of the UCS previously discussed with the same factors highlighted affecting the stiffness of the samples. In the final analysis, the grout mix with higher magnesia content (mixes 2, 5 and 7) led to higher values of stiffness than the one with higher phosphate content (mixes 1 and 6). It was observed that compost content did not cause significant negative impact on stiffness ($p = 0.46$) when compared to the uncontaminated control (Figure 5), but the difference between both mixes over time was significant at the 5% level. As compressibility is the reciprocal of stiffness, the results suggest that with the contaminated samples, 25% compost addition to soil increases the compressibility of the monolith formed, while 10% compost addition gives a stronger and less compressible material. The apparent decrease in stiffness of the uncontaminated control samples with both grout mixes (mixes 6 and 7) at 140 days compared to the 84-day value is interesting. However, it was not statistically significant ($p = 0.06$). Samples with mixed contamination had lower compressibility than uncontaminated samples with both grout mixes at 140 days. The effect of contamination was

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1 significant in the lower pH mixes (p = 0.012) but was not statistically significant (p = 0.08) in

2 the higher pH mixes.

3
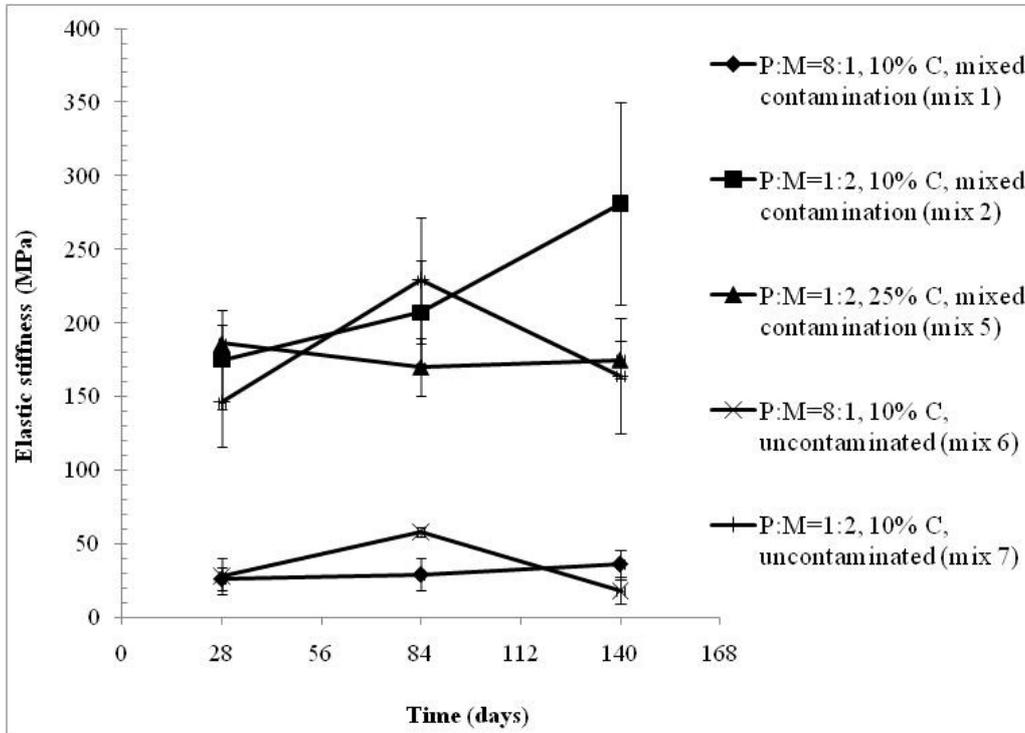
P: triple super phosphate, M: dead burned magnesia, C: compost

**Figure 5. Elastic stiffness for the mixes**

8 Figure 6 shows the permeability of soil-cement systems with both grout mixes, with and

9 without contaminants. These served to evaluate the effect of contaminant immobilisation and

10 degradation on permeability of the treated soils. The higher pH cement formulation, which

11 had clear evidence of microbial activity, was monitored for a longer period (140 days), while

12 the lower pH formulation without clear evidence of microbial activity was monitored for 84

13 days. Therefore, analysis for P:M=1:2 soil-cement systems (mixes 2 and 7) was done at 28,

14 84 and 140 days, while that of P:M=8:1 soil-cement systems (mixes 1 and 6) was done at 28

15 and 84 days. Samples treated with the higher phosphate content grout were found to be more

16 permeable (p = 0.005) than those treated with the higher magnesia content grout. This

17 corroborates the aforementioned UCS results. The permeability of the former was relatively

18 constant over time, around 4.49×10^{-9} m/s for contaminated samples, and 3.4×10^{-9} m/s for

19 uncontaminated samples, while that of the latter slightly varied over time with 140-day values

20 at 1.38×10^{-9} m/s and 0.72×10^{-9} m/s for contaminated and uncontaminated samples

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respectively. There was significant difference in permeability due to the presence of contaminants at 0.1% level in the higher pH mixes. In the lower pH mixes, the effect of contaminants was significant at the 5% level. One of the contaminants used, zinc, has been found to increase the permeability of Portland cement, probably by promoting ettringite formation, and some other organics have been reported to increase the porosity, and hence permeability of cement (Trussell and Spence 1994). Thus, the presence of contaminants is likely to cause a significant difference in permeability.

In some mixes (e.g. mix 7, 28 days), there is high variation between the duplicate samples tested. This is probably a reflection of imperfections in recreating conditions from one sample to the next during sample preparation. Permeability measurement is sensitive to changes that have occurred during the experiments, for example, different patterns of cracks being formed. The differences in permeability between contaminated and uncontaminated samples confirm the findings of Smith and Al-Tabbaa (2007) in which contaminated S/S treated soils (contaminated with lead and zinc) were found to exhibit higher values of permeability than their uncontaminated counterparts. These values conform to acceptable standards. The permeability limit is usually taken as 10^{-9} m/s in the UK for in-ground treatment. The United States Environmental Protection Agency tends to use the same value for disposal to landfill. The same value is used in Canada for utilisation, while a higher limit value of 10^{-8} m/s is used for disposal scenarios (Al-Tabbaa and Stegemann 2005). Generally, permeability demonstrates a decreasing tendency as age increases ($p < 0.001$) save for the 28-day result of mix 2. The decreasing tendency in permeability with age is possibly due to continued condensation and hydration reactions in the cementitious system, as opposed to previous studies where permeability was found to increase with age. However, it appears to support the durability of MPCs reported in the literature.
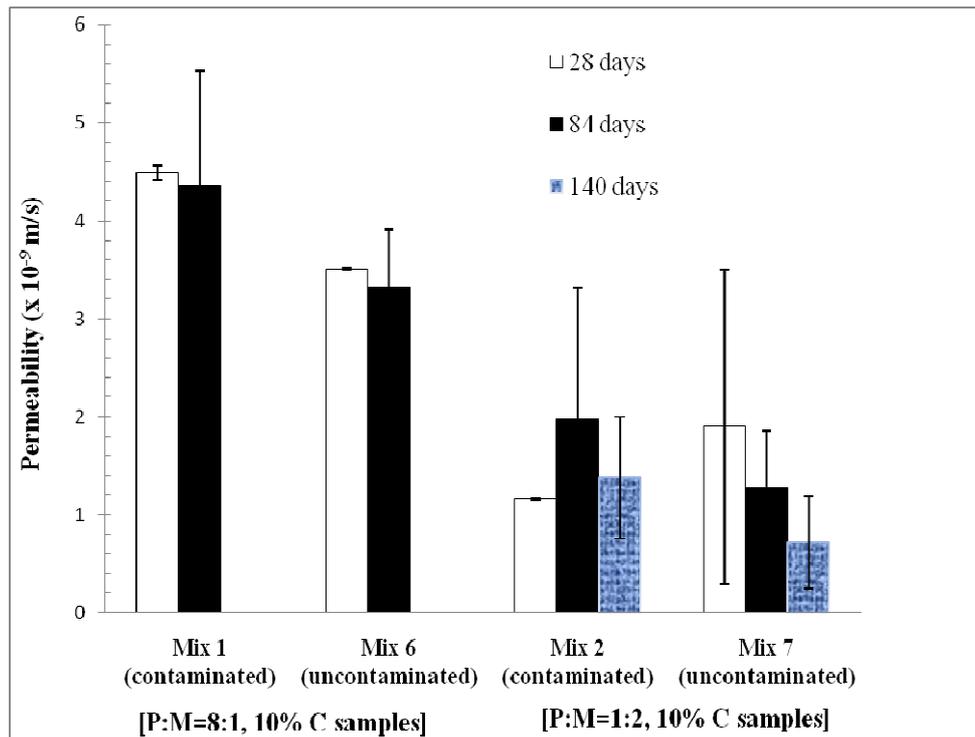
P: triple super phosphate, M: dead burned magnesia, C: compost

Figure 6. Permeability for the mixes

4. Conclusions

This work presented details of investigations on facilitating contaminant immobilisation and biodegradation within a S/S treatment system employing two MPC formulations as binder. A number of tests were carried out at set periods to assess biodegradation of the organic contaminant and immobilisation of the heavy metal contaminants, as well as the engineering behaviour of the cement-stabilised material.

The findings of this research raise the question of suitability of the dehydrogenase assay for evaluating biological activity in the MPC systems due to the apparent stimulatory and inhibitory effects exhibited by the cement constituents on the test result. Biotic and abiotic dehydrogenase activities were observed in mixes with higher magnesia content while TSP was found to inhibit dehydrogenase activity in mixes with higher phosphate content. There was a reduction in organic contaminant concentration, down to ~56% of the initial value, in mixes with both cement formulations after 140 days. The Standard mixes indicated higher contaminant reduction than the abiotic controls after 84 days. Soil-cement mix with 25% compost content was found to exhibit higher dehydrogenase activity but lower reduction in organic contaminant concentration than mixes with 10% compost content. Further

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investigations are required to elucidate the influence of microbes in the observed contaminant degradation. The leached concentrations of heavy metals were significantly reduced in both cement formulations to <0.01 and 0.1 mg/kg for lead and zinc respectively. Generally, the engineering behaviour of the treated soils conformed to acceptable standards.

The results of the study showed that with the appropriate magnesia content, contaminant immobilisation and biodegradation could occur simultaneously without detrimental impacts on the structural integrity of the stabilised material. The application of such MPC grout mix appeared to stimulate microbial activity in a heavily contaminated soil and the fact that microbes could still survive and remain active at pH levels slightly above the upper limit for microbial survival (pH 8.5) further supports the view.

This work presented a useful assessment of the effectiveness of MPC formulations for stabilisation/solidification of contaminated soils. Although, the research was limited to an organic contaminant and two heavy metals, it has highlighted the strong and weak aspects of the treatment system and areas that require further investigations. The results so far are promising for the application of the cement in contaminated land remediation.

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