



## Comparison of properties of traditional and accelerated carbonated solidified/stabilized contaminated soils

LIU Jiangying<sup>1,2</sup>, XU Dimin<sup>1</sup>, XIONG Lan<sup>1,2,\*</sup>, Colin HILLS<sup>3</sup>,  
Paula CAREY<sup>3</sup>, Kevin GARDNER<sup>4</sup>

1. State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China. E-mail: [jiangying.liu@gmail.com](mailto:jiangying.liu@gmail.com)

2. Department of Civil Engineering, University of Birmingham, Edgbaston, Birmingham, B15 2TT, United Kingdom

3. Centre for Contaminated Land Remediation, Department of Earth and Environmental Sciences, University of Greenwich, Chatham Maritime, Kent, ME4 4TB, United Kingdom

4. Department of Civil Engineering, University of New Hampshire, Durham, NH 03824, USA

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### Abstract

The investigation of the long-term performance of solidified/stabilized (S/S) contaminated soils was carried out in a trial site in southeast UK. The soils were exposed to the maximum natural weathering for four years and sampled at various depths in a controlled manner. The chemical properties (e.g., degree of carbonation (DOC), pH, electrical conductivity (EC)) and physical properties (e.g., moisture content (MC), liquid limit (LL), plastic limit (PL), plasticity index (PI)) of the samples untreated and treated with the traditional and accelerated carbonated S/S processes were analyzed. Their variations on the depths of the soils were also studied. The result showed that the broad geotechnical properties of the soils, manifested in their PIs, were related to the concentration of the water soluble ions and in particular the free calcium ions. The samples treated with the accelerated carbonation technology (ACT), and the untreated samples contained limited number of free calcium ions in solutions and consequently interacted with waters in a similar way. Compared with the traditional cement-based S/S technology, e.g., treatment with ordinary portland cement (OPC) or EnviroCem, ACT caused the increase of the PI of the treated soil and made it more stable during long-term weathering. The PI values for the four soils ascended according to the order: the EnviroCem soil, the OPC soil, the ACT soil, and the untreated soil while their pH and EC values descended according to the same order.

**Key words:** solidified/stabilized; accelerated carbonation; contaminated soil; electrical conductivity; liquid limit; plastic limit; plasticity index

### Introduction

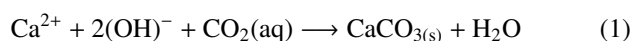
Solidification refers to processes that encapsulate a waste to form a solid material and to restrict contaminant migration by either decreasing the surface area exposed to leaching or coating the waste with low-permeability materials or both. During solidification process, the changes in the physical properties of the waste forms usually include an increase of compressive strength, a decrease of permeability, and the encapsulation of hazardous constituents.

Stabilization refers to processes that involve chemical reactions that reduce the leachability of a waste by chemically immobilizing the waste or converting the constituents into a less soluble, mobile, or toxic form.

Solidified/stabilized (S/S) technology involves the mixing of binding agents into contaminated media, such as mixing contaminated soil or hazardous waste to create a solidified and stabilized product. In S/S waste form, pollutants are chemically stabilized and physically encapsulated

(Hausman, 1999; Sherwood, 1993; Liu *et al.*, 2005).

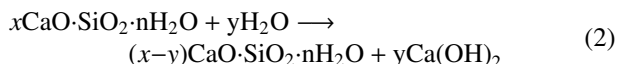
The S/S contaminant-stabilizer mix need to be carefully designed because there is a risk of negative environmental impact due to degradation in the long term. Among the environmental stresses on the degradation of S/S materials, carbonation is a significant surface process that can affect performance in both the short and long term curing periods (Al-Tabbaa and Stegemann, 2005; Bone *et al.*, 2004; Liu *et al.*, 2005; Liu *et al.*, 2006). Carbonation mainly involves the chief hydration products: calcium silicate hydrate (CSH) and calcium hydroxide (Ca(OH)<sub>2</sub>), which are converted to calcium carbonate (CaCO<sub>3</sub>) according to the following stoichiometry (Bin Shafique *et al.*, 1998; Bonen and Sarkar, 1995; Liu *et al.*, 2005; Mollah, 1993; Papadakis *et al.*, 1989; Papadakis *et al.*, 1991):



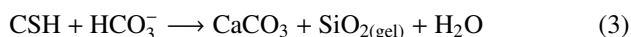
This assumption is based on the abundance of calcium ions in the pore water because of dissolution of portlandite. The carbonation reaction is supported by calcium hydrox-

\* Corresponding author. E-mail: [xionglan@mail.tongji.edu.cn](mailto:xionglan@mail.tongji.edu.cn).

ide provided by the decalcification of CSH gel after the original level of portlandite formed during depletion of ordinary portland cement (OPC) hydration (Gervais *et al.*, 2004).



Long-term attack by carbonic acid decomposes the CSH gel into calcium carbonate, acid-insoluble silica gel and water.



By affecting the chemical properties, carbonation can change the geotechnical properties and durability of S/S soils (Garraabrants *et al.*, 2004; Liu *et al.*, 2006).

The recent literature survey show that S/S technology in the high concentration  $\text{CO}_2$  atmosphere may have the beneficial impacts on contaminants immobilization although carbonation can impose the deleterious effects on the traditional cement-based S/S materials (Conner and Hoeffner, 1998; Fernandez Bertos *et al.*, 2004; Hills *et al.*, 1999; Lange *et al.*, 1996; Lange *et al.*, 1997; Van Gerven *et al.*, 2004). Accelerated carbonation technology (ACT) on S/S treatment is a novel technology and has been proved to have a great potential of stabilization for a range of heavy metals. In the presence of high concentration  $\text{CO}_2$  gas, the contaminated soil containing with heavy metals is treated through mixing with an appropriate binder such as portland cement, quick lime and industry byproducts. Compared with the traditional cementitious S/S technology which is based on hydration reactions and requires longer setting time, ACT needs only several minutes to obtain a hardened mass where the contaminants are encapsulated by carbonate-based products. Optimum carbonation conditions were established for a range of waste materials and binder types, and it was concluded that the substantial improvements in waste encapsulation properties resulted from precipitation of calcite and calcium-metal double salts in pore water and formation of metal-silanol complexes (Fernandez Bertos *et al.*, 2004; Hills *et al.*, 1999).

The purpose of this project was to evaluate the performance of traditional and ACT S/S contaminated soils through a pilot-scale experiment. This work will provide the data on the long-term behavior of S/S contaminated soils under the environmental stresses of degradation so that it may direct the practice of S/S technology on the redevelopment and remediation of contaminated land. The detailed goals for this project are to identify and quantify some geotechnical and chemical properties of untreated, traditional and accelerated carbonated S/S contaminated soils after long-term maximum natural weathering. This paper discusses the outcomes of part of the field research to date.

## 1 Materials and methods

### 1.1 Working site

The field research focuses on the site which is located at Dartford, Kent, UK. The annual precipitation, temperature, relative humidity in this area is 1200–1700 mm, 5–18°C, 70%–90%, respectively. The soil is London clay contaminated by firework manufacturing and the main pollutants include cadmium, chromium, copper, lead, calcium, iron and magnesium. The concentration of the main pollutants in 1999 and the corresponding threshold limits from British Inter-Developmental Committee on the Redevelopment of Contaminated Land (ICRCL) are listed in Table 1. The pilot-scale S/S remediation of the contaminated soil was completed by the University of Greenwich in September 2000 (Figs.1 and 2). The treated area of the site consists of four cells (Cell 1–4) with a size of 10 m × 5 m × 0.5 m which are lined with an impermeable membrane to enable leachate collection and open to the atmosphere. The soil in each cell was *ex-situ* treated using different S/S binder materials and backfilled.

### 1.2 S/S treatment

The excavated material was first reduced in size through a Rotamill crusher for several cycles to shred the soil and allow thorough blending of the hotspot material with the surround test plot soil. This process had a dual purpose: the shredded soil proved less cohesive and prevented

**Table 1** Characterisation of contaminants in the soil in 1999

Element	Concentration (mg/kg)	ICRCL threshold limits (mg/kg)
Cadmium	0	3
Total chromium	9	600
Copper	17,498	130
Nickel	0	70
Lead	203	500
Zinc	64,049	300
Calcium	19,415	N/A
Iron	37,745	N/A
Potassium	3,026	N/A
Lithium	10	N/A
Magnesium	3,710	N/A
Sodium	0	N/A



**Fig. 1** Construction of four pilot-scale cells in the site. Cell 1: untreated soil; Cell 2: EnvirOceM soil; Cell 3: OPC soil; Cell 4: ACT soil.



Fig. 2 Accelerated carbonation treatment equipment.



Fig. 3 Sampling pit at the cell.

agglomeration during subsequent treatment stages; a more homogenous material was created for the trial to minimize variability of the test cells. A portion of this shredded soil was then used to fill Cell 1 and the untreated soil cell. Cell 2 contained soil and 20% (on a total dry weight basis) OPC addition that had passed through the Rotamill for mixing. A similar procedure was performed for Cell 3, using 20% of a proprietary environmental cement-EnvirOceM, a formulation of cement with pulverised fuel ash (PFA) as the binder instead of OPC.

The material for Cell 4 was the contaminated soil with 20% EnvirOceM. The mixed binder and soil were fed into the carbonation chamber along an open conveyor belt and through a feeder hopper (Fig.2). The chamber was then closed and carbon dioxide added to the system and the chamber rotated. Carbon dioxide was supplied as liquid  $\text{CO}_2$ , and stored under pressure ( $19 \times 10^5$  Pa) in a 12-t stainless steel container. The liquid was converted to a gaseous form through vaporisers and fed through to the carbonation chamber. A 2-min period was allowed to purge the chamber, then the binder and soil mixture was dynamically carbonated for 20 min. The carbon dioxide flow was then turned off and the treated material was allowed to cool slightly before emptying into a dump truck and placement into Cell 4.

Materials were loosely filled into the four cells without any compaction and barrier cover on the surface so that the three kinds of different S/S treated soils and the untreated soils would expose to the maximum natural weathering. The treated soils in each cell are considered to be completely homogenous.

### 1.3 Sampling and properties tests

Samples were taken at depths of 0–50 mm, 50–150 mm, 150–230 mm, 230–300 mm, 300–390 mm, 390–500 mm at 800 mm × 800 mm × 500 mm trial pit in each cell four years after the treatment (Fig.3). For specimen preparation, desiccant (Geejay Chemicals Ltd., UK) was used to remove the moisture content of the soil to prevent the chemical structure of the soil changing due to the ordinary heating process. The air drying lasted for several days until no further weight change was observed. The chemical properties of the soils (degree of carbonation (DOC), pH, electrical conductivity (EC)) and physical properties (moisture content (MC), liquid limit (LL), plastic limit

(PL), density) were measured. All the experiments were run thrice, the data were the mathematical mean values. MC was determined by air drying until the weight was constant with time. LL was tested by the cone penetrometer method and PL was measured according to British Standard BS 1377 (1990). pH and EC were determined by pH meter (Combo pH Meter 131-6582, UK) and electrical conductivity meter (Hanna Instruments Ltd. HI-993310-agri, UK) through U.S.EPA toxicity characteristic leaching procedure (TCLP).

Thermo-gravimetric method was adopted to measure the degree of carbonation on the basis of burning material at 105, 450 and 900°C, respectively. In detail, the dried soil samples were screened by 2-mm sieve. Approximate 5 g specimen was taken from each sample and placed in the crucible. The specimen was heating at 105°C for 2 h and weighed after cooling at room temperature, then burned it at 450 and 900°C for 2 h and weighed after cooling at room temperature sequentially. The weight loss between the two high temperatures is called DOC.

## 2 Results and discussions

The field results are shown in Figs.4–8. The definitions of MC, DOC and pH are self-explanatory. LL is the empirically established moisture content at which a soil passes from the liquid state to the plastic state. PL is the empirically established moisture content at which a soil

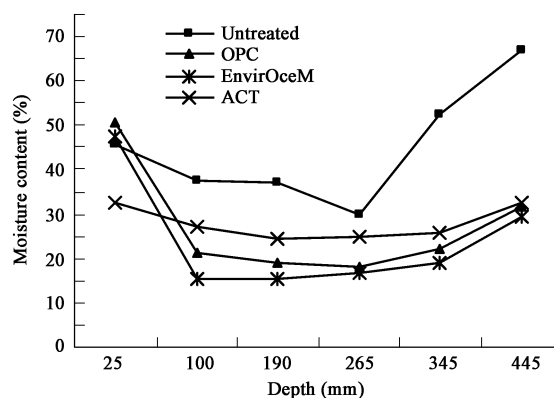


Fig. 4 Moisture contents of the soils in the four cells.

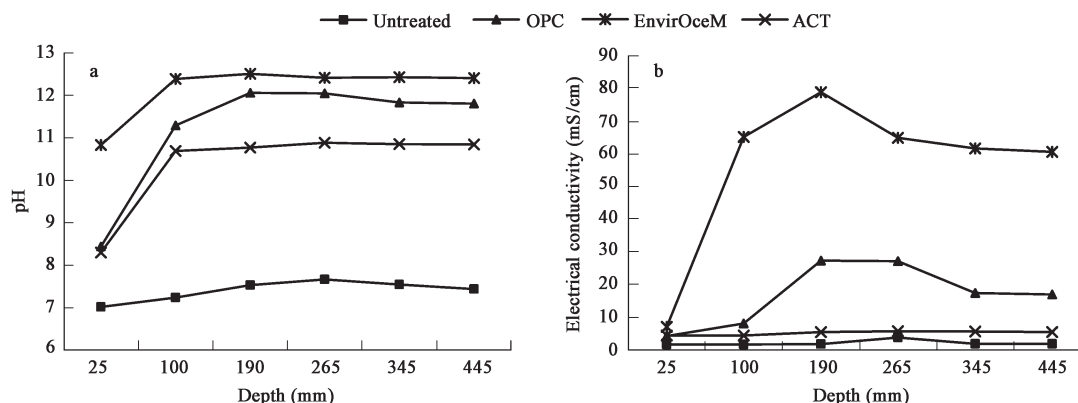


Fig. 5 pHs (a) and electrical conductivities (b) of the soils in the four cells.

becomes too dry to be plastic. The difference between the PL and LL of the soils is called PI which characterizes the potential water content range. Soil electrical conductivity is the ability of soil to conduct electrical current. pH and EC of the soil solution were chosen to characterize the leachability of ions in the soil. It is evident that variations of all parameters except DOC exhibited two phases with the depth. The maximum or minimum values of these parameters were at the mid-height of the cells, while DOCs decrease from surface to bottom of all cells.

### 2.1 Moisture contents

Figure 4 shows that all the cells exhibit a characteristic reduction in the MC from the surface to the mid-height of the cell and then MC increases between the middle and the bottom of the cell. It is most likely that this result is influenced by recent rainfall on the surface (sampling conducted in October) and water collecting on the bottom at the liner interface. The untreated Cell 1 has the highest MC throughout its depth, this is most likely because of a higher permeability, and clay mineral properties which allow it to absorb more water. This is evidenced by the higher liquid limits of samples from Cell 1, suggesting that the material has a larger diffuse double layer. It is significant that ACT soil contains more moisture contents than traditional S/S soils, i.e. OPC soil and EnvirOceM soil.

### 2.2 pH and electrical conductivity

According to Fig.5, the untreated soil is neutral or slightly alkaline, while OPC soil, EnvirOceM soil, or ACT soil is very strong alkaline because of the addition of cement. The lowest pH at the surface of each cell could be due to the vegetation and weathering. As expected, pH of ACT soil is lower than that of OPC or EnvirOceM soil due to carbonation.

Electrical conductivity characterizes the concentration of water soluble ions in the soil. All the cells exhibit a characteristic increase in the MC from the surface to the mid-height of the cell and then EC decreases between the middle and the bottom of the cell. The untreated soil has the lowest EC because there are much more soluble ions in cement in the other cells (2, 3, 4). In Fig.5b, the pattern of lowest to highest EC follows that of pH. The lowest EC

of the soil in each cell is in the surface layer. It can be considered as that the weathering, vegetation, carbonation and other environmental factors changed the permeability and leachability of the surface soils so that the ions were mobilised downwards. Because of clay mineral properties of the untreated or treated soil although dilution due to the addition of cement in the cells (2, 3, 4), the more ions, the smaller diffuse double layer, consequently, the less water content range it has. This observation is validated by the results of LL and PL of the soils and by the study on total metal concentration in the four cells from the University of Greenwich. It shows the metals were being progressively mobilised and were being concentrated towards the bottom of the soil column, although the levels of metal leaching from the three kinds of different treated soils were below the regulatory limits for all elements of concern (Antemir *et al.*, 2006). Therefore, the two-phase variations of pH and EC may well explain the changes of other geotechnical properties with the depth.

### 2.3 Degree of carbonation

In Fig.6, the untreated Cell 1 has the lowest DOC at all depths, as expected. All the treated cells (2, 3, 4) have similar surface DOC values, which are higher than that of Cell 1 due to the cement content. It is significant that the DOC of the sample in Cell 4 subjected to accelerated carbonation exhibits a linear reduction in DOC with the depth,

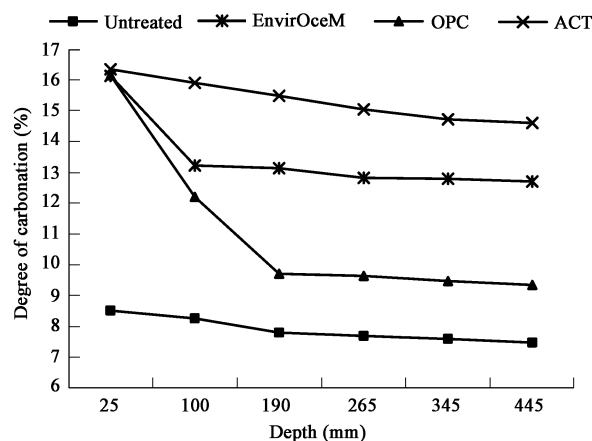


Fig. 6 Degrees of carbonation of the soils in the four cells.

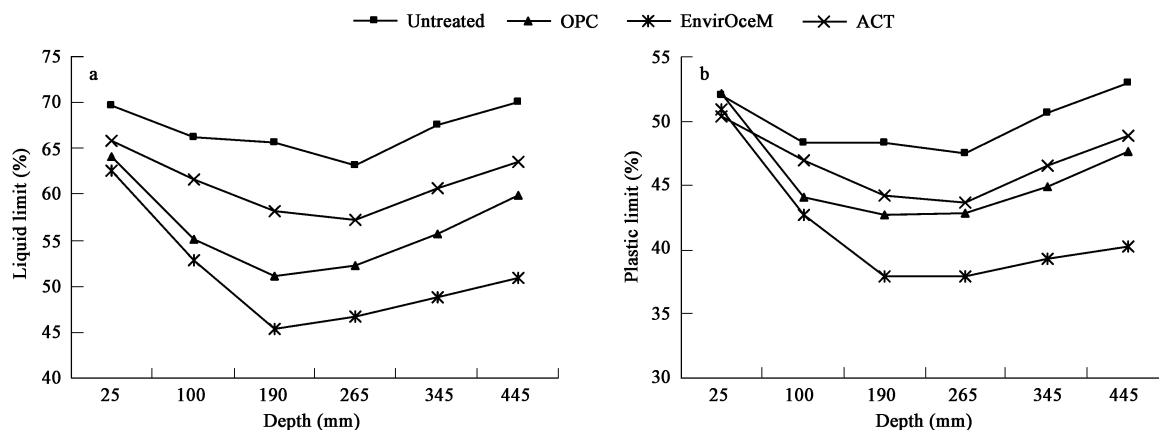


Fig. 7 Liquid limits (a) and plastic limits (b) of the soils in the four cells.

similar to the untreated samples, whilst the cement treated samples in Cells 2 and 3 exhibit significant decreases from the surface to mid-height followed by a smaller reduction to the base of the cells. It is thought that this is due to the availability of un-carbonated calcium compounds as well as the gaseous permeability of the samples.

## 2.4 Liquid limit and plastic limit

The LL and PL in each cell change with the depth in similar pattern in Fig.7. Compared with the other two different cement-based soils, ACT greatly increased the PI of the treated soil and made PI more stable in the long-term weathering (Fig.8).

The LL and PL data are best explained by considering the difference between the two values, i.e., the PI value. It is obvious in Fig.8 that PIs of the materials in the cells increase according to the following sequence:

EnviroceM soil < OPC soil < ACT soil < untreated soil

Moreover, the pH and EC increase according to the following sequence:

Untreated soil < ACT soil < OPC soil < EnviroceM soil

Evidently the sequences are inversely related, reflecting how the PI is affected by the pH and conductivity. This is most likely due to the effect of ions on the size of the diffuse double layer of the clay mineral particles. This observation is reinforced by the fact that the cement treated samples in Cells 2 and 3 have PIs that change similarly

with the depth, while the PIs of the untreated and ACT treated Cells 1 and 4 also change similarly with the depth. The similar variations in PI with the depth between these pairs of samples also match variations in the DOC with the depth, indicating that free calcium ions are particularly important in the control of the PI and consequently broader geotechnical properties.

## 3 Conclusions

Compared with the traditional cement-based soils, ACT greatly increased the PI of the treated soil and made PI more stable in the long-term weathering. The increase sequence of PIs is inverse to that of pH and EC of the four materials: for PI, EnviroceM soil < OPC soil < ACT soil < untreated soil; for pH and EC, untreated soil < ACT soil < OPC soil < EnviroceM soil.

The experimental results showed that the way in which the material from the trial site interacts with water (PI), and hence its broader geotechnical properties, is related to the dissolved solids and most likely the free calcium ion concentration. This in turn is related to the leaching profile and the DOC. Early signs suggest that the aged ACT treated samples and untreated samples have limited free calcium ions in solution and consequently interact with water in a similar way.

The future research will be needed to carry out to assess the effect of accelerated CO<sub>2</sub> weathering on the properties of cementitious S/S contaminated and un-contaminated soils.

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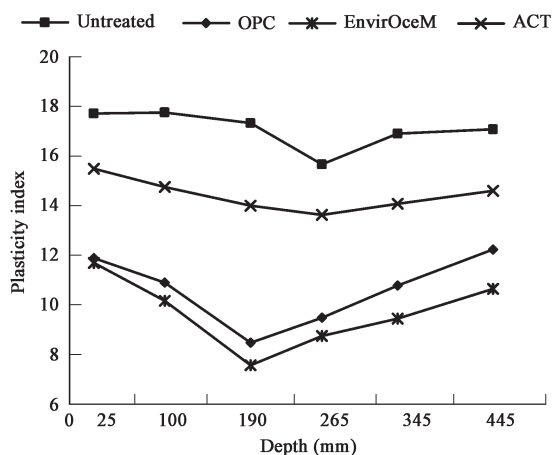


Fig. 8 Plasticity indices of the soils in the four cells.

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