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Stabilisation/Solidification of Pb Polluted Soils: Influence of Contamination Level and Soil:Binder Ratio on the Properties of Cement-Fly Ash Treated Soils

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Two soils spiked with lead at different rates were stabilised/solidified using Portland cement and fly ash at different soil:binder ratios and tested for their setting time, unconfined compressive strength (UCS), leachability and durability. Results show that soil texture, percentage of binders and lead concentration play an important part in the treatment, significantly influencing the performance of the resulting products in terms of curing, compressive strength and durability. Pb soil concentrations higher than 15,000 mg kg^{-1} were found to heavily reduce the applicability of the treatment requiring the maximum amount of binder in order to satisfy the performance criteria. The performance of sandy soils was shown to be limited by setting time and UCS features due to the retardation of the hydration reactions and also by its leaching behaviour, whereas for silt-clayey soils the critical parameter is the mechanical resistance.

1. Introduction

Lead (Pb)-based compounds have been a major source of environmental contamination in the past few decades (Tang and Yang, 2012).

Reported chemical-physical treatment options for Pb polluted soils could be expensive, e.g.: soil washing, require intensive energy use, e.g.: electrokinetic remediation, time consuming, e.g.: biological methods such as bioleaching or phytoremediation, or environmentally unsustainable such as disposal in landfills (Harbottle et al. 2007). Thermal treatments can be successfully applied only for organic pollutants removal (Falciglia et al., 2011).

Recent studies (Leonard and Stegemann, 2010) have also shown the possibility of using stabilisation/solidification (S/S) with hydraulic binders as a possible treatment option, with the potential of using the S/S product for useful purposes. S/S has been widely used due to its versatility, efficiency, time and costs to dispose of low-level radioactive and hazardous wastes, as well as to remedy metal or radionuclides contaminated soils (Falciglia et al., 2012).

S/S is a treatment by which contaminated soils, sediments or waste are mixed with a binder and/or specific additives with the aims of reducing the mobility of the toxic contaminants by increasing the pH and fully or partially binding the contaminants in the solid matrix (stabilisation), but also of improving the physical properties (strength, compressibility, permeability and durability) of the final treatment products (solidification) (Antemir et al., 2010).

For Pb-polluted soil treatment, most applications of S/S are cement-based, and rely on Portland cement (PC) as the primary binder (Svensson and Allard, 2008). More recently PC has been combined in blends with other minerals such as lime, blast-furnace slag, clays and fly ash. Fly ash (FA), also known as pulverised fuel ash (PFA), is a by-product generated from coal fired power plants.

However, several studies have demonstrated that the hydration processes of cement, and materials such as FA, can be highly modified by heavy metal concentration due to coating around binder grains resulting in a worsening of characteristics of the S/S treated matrices (Malviya and Chaudhary, 2006). Therefore, the presence of a high Pb concentration in soil may result in an inapplicability of the S/S treatment or a reduction of its effectiveness.

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However the correlation between metal contamination level variation and the performance of S/S treated matrices has not been investigated in any detail and in particular, the limits for the application of S/S techniques to treat high Pb concentration polluted soils are not clear.
Hence, the general objective of this work was to better understand the potential of S/S for the treatment of Pb polluted soils and in particular the effects of Pb concentration and soil:binder ratio on the physical and mechanical properties of soil treated with PC and FA which were assessed analyzing the setting time, unconfined compressive strength (UCS), leachability and durability of the treatment products.

2. Materials and methods

2.1 Soil contamination, binder systems and S/S sample production

A sandy soil (soil A) and a silty-clay soil (soil B), with properties shown in Table 1, were spiked with Pb at different rates (C) (1,000, 2,000, 4,000, 8,000, 15,000 and 25,000 mg kg^{-1}), by adding a known quantity of a contaminant solution containing deionized water and reagent grade lead (II) nitrate, purchased from Merck KGaA (Darmstadt, Germany). After the contamination procedure, the soils were kept in a closed vessel and stored in a dark room at 4 °C for 1 month then five samples for each contamination level were collected and analysed for Pb content before S/S treatments. Pb content was performed by ICP-OES (Perkin Elmer Optima 4300 with Dual View).

Table 1: Characteristics of the soils

Parameter	Soil A	Soil B
Texture	sandy	silty-clay
Sand (silica s. 75-350 μm) [%]	80	20
Silt (silica flour 10-75 μm) [%]	10	56
Clay (kaolin <75 μm) [%]	10	24
pH (L:S of 10)	8.73	8.39
Organic matter [%]	2.79	2.98
Total Organic Carbon [%]	1.67	1.75
Bulk density [g cm^{-3}]	1.42	1.31
Surface area [m^2 g^{-1}]	3.33	14.1
Moisture content [%]	14	25.5

The cement used was purchased as type CEM I Portland cement (PC) CEM 11/B-LL 32.5R from *Italcementi S.p.A.* (Italy). Class F fly ash (FA) was obtained from *Buzzi Unicem S.p.A.* (Italy).
The S/S treatment was performed by mixing control or spiked soil (S) samples with a binder mixture (B) of PC and FA (PC:FA 1:1) at three different S:B ratios (3.3:1, 4.0:1, 5.0:1), applied wet using a water (W) to dry binder (DB) ratio of 0.42:1. The mixing was performed by means of a food mixer for 15 min to a homogeneous consistency and the treated soil samples were then cast and compacted into cylindrical moulds (100.0 mm in height and 50.0 mm in diameter) in accordance with the ASTM D1557-91 standard. After 1 day, the samples were demoulded then cured for 28 days in sealed sample bags at a temperature of 20 ± 2 °C and a relative humidity of 95 ± 3 % prior to UCS and durability testing.

2.2 Testing protocol and quality criteria

To verify the effectiveness of the S/S treatment, it is necessary to assess the characteristics of the treatment products and compare them with specific performance criteria. It is appropriate to establish a testing regime that addresses the relevant issues for the management scenario of the treatment products (e.g., disposal or utilisation) being considered (Perera et al., 2004). The testing protocol on control and soils contaminated at different C included: (i) setting time, (ii) UCS, (iii) leaching and (iv) wet-dry and freeze-thaw durability values.
The initial and final setting times of the mixtures were determined by using the ASTM C191-82 method.
UCS test relates to the mechanical resistance of the S/S products. UCS values were measured according to ASTM test method D1633 by applying a vertical load axially at a constant strain rate of 0.5 MPa s^{-1} using a *Laumas Electronics CTS* compressive strength testing apparatus until failure of the cylindrical specimen.
Durability test methods are applied to analyze the long-term performance of the S/S products and in particular the resistance of the material to repeated cycles of weathering. Cured test specimen were subjected to twelve wet/dry (W/D) and freeze/thaw (F/T) cycles according to ASTM D4843 and ASTM D4842 methods, respectively.

Pb^{2+} leaching behaviour of the products was investigated applying the EN 12457-2 test and the results were compared with E.U. landfill acceptance criteria (Council Decision 2003/33/EC).
The criteria refer to some physical and chemical properties of the S/S solids, measured at 28 days, considering the specific methods adopted for the experiments. The quality criteria were extracted from regulatory limits proposed by US Environmental Protection Agency (US EPA) and United Kingdom Environmental Agency (UK EA).

3. Results and discussion

3.1 Setting time

Figure 1 shows the effects of Pb soil concentration (C) on the initial and final setting times of the S/S treated soils for a S:B ratio of 3.3:1, 4.0:1 and 5.0:1 and for soils A and B. Results indicate that, especially for soil A, C and S:B ratio significantly influenced the setting times of the S/S treated soils. In particular, setting times increased for both soils, with increasing C and decreased with decreasing the S:B ratio. Higher setting times were observed for soil A, where the presence of Pb at a S:B ratio of 5.0 strongly delayed the hydration reactions and significantly lengthened setting time values (up to 240 h) for C higher than 15,000 mg kg^{-1}. This specific behaviour suggests that when a Pb:B threshold ratio is exceeded, a significant increase in the setting time occurs.
This is consistent with the literature findings where Pb has been reported to suppress cement hydration and lengthen the setting times due to the precipitation of protective coatings of gelatinous hydroxide around the cement grain surface (Chen et al., 2009; Gervais and Ouki, 2002).
Considering the less rigorous US EPA acceptance quality criteria of 72 h for final setting time, inadequate values were obtained for soil A at a S:B ratio of 5.0 for any Pb contamination level and at a S:B ratio of 4.0 only for a C of 25,000 mg kg^{-1}. Adequate values were obtained for soil B for all the experimental conditions tested. If the BS EN criteria is considered (initial setting time < 8 h, final setting time < 24 h), adequate values were obtained only for soil B contaminated at the maximum level of 2,000 mg kg^{-1} for all the S:B ratios investigated.

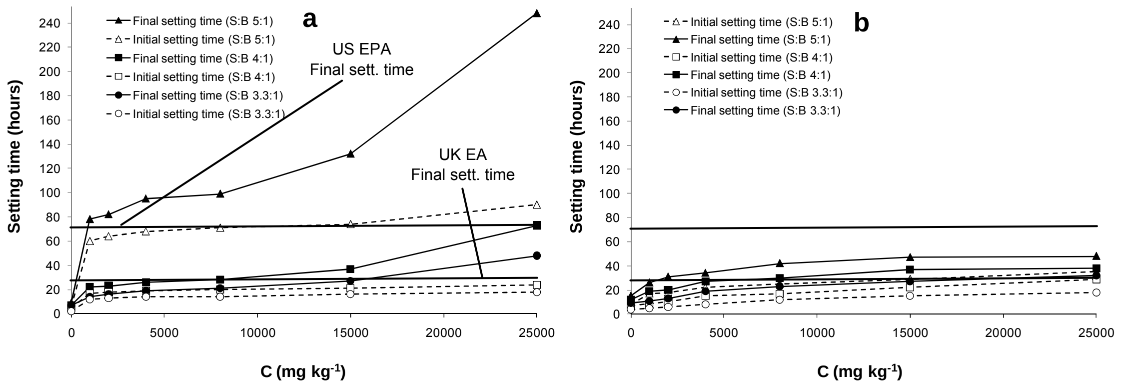

Figure 1: Setting times of S/S treated soils vs Pb soil concentration (C) for soil A (a) and soil B (b) (S:B ratio of 3.3, 4.0 and 5.0)

3.2 UCS

Results of compressive strength (UCS) tested at 28 days of curing for control and treated polluted soils (soil A and B) are presented as a function of C in Figure 2. Results showed that C highly influenced UCS and the same trend between UCS and C was observed for both tested soils. Specifically, for all the S:B ratios tested, an increase of UCS was observed for a C = 1,000 mg kg^{-1} (up to 13,000 KPa) respect to the control, followed by a decrease with increasing C for the highest values. As expected, UCS of the samples increased with decreasing S:B ratio, and highest values were measured for sandy soil. Overall, excluding the data referred to a C = 25,000 mg kg^{-1}, a difference of between 3,000 and 6,000 KPa was recorded between UCS of soil A and B for all the B:S ratios. For the samples spiked at a C = 25,000 mg kg^{-1}, a drastic UCS decrease was observed only for the sandy soil. Therefore, it is clear that the presence of low C (< 4,000 mg kg^{-1}) results in an improvement of the mechanic characteristics of the S/S treated soils respect to the control samples, whereas for higher C, UCS decreased, doing so more rapidly for sandy soil up to values lower than 100 KPa.

This specific behaviour is probably due to the lengthening of the hydration reaction that was observed to be more consistent for the sandy soils. As a matter of fact, the better strength performances of the sandy soils are hindered by the higher setting times recorded, especially for high values of C. But, for the lowest C, it seems that the presence of Pb in the structure of the S/S treated soils gave them an improvement in the mechanical features that are not weakened by a significant retardation of the hydration reactions.
In terms of quality acceptance, considering the US EPA criteria, insufficient strength values were obtained only for soil A considering a S:B ratio equal to or higher than 4.0 and the maximum C (25,000 mg kg^{-1}) in the cases of S/S treated soils landfill disposal (UCS > 0.35 MPa). If the more restrictive limit for construction application (UCS > 3.45 MPa) is considered, sufficient UCS values were reached for C equal to or lower than 15,000 mg kg^{-1} for sandy soil and 4000 mg kg^{-1} for silty-clay soil. Higher C silty-clay soils (up to 8,000 mg kg^{-1}) could be successfully treated using a S:B ratio of 3.3 or changing the composition of the binder (i.e.: increasing the PC content).

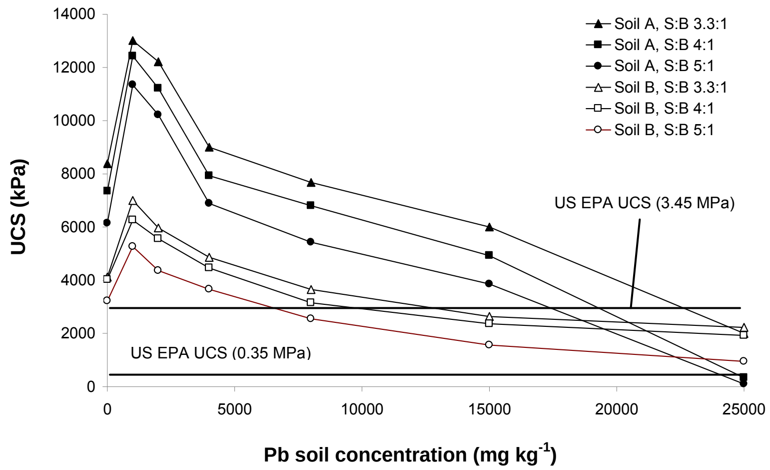

Figure 2: Effect of Pb soil concentration on the UCS development of S/S soils for soil A and B (S:B ratio of 3.3, 4.0 and 5.0)

3.3 Leachability

Results on the Pb leachability were showed in Figure 3. For all the single batch extractions low values of leached Pb were observed for C values up to 8,000 mg kg^{-1}, while for higher C a significant increase was observed in soil A and a slight increase in soil B. This specific behaviour corresponded to pH values which were above 9.8 for soil B but decreased down to a value of 8.0 for soil A at the highest C, indicating the higher buffering capacity of the treated samples of soil B compared to those of soil A. As expected, an increase of leached Pb and a decrease of pH values were observed with increasing S:B ratio. Generally, for most alkaline materials the leaching concentration of Pb decreases for a pH reduction from 10 to 8, but in this case a different trend was observed, probably due to the higher concentration tested that determined an increase in the leaching value even though the reduction in pH would have yielded a lower concentration.
Furthermore, the theory for which leaching of contaminants such as Pb is reduced with increasing the percentage of fine texture soil and/or humidity (i.e.: soil B) seems to be confirmed. Indeed, an increase of the specific surface area of the S/S matrices and, therefore an increased adsorption of contaminant onto the clay fraction of the soil may produce a decrease in the amount of coating on the cement grains allowing the cement hydration. Moreover, for soil B, the presence of kaolin, that is known to be a good Pb^{2+} adsorbent (Jiang et al., 2009), especially for high pH values, improved the adsorption phenomena reducing Pb leaching. This phenomena is more relevant for Pb concentration equal to or higher than 8,000 mg kg^{-1}. For both types of soil, the good results obtained, in terms of leachability, are also probably due the presence of a low concentration of organic matter. This condition is in fact known to play an important role in the increase of the immobilization phenomena of Pb (Janoš et al., 2010).
Comparing the obtained results with E.U. landfill acceptance criteria (Council Decision 2003/33/EC), the leached Pb for soil B (all treatments) was below the limit of 0.5 mg kg^{-1} for inert waste landfill disposal. For soil A, the limit of 0.5 mg kg^{-1} was respected only for C equal to or lower than 15,000 mg kg^{-1}. For the other treatments, leached Pb was in each case below the limit of 10 mg kg^{-1} for non hazardous waste landfill

disposal. Results confirm that the main factor controlling the Pb concentration in the leachate is the final pH, and they are in agreement with Jing et al. (2004) which highlights the possibility of successfully treating also heavy Pb soil contamination using minimal binder percentage (i.e.: S:B = 5.0:1) for silty-clayey soils or using higher binder percentages (depending on the objectives of the treatment) for sandy soils.

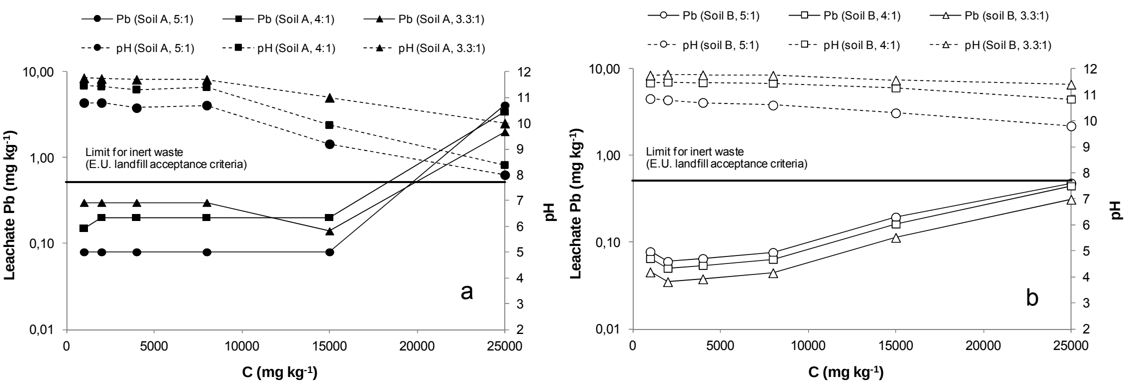

Figure 3: Effect of Pb concentration on the leachability of Pb and pH of S/S soils for soil A (a) and B (b)

3.4 Durability

For the F/T test (Figure 4) a slight increase of the weight loss was observed with increasing C for C ≤ 15,000 mg kg^{-1}. A significant average variation (about 15%) in terms of mass loss was observed between both tested soils. C > 15,000 mg kg^{-1} significantly worsened the performance of the S/S matrices, shown by an in-crease of the mass loss during the durability cycles. Specifically, for the samples where C was 25,000 mg kg^{-1} a weight loss of 21, 24 and 49 % was achieved respectively for the soil A (S:B 3.3:1), soil B (S:B 3.3:1) and soil B (4.0:1). For the other experimental conditions, all the tested samples were disintegrated after 2 cycles, for soils A (S:B 5.0:1) and B (S:B 5.0:1) and after 8 cycles for soil A (S:B 4.0:1). This clearly shows that, despite the overall best durability performance of the sandy soils, at high Pb contamination level, they could be more vulnerable than fine texture soils such as soil B. This confirms that in sandy soil, the large retardation of the hydration reactions observed, due to the high Pb level, may significantly worsen the characteristics of the S/S treated soils and consequently their performance.

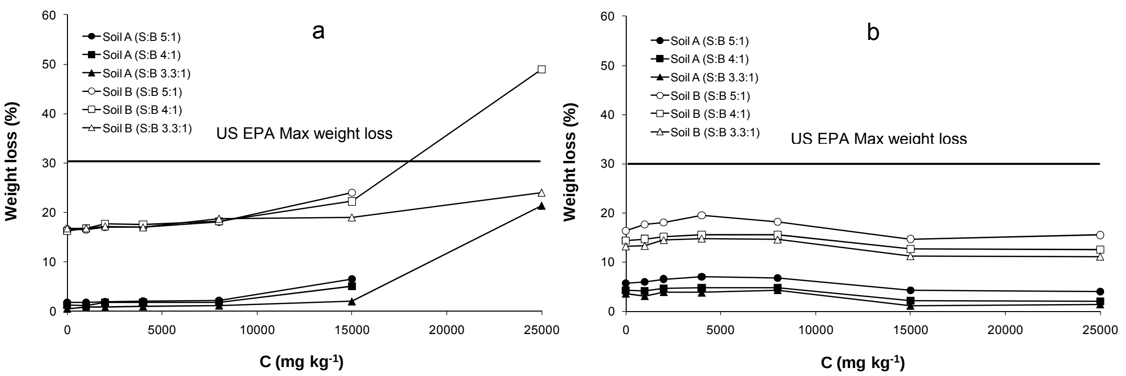

Figure 4: Effect of Pb soil concentration on the weight loss of S/S treated soils during freeze-thaw (a) and wet-dry (b) durability test for soil A and B (S:B ratio of 3.3, 4.0 and 5.0)

For the W/D test a small increase in the weight loss was observed with an increasing of C for C equal to or lower than 8,000 mg kg^{-1}. For all the samples no difference was observed between C = 15,000 and 25,000 mg kg^{-1}, whereas an increase of about 10% was observed for soil B in comparison with soil A. The observed decrease in weight loss with an increasing Pb level in soil may be attributed to the water saturation phenomena regarding the samples during their immersion in water for 5 h at each cycle of W/D. The presence of a higher amount of water in the sample matrix could play an important role in the improvement of the hydration kinetics that gave the best performance in terms of W/D durability to the treated soils. Based on the durability acceptance criteria proposed by WTC 1991 (weight loss < 30%), a minimal S:B ratio is sufficient to successfully treat a Pb contamination level equal to or lower than 15,000 mg kg^{-1}, whereas a S:B ratio of 3.3 is needed to treat contamination levels up to 25,000 mg kg^{-1}.

4. Conclusions

The following conclusions have been drawn according to the results presented above:

1. Soil texture, the percentage of binders used and lead concentration in soil significantly influence the performance of the S/S treated soils in terms of curing, compressive and weather cycling strength.
2. The observed influence of lead content on studied parameters may be useful in predicting setting time, UCS, leaching and durability of soils treated by PC and FA at any contamination level.
3. Lead soil concentration higher than 15,000 mg kg^{-1} heavily reduces the applicability of the S/S techniques requiring a large amount of binder to satisfy the selected performance criteria; this could make the treatment very expensive. Specifically, despite the best compressive strength observed at the lowest lead concentration values, soils performance was shown to be limited by setting time and UCS features due to the lengthening of the hydration reaction.
4. In terms of leachability, Pb soil concentration does not represent a limitation, indeed also heavy contamination may be successfully treatable also using minimal binder percentage for any type of soil, except for the in situ and inert waste landfill disposal scenarios, for which, due to the severe limits adopted, a higher soil:binder ratio of 4.0 is required.

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