Contaminated soil treatment: Summary of PhD thesis on stabilisation/solidification combined with biodegradation

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Abstract

This work investigated development of operating envelopes for stabilisation/solidification (S/S) treatment, and facilitation of biodegradation within S/S treated contaminated soils, with the aim of improving the robustness and sustainability of S/S technology. The ‘process envelopes’ study utilised different conventional cementitious binders for treatment of contaminated soil, and generated extensive data from which the range of operating conditions that led to acceptable mechanical and leaching performance of the treated soil was determined. While the S/S and biodegradation study indicated that use of magnesium phosphate cement(s) could facilitate effective immobilisation of heavy metals alongside parallel biodegradation of organics in S/S treated soils.

The above paragraph provides a 100-word summary (or brief abstract) of the PhD thesis at Cambridge University entitled “Process envelopes for and biodegradation within stabilised/solidified contaminated soils” submitted in March 2011. A more detailed summary (of roughly 4300 words) follows thereafter.

Keywords: Binder dosage; cementitious binders; compressive strength; hydraulic conductivity; leaching; magnesium phosphate cements, heavy metals, organics.
Detailed Summary of Thesis

This research involved investigations aimed at improving aspects of the robustness and sustainability of stabilisation/solidification (S/S) technology as well as increasing confidence in the technology by increasing its transparency. Therefore, a coherent body of data was generated in a series of laboratory tests in order to develop correlations and comparisons culminating in the development of operating envelopes for S/S treatment of a contaminated soil. Investigations on utilising magnesium phosphate cements (MPCs) to facilitate biodegradation within a stabilised/solidified contaminated soil were also carried out.

It is evident that in view of the increasing pressure by the UK government to build 60% of new homes on brownfield sites, that S/S has emerged as an ideal remedial measure for such contaminated sites. Hence, in order to enhance the applicability of S/S technology for the treatment of a wide range of contaminated soils, it is important to develop process envelopes for S/S treated soils, which define the limits of operating variables that result in acceptable performance. Long-term performance concerns related to S/S technology was addressed by investigating the utilisation of relatively low-pH MPCs to facilitate biodegradation of organic contaminants within S/S treated soils over time.

In Chapter 2, a comprehensive review of literature on various aspects of S/S technology, its combination with biodegradation and the concept of process envelopes is presented. A brief history of S/S technology and its applications to date, as well as design criteria for S/S process and sustainability concerns of the technology, were also reviewed. The chapter further reviewed the conventional S/S binder materials, namely, Portland cement (CEMI), hydrated lime (hlime), pulverised fuel ash (PFA) and ground granulated blast furnace slag (GGBS), and the novel binder considered in this work, namely MPCs, and their interaction with soils. The generic stabilisation mechanisms of contaminants were also identified. The performance of S/S treated soils utilising the binder formulations considered in this work in terms of the design criteria used here were also reviewed. It was observed from the literature that previous related studies focussed on density, unconfined compressive strength (UCS) and leachability hence these parameters were discussed for each of the four binder systems. Other parameters, namely, compaction, permeability and porosity, where there is far less information available were discussed collectively.
It was shown that contaminated soils generally achieve higher strengths after S/S treatment and the presence of contaminants interferes with cement hydration processes and leads to complicated strength development. It was observed that the UCS was optimum around the optimum water content and increased with binder dosage for all binders. Although GGBS activated by cement and lime has been extensively used in ground improvement works, very few studies have deployed CEMI-GGBS and lime-GGBS blends for the treatment of contaminated soils. The optimum mix for maximum strength of CEMI-PFA was found to vary with the chemical, physical and mineralogical properties of the PFA used, but typically the optimum proportion required about 30 – 50% PFA content of the blend. The optimum mix for maximum strength of CEMI-GGBS blend was found to require about 50 – 60% of GGBS in the blend, while the optimum mix for lime-GGBS blend would require about 1 part lime to 4 parts GGBS. In general, the strength of uncontaminated soil stabilised with the optimum mix of CEMI-GGBS and lime-GGBS were higher than those stabilised with CEMI.

For evaluation of the leachability performance of S/S soils, most of the reported literature used the toxicity characteristic leaching procedure (TCLP) and other batch leaching tests and there is a dearth of literature on pH-dependent leaching of metals from S/S contaminated soils. Nevertheless, there are quite a number of studies on the pH-dependent leaching of contaminants in a range of similar waste materials such as municipal solid waste incinerator bottom ash. It was observed from the literature that about 15 – 20% CEMI dosage is required to reduce the leachability of the average metal concentrations found in soils to acceptable levels, while 10 – 20% CEMI-PFA dosage was required for effective leachability reduction. PFA addition to CEMI or lime was found to increase the immobilisation pH region for Pb. Although very few studies have used lime-GGBS blend for treatment of contaminated soils, lime alone has been frequently used for the treatment of Cu and Pb and about 10% dosage was adequate in reducing their leachability. Lime also showed good leachability reduction for TPH but the reduction was found to be independent of binder dosage. Generally, the literature review showed that good leachability reduction was recorded with about 20% dosage of the different binders.

Comparative studies between different binders are limited. Those presented showed that the permeability of contaminated soils treated by different binder systems increased over time probably due to interactions of the contaminants with the soil-grout material superseding the
effect of the continued hydration of the cementitious materials. Leachability comparative studies using the TCLP test showed that CEMI and CEMI-PFA were effective for Cd, but at lower dosages, lime-GGBS was observed to be significantly less effective for the metal. Lead was found to present problems with both rate of setting and leachability in CEMI. However, it was observed that inclusion of GGBS in a binder blend offered superior performance compared to PFA. In particular, GGBS-based binders were notably effective for Pb immobilisation. It was concluded that CEMI is a very versatile and dependable binder compared to the other blended binders. In every case, inclusion of CEMI resulted in leachate concentrations as low as or lower than the corresponding mixture without CEMI. Long-term performance of S/S treated soils showed consistent effectiveness over a period of 5-years with the occurrence of fluctuations in mechanical and leaching behaviour owing to the complex nature and variability of S/S treated soils. The effect of the long-term interaction between contaminants and soil-grout materials seems to be dominant over those of small differences in grout constituents over a long period.

A review of literature on the possibility of combining S/S with biodegradation showed that biodegradation could be facilitated in a Portland cement-based S/S system as well as in low-pH MPCs. It is reported that the maximum levels of Pb and Zn that microbes can tolerate is about 1,000 mg/kg. It was observed that MPCs have the potential to significantly reduce the leachate concentrations of Pb and Zn. Work presented in combining S/S and biodegradation showed that the addition of compost was important in encouraging the survival and possible growth of microbial life within soil-grout systems. The effectiveness of using dehydrogenase activity for evaluation of microbial activity in the S/S treatment system was also shown. The overall conclusion from the studies was that organic contaminant degradation could occur in S/S treated soils, but the role of microbes in this removal is not certain. The studies showed that the use of cement with relatively lower pH would lead to the survival of microbes for significant periods. Hence, the possibility for contaminant attenuation could be confirmed or engineered in the future.

The literature review chapter was concluded by reviewing the concept of process envelopes and an overview of the ProCeSS project. It was shown that process envelopes are called for in stochastic systems with significant variability and since S/S technology is used to treat variable waste types including contaminated soils; it is desirable to develop generally applicable S/S
process envelopes. This provided the impetus for the ProCeSS project, which sought to develop process envelopes for different waste types including contaminated soil.

In Chapter 3, the materials used in the experiments were presented and the experimental procedures elucidated. In the process envelopes study, four different binder formulations were employed for treatment of a real site soil spiked with a cocktail of heavy metals, including Cd, Cu, Pb, Ni and Zn, and diesel. The binder formulations were CEMI, CEMI:PFA = 1:4, CEMI:GGBS = 1:9 and lime:GGBS = 1:4. In the combined S/S and biodegradation studies, two MPC formulations, with dead burned magnesia (MgO) to triple super phosphate (TSP) ratio, MgO:TSP = 8:1 and MgO:TSP = 1:2, were used to treat a model soil spiked with Pb, Zn and 2-chlorobenzoic acid (2CBA). The composition of the different S/S soil mixes used in the experiments was described in the chapter. A description of the sample preparation procedures, curing environment and sampling techniques was also made. The different types of testing carried out to assess the mechanical and leaching performance of S/S treated soils in the course of the experiments were elucidated. The testing times were also stated and the procedures involved in the tests described.

In Chapter 4, the results of investigations on the performance of the S/S soil systems and resulting process envelopes for S/S treatment using conventional binder materials were presented and discussed. The performance of soils treated by each of the four different binders were evaluated in terms of compaction, bulk density and UCS, permeability and porosity, leachate pH, acid neutralisation capacity (ANC) and leachability of contaminants and monolithic tank leaching as well as interrelationships between the various properties followed by comparisons between the binder systems. Performance thresholds are usually required to define process envelopes and they are usually end-use driven. Therefore, the range of binder dosage and water content that led to acceptable mechanical and leaching properties, i.e. the process envelopes, of all four soil-binder systems were compared.

The compaction characteristics of all four binder systems were similar as the optimum moisture content (OMC) of the different mixes varied within a 2 – 3% range depending on the binder dosage. The MDD of all four binder systems ranged from 1.73 – 1.87 Mg/m³ depending on the binder dosage. The compaction results demonstrate that soil contamination and binder
addition up to 20% dosage does not alter the compaction behaviour of the mixture significantly.

The binders had similar trends of variation of 28-day bulk density with water content and binder dosage, and the bulk density of the different water content and binder dosage mixes ranged from 1.5 – 1.9 Mg/m³. There was generally a slight increase in bulk density between 28 and 84 days. Generally, the trend in variation of 28-day UCS of the blended binders (i.e. CEMI-PFA, hlime-GGBS and CEMI-GGBS), with respect to water and binder proportions, was similar. However, that of CEMI-treated soil was markedly different from the others. The order of binder mix densities was: CEMI > CEMI-GGBS > hlime-GGBS > CEMI-PFA. The UCS was generally optimum around the OMC. Apart from CEMI mixes, the strength gain over time in 5% dosage mixes of the blended binders was similar across the different binder systems. However, 10% dosage caused significantly different patterns of strength gain. The results of the study suggest that the presence of contaminants has a greater deleterious effect on lime-activated GGBS than on CEMI and CEMI-activated GGBS. The general ranking of the UCS was the same as that of the bulk density stated above. Generally, UCS correlated with bulk density in the different binder systems as the highest UCS was obtained around the highest bulk densities.

It was deduced from the UCS before immersion results that in the presence of mixed contamination, stabilisation of sandy soil with CEMI leads to higher strength than with lime-GGBS as opposed to some previous studies on uncontaminated soils where the reverse was the case. Further, the presence of PFA in CEMI was observed to lead to lower strength under the same condition. A comparison of the 49-day UCS before and UCS after immersion data showed that among the four binder systems, GGBS-based binders were least affected by immersion in water, while CEMI was worst affected. The ranking of the resistance of the UCS of the soil-binder systems to deleterious swelling with water immersion was in the order, hlime-GGBS > CEMI-GGBS > CEMI-PFA > CEMI.

The permeability of the three CEMI-containing binders with respect to water and binder proportions was generally similar but the higher permeability associated with the presence of lime was reflected in hlime-GGBS mixes, whose permeability was higher than that of the other binders. The permeability behaviour of hlime-GGBS mixes was markedly different from that
of the other binders as it clearly increased with increasing binder dosage. The optimum permeability was generally obtained around the OMC. The general order of permeability was CEMI < CEMI-GGBS ≈ CEMI-PFA < hlime-GGBS. In the final analysis, irrespective of the binder used, the permeability of S/S contaminated soils slightly increased with time. The highest porosities at 28 days were observed in 10% and 20% hlime-GGBS dosage mixes, which on some level corroborates the aforementioned permeability results although permeability did not correlate with porosity in the different binder systems. There was no clear trend in porosity variation with time in the different binder systems.

The ANC or buffering capacities of the binder formulations alone were observed to be in the order, hlime-GGBS > CEMI > CEMI-GGBS > CEMI-PFA. Although the hlime-GGBS binder formulation had a slightly better buffering capacity than CEMI, CEMI-treated soils showed a better buffering capacity than hlime-GGBS-treated soils. This corroborates the aforementioned position that the presence of contaminants has a greater deleterious effect on hlime-GGBS than on CEMI. The results showed that the leaching behaviour of the metals studied mainly depended on the pH attained by a given binder during the leaching test and the leachate pH is influenced by the binder dosage applied. However, there was no significant effect of binder dosage or pH on total petroleum hydrocarbon (TPH) leachability and the water content had no significant effect on the leachability. Leachability of all metals generally increased with decreasing pH and decreased with increasing binder dosage. The exceptions to this were the leaching behaviour of Cu, Pb and Zn. The metals exhibited their characteristic amphoteric behaviours such that in CEMI and hlime-GGBS mixes, the leachability of the metals increased at a higher pH. CEMI-PFA and CEMI-GGBS were the best binders for Pb, with CEMI-PFA being slightly better at zero acid addition and CEMI-GGBS was more effective in acidic solution due to its better buffering capacity. CEMI showed poor immobilisation capacity for Pb as Pb leachability increased with increase in CEMI dosage under highly alkaline conditions.

The speciation of contaminants was similar in all binder systems. The leaching behaviour of Cd, Cu, Pb and Zn generally followed the hydroxide profile of the metals in all binder systems, although the leachate concentration of Pb was much closer to the estimated solubility values of the metal in an equilibrium solution containing all the metals studied. The leaching behaviour of Ni suggests the existence of the metal in more soluble phases other than the hydroxide. It is highly likely that Ni existed as carbonate-complexes in the cementitious systems. Compared to
the untreated soil, the 20% dosage mix of all binder systems showed the potential for chemical immobilisation of the metals, as in some cases the leachability of the metals were lower in the said mixes than in the untreated soil even at the same pH. Generally, CEMI and lime-GGBS showed better immobilisation capacities for the more soluble metals (Cd, Ni and Zn), while CEMI-GGBS and CEMI-PFA was better for the more amphoteric metals (Cu and Pb). There was no clear trend with TPH leachability but lime-GGBS was marginally better for leachability reduction of the contaminant than the other binders were.

Generally, the leachability of the metals in the mixes was either stable or decreased by over half an order of magnitude between 28 and 84 days after S/S treatment. There was a general increase in TPH leachability at 84 days over the 28-day values in all binder systems. However, this increase was more pronounced in CEMI-PFA mixes especially under acidic influence, probably due to the hydrocarbon origins of PFA. Hence, CEMI-PFA appears to be the least suitable binder for reducing TPH leachability. CEMI-GGBS mixes showed a unique leachability trend between 49 and 84 days as there was a decline in the leachate concentrations of all metals between both curing ages, and this corroborated the strength increase observed during the said period.

The leachate concentrations of the metals in all soil-binder systems in the monolithic leaching test were very low even in 5% binder dosage mixes. Generally, the predominant mechanism of release in all soil-binder systems was surface wash-off of contaminants otherwise physically encapsulated within the cementitious matrix, although diffusion-controlled leaching was observed in some cases. CEMI-GGBS mixes demonstrated a unique effectiveness for Pb as mixes with the other binders leached out higher concentrations of the metal with 10% binder dosage than with 5% dosage in line with the amphoteric behaviour of the metal but CEMI-GGBS mixes did not.

Generally, higher UCS was correlated with lower permeability in CEMI and CEMI-PFA binder systems, but UCS did not correlate well with permeability in CEMI-GGBS and lime-GGBS binder systems. UCS and permeability generally correlated with monolithic leaching in all soil-binder systems, which shows that leaching of contaminants from monolithic samples is lower in stronger and less permeable samples. UCS and permeability generally correlated with granular leachability in the binder systems, especially in the binders containing cement.
However, there were some deviations from this rule. The most obvious was in lime-GGBS mixes where permeability did not correlate with granular leachability due to the aforementioned permeability behaviour of lime-GGBS mixes. Overall, this implies that the higher the UCS and the lower the permeability, the more likely the immobilisation will be better.

A comparison of the process envelopes for the different soil-binder systems showed that generally the optimum values of performance properties were obtained around the OMC. The 1,000 kPa UCS criterion imposed in the UK for landfill disposal of S/S treated wastes was satisfied by only CEMI with 10% dosage; greater than 20% dosage would be required for the other binders. However, the US/Canada ~450 kPa UCS criterion for controlled utilisation was satisfied by all soil-binder systems with 10% dosage, but this depended on the choice of water contents. Generally, water contents at the OMC and 2 – 4% wet of OMC were required to satisfy the criterion. None of the binders satisfied the $10^{-9}$ m/s permeability criterion with 20% dosage, thus higher binder dosages would be required to meet that criterion. Nevertheless, but for lime-GGBS mixes, whose permeability behaviour was uniquely different, the $10^{-8}$ m/s permeability criterion was satisfied by the other binder systems with up to 20% binder dosage at certain water contents.

Leachability data showed that about 20% binder dosage was required for all binders to satisfy the Environmental Quality Standards (EQS) for inland surface waters and the inert waste landfill WAC for the metals. All binders with up to 20% dosage satisfied the WAC for the other types of landfill. With CEMI and lime-GGBS, there were problems with meeting some leaching criteria for Pb at higher binder dosages even when the same criteria were satisfied at low binder dosages due to the characteristic amphoteric behaviour of the metal. Hence, it is suggested that both binders are not suitable for similar soils with high concentrations of Pb destined for stable non-reactive hazardous waste and inert waste landfills. Furthermore, the pH-dependent leachability data suggest that with a higher binder dosage (> 20%); the leaching criteria for most of the metals could be met over a long time. Hence, higher binder dosages than the range studied may be required for soils with similar contamination to fully satisfy long term clean up targets.
The results in chapter 4 highlighted the utility of the binders studied in bringing about significant reduction in leachability of different types of contaminants. Overall, the study showed that compacting samples to the OMC gives the best possible balance between acceptable mechanical and leaching properties. Generally, improved mechanical and leaching properties were observed with increasing binder dosage, with a few exceptions. Hence, depending on the types of contaminants present and other site-specific conditions, with higher (> 20%) binder dosages, soils treated by the binders could be put to beneficial uses, like redevelopment for housing purposes or as fill material in road construction.

The results of investigations on combining S/S and biodegradation using MPCs are presented and discussed in Chapter 5. The performance of the S/S soil systems were assessed using soil-cement paste pH, moisture content, organic contaminant extraction and analysis, dehydrogenase activity, batch leaching and leachate pH, UCS and permeability. The linkage between the performance properties was also explained. The pH of the treated soils was constant over time as no treatment kind caused any significant change in the parameter over time. Generally, the pH of the system was governed by the pH of the grout constituent in relative abundance. Moisture loss was of major concern in the study. Amidst the high relative humidity of the incubator in which the S/S soil samples were stored, there was still a problem with maintaining sufficient moisture in them, as they were prone to drying out over time. This in turn had some effect on dehydrogenase activity in the higher-magnesia-content soil-grout mixes as moisture loss led to decreased microbial activity.

There was reduction in 2CBA concentration over time in both treated and untreated soils, but more contaminant attenuation was found in the treated soils. Contaminant recovery analysis after 140 days indicated a similar reduction in 2CBA concentration to ~57% within the low and high pH mixes with mixed contamination. Contaminant reduction was also recorded in the untreated soil and the aseptic controls of both cement formulations down to ~75% of the initial value at 84 days compared to the corresponding treatment mixes, whose reduction was down to ~57% at the same time. The results indicated the need for further investigation in order to elucidate the exact mechanism(s) responsible for contaminant loss in the systems.

The findings of this work raise the question of suitability of the dehydrogenase assay for evaluating biological activity in cementitious systems especially for MPCs whose constituents
exhibit stimulatory and inhibitory effects on the test result. It also evokes the need for investigating the best biological test(s) that could effectively account for contaminant biodegradation in the cementitious system without any interference from the cement. Nevertheless, the results showed that in soil-grout mixes with more magnesia than phosphate, there was clear evidence of biological activity amidst the abiotic dehydrogenase activity exhibited by the grout constituents. Furthermore, samples treated with the higher-phosphate-content grout, with only organic contamination, later indicated dehydrogenase activity towards the end of the study period, although that was not the case at the initial stage due to TSP inhibition. Further work is necessary in order to improve our understanding of such anomalous behaviour. Moreover, this study adds magnesia and TSP to the list of substances that can cause stimulatory and inhibitory effect on soil dehydrogenase activity noted in the literature.

In the final analysis, it is thought that loss of the contaminant in the soil-cement mixes is due to the combined effect of biodegradation and some abiotic factors, especially for those that indicated dehydrogenase activity. Abiotic factors that may be called for include immobilisation of the contaminant in the cementitious system and reduced solvent extraction due to the effect of aging. The latter factor may well account for contaminant loss in the untreated soil. Overall, the amount of contaminant loss due to biodegradation cannot really be quantified due to the complex behaviour of the soil-cement systems as the effectiveness of both cement formulations were similar even though dehydrogenase activity was not observed in the lower pH formulation. It was observed from the leachability results that the presence of heavy metals retarded contaminant reduction in the untreated contaminated soil but that was not the case with the treated counterparts. The results further indicated that both cement formulations were as effective in heavy metal immobilisation.

The results of the combined S/S and biodegradation study showed that with the appropriate magnesia content, contaminant immobilisation and degradation could occur simultaneously without detrimental impacts on mechanical properties like UCS and permeability. Further, the results suggest that to achieve biodegradation without compromising the mechanical behaviour of the treatment system, proportioning the cement constituents to give a mix with adequate magnesia content should take precedence over pH considerations for which reason a mix with greater phosphate content is desirable. The application of such 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.

The major contributions of this work to S/S technology include the investigations on comparison of soil contaminated by a cocktail of heavy metals and petroleum hydrocarbons and treated by different binder formulations, in terms of mechanical and leaching behaviour. Specifically, the granular leachability of different contaminants in the soil-binder systems under different pH conditions, over a period of 84 days is relatively new as there is a paucity of literature on such testing for soils. The attempt to develop process envelopes for different performance properties is novel and this work has provided some insights for a given soil type which may broadly apply to other soils of the same type impacted with the same type of contaminants. Furthermore, the contribution of this research also encompasses investigations utilising MPCs to facilitate biodegradation within a mixed contaminated soil treated by S/S without compromising the structural integrity of the treated soil.

Based on the outcome of the investigations, it is concluded from the process envelopes studies that compaction around the OMC can be used to achieve improved mechanical and leaching properties. The quality of immobilisation of contaminants during S/S treatment would mainly be determined by adjustment of pH, for metals, and provision of sorption sites for organics. The continued retention of contaminants within the S/S matrix would depend on production of a high quality cementitious matrix with low porosity and solubility. It is concluded from the combined S/S and biodegradation studies that with the appropriate magnesia content, contaminant immobilisation and biodegradation can occur simultaneously without detrimental impacts on the structural integrity of the treated soil. The results so far are promising for the application of MPC in contaminated land remediation.

Note: This PhD thesis resulted in 9 journal articles and an award-winning conference paper. These are presented as ‘further references’ in the References section for a deeper understanding of the work summarised here.

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