Performance assessment of stabilised/solidified waste-forms

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ABSTRACT

A method to treat contaminated land is stabilisation/solidification (S/S), which physically encapsulates and chemically stabilises the contaminants. The current knowledge on the behaviour of S/S systems is based upon scarce and incomplete data, mostly obtained from laboratory simulations or small scale trials of the technology. The field performance of S/S soils is largely unknown.

The aim of this research was to improve the understanding of the long-term performance of S/S soils, by examining samples retrieved from eight full-scale remedial operations. The sites were selected to emcompass a broad range of contaminants, binder systems, environmental exposures, and ages since the remediation.

Conceptual models for each site were developed, based upon historical information from the literature. The models were used to identify the environmental loads, acting at the sites, and to predict their likely impact on the S/S soils. These impacts were considered by examining the microstructure, mineralogy, leaching behaviours and mechanical properties of the aged soils. Risk indicators for the performance of S/S soils were identified and they included reactions involving sulfates, carbonation, microcracking and the presence of weathered minerals.

There was no link between the age of the S/S soils and degradation. The performance of the S/S soils was site specific and was infuenced by the design of the remediation formulation, the implementation of the treatment and not least the environment of exposure.

The behaviour of S/S soils is commonly compared to that of concrete. However, whilst the results suggested that same degradation mechanism occur, properties such as permeability and unconfined compressive strength differed. The S/S soils were two orders of magnitude weaker and five order of magnitude more permeable than normal concretes.

Microstructural investigations revealed that although expansive phases developed with time in the S/S soils, there was no damage associated with them. According to their mechanical properties seven out of eight soils performed to their design criteria, up to 16 years after remediation. However, three sites failed to meet the limits following pass/fail leaching tests. This was due in part to the choice of leaching test carried out for the evaluation and the use of inappropriate remedial leaching limits, such as Drinking Water Quality values. However, the pH dependent leaching test showed that the contaminants were well immobilised in the old S/S soils and their release, at the natural pH of these soils did not exceed 1 mg/l.

The acid resistance of the aged S/S soil was low to moderate and was mainly assured by the carbonates present. This fact will impact on the durability of S/S soils; however, estimates from the literature indicate that the acid resistence of carbonated materials would be exhausted in thousands of years.

Based upon these results, the integrity of the soils had endured, and no obvious signs of impending failure were observed.

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Chapter 1 Introduction

1. Background

Contaminated land is a worldwide environmental issue. The links between chemicals, the quality of air and water and human health was known since the 18th – 19th centuries, but very little concern was placed on the contamination of soils (Cairney and Hobson, 1998). Previously only known because of infamous events such as Love Canal, Times Beach, USA, Minimata, Japan, contaminated land is now a field in its own right, subject to strict regulations and controls, at least in most developed countries (Nathanail and Bardos, 2005; Cairney and Hobson, 1998).

Contaminated land or contaminated soil is the result of unregulated waste disposal arising from intensive industrial activities. This soil contains 'harmful substances to the point, where it poses a serious risk to human health and the environment' (Environment Agency, 2008a). This term must be distinguished from brownfield land which defines land or premises that have previously been used or developed (Environment Agency, 2008a).

The management of contaminated land was first initiated in the United States in the 1970s and slowly adopted in several European Countries, including the United Kingdom where it was harmonized towards the end of 1990s, through the Environment Protection Act. There is no uniform approach to contaminated land across the globe; each country has developed its own policy for dealing with contaminated land, which ultimately aims at identifying and treating the soil.

Stabilisation/Solidification (S/S) is an effective method for treating a variety of hazardous and radioactive wastes and contaminated soils, which involves mixing cementitious binders to encapsulate and chemically stabilize the contaminants. Although S/S has been often used in Europe as a risk management technique for hazardous and radioactive waste, its application to contaminated land has been relatively limited. The practical application of S/S for the treatment of soils has raised questions regarding the long-term durability and the permanence of contaminant immobilization within the stabilized matrix.

The need for data on the durability of S/S wastes led to the establishment of an international collaborative research program (PASSiFy) comprising a number of key commercial, academic research partners and regulators such as the US Environmental Protection Agency (EPA), the Environment Agency (England and Wales) (EA) and the Environment Agency of France (ADEME). The proposed work is unique and aimed at accessing and testing a number of well-characterised, full scale sites treated by S/S many years ago, to provide field data on their long-term performance.

2. Aims and objectives

The aim of this work is to improve the understanding and confidence in the long-term performance of the soils treated by Stabilisation/Solidification.

The objectives are:

1. to evaluate the extent of weathering of a four year old cement treated soil opened to the atmosphere and identification of degradation risk indicators;
2. to examine the mechanical properties, the mineralogy and microstructure of seven aged cement treated soils, up to 16 years old;
3. to evaluate of the efficacy of contaminant immobilization in the aged S/S soils.

3. Thesis structure

Chapter 2 is a literature review of contaminated soil and methods of treatment for contaminated soil, the focus being placed on Stabilisation/Solidification. The current understanding of the mechanism of metal immobilization and the durability of the S/S soils is discussed.

Chapter 3 introduces the materials and methods used to characterize the S/S soils and evaluate their performance with time.

Chapter 4 describes in detail the S/S sites studied. Conceptual models for each site are presented to analyse the loads likely to influence the S/S soils performance, in their environment of service. The histories of the sites are examined for information on the sources of contamination, and the methods used to extract samples from the sites are described.

Chapter 5 is devoted to the study of soils obtained from a pilot scale demonstration of S/S. Samples were extracted four years after treatment and tested for physical, microstructural, mineralogical and chemical characteristics, to inform the testing strategy in next chapters.

Chapter 6 examines the physical, chemical and microstructural properties of the samples obtained from full-scale S/S remedial operations, to evaluate their performance with time.

Chapter 7 explores the efficacy of metal immobilization in the aged S/S soils, following up to 16 years of exposure in the environment. The acid resistance of these soils is also studied.

Chapter 8 contains a summary of the findings in this thesis, conclusions and suggestions for further work.

Chapter 2 Literature review

1. Introduction

The current work aims to evaluate the performance with time of contaminated soils treated by Stabilisation/Solidification, by studying sites in two different countries. This chapter provides a general introduction to contaminated land, the legislation and practices relating to contaminated land in the UK and the USA are given. The methods available for treating contamination in soils are reviewed with the focus placed on Stabilisation/Solidification (S/S). The principle of S/S, the methods of applying S/S, typical binder systems used and their chemistry are also explored. A detailed review of the contaminant immobilisation mechanisms acting in S/S soils and the processes affecting their performance with time is provided. This chapter concludes with the previous studies and the current understanding of the long-term performance of S/S soils.

2. Contaminated land

Contaminated soil is the result of industrial activities, unregulated discharge of waste, spillages, application of pesticides or percolation of contaminated surface water to subsurface strata (Sarsby, 2000). The most common chemicals involved in soil contamination are petroleum hydrocarbons, solvents, pesticides, lead and other heavy metals and metalloids. According to recent estimates, between 50,000 and 300,000 hectares of contaminated soil exist across the UK, representing 1.2% of the total land area (Nathanail and Bardos, 2004).

The main method of dealing with contaminated soil has been excavation and disposal to landfill, but this is no longer considered a sustainable approach. With the increasing pressure for land resources, increasing landfill costs and the prospective removal of the exemption from paying landfill tax, the focus was firmly placed on developing remediation technologies for contaminated soils (NetRegs, 2010).

The basis of contaminated soil remediation is risk minimisation. In order for a risk to be realised in a soil affected by contamination, a 'pollutant linkage' must exist (Figure 2.1). A pollutant linkage requires the presence of three elements, a source of contamination, a receptor capable of being harmed, and a pathway capable of exposing a receptor to the contaminant (Environment Agency, 2008). By breaking the pollutant linkage (source-pathway-receptor), through either i) managing (removing, destroying, modifying or immobilising) the source; ii) interrupting the pathway (e.g. using a cover) or iii) modifying the receptor (e.g. restricting access to site) the risk is eliminated or minimized (Bardos *et al.*, 2000).

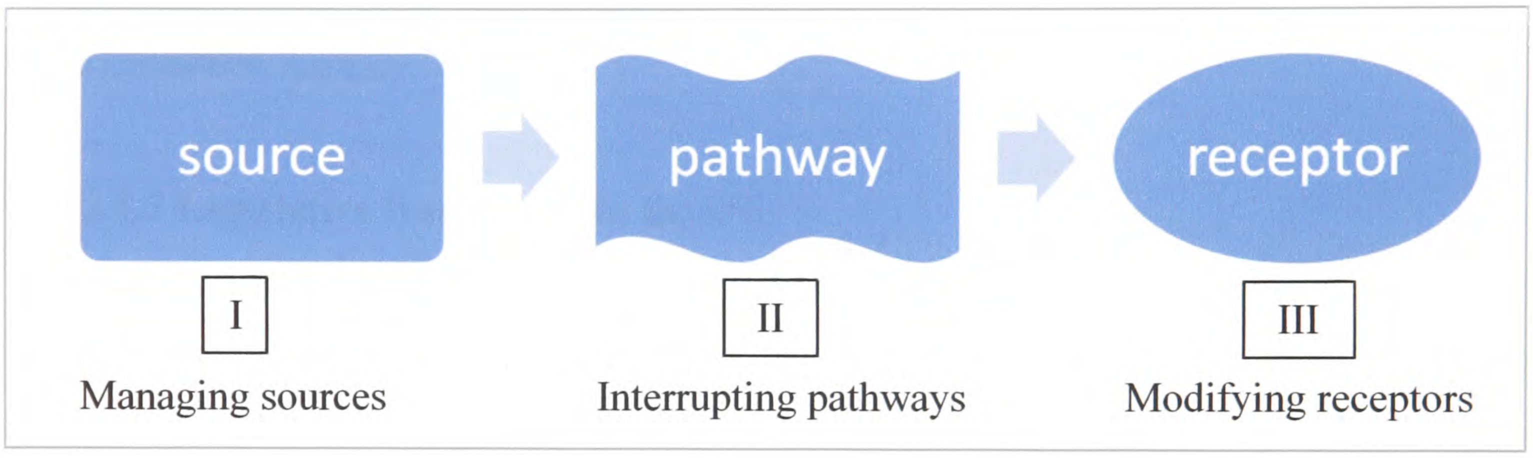


Figure 2.1 – Key actions for the reduction of risk posed by soil contamination

2.1 Legislative framework for contaminated land

The legal framework for management of contaminated soil was first introduced in the United States in the 1970s and slowly adopted in several European Countries, including the United Kingdom towards the end of 1990s, through the Environmental Protection Act. There is no uniform approach to contaminated land across the globe; each country developing its own policy for dealing with contaminated land. The main differences between each country's policies are in identification of risk where this is based on national needs, environmental setting, population etc. Two contaminated land systems are presented below.

2.1.1 Legislative framework in the UK

The approach to the management of contaminated land is covered by the Part IIA of the Environmental Protection Act 1990. This ensures that 'unacceptable risks to human health and environment are identified and removed, the damaged land is brought back into use and the costs related to the remediation are proportionate, manageable and economically sustainable' (DETR, 2000).

A soil containing contaminants is only considered contaminated, if a significant potential of significant harm (SPOSH) can be demonstrated. In other words, if the contaminant concentrations in the soil exceed the soil guideline value (SGV), for the planned land use, and a pollutant linkage (source-pathway-receptor) is identified, the contamination poses a risk and requires further investigation and/or remediation. The process of identification of contaminated sites does not constitute the focus of this work, therefore it will not be addressed here. More information of the various stages in this process can be found in the Guidance for the Safe Development of Housing on Land Affected by Contamination (Environment Agency, 2008b).

2.1.2 Legislative framework in the US

In the US, a structured approach, for assessing whether a site is contaminated and whether it requires remediation, was brought in by the US Environmental Protection Agency (USEPA). This approach consists of a preliminary assessment of the contaminated land by ascribing a numerical value to a series of risk factors which will determine its insertion on the National Priorities List (NPL) and subsequent eligibility for remediation under the Superfund programme (Bergius and Oberg, 2007). The programme was introduced in 1980, following the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), and deals with the remediation of uncontrolled hazardous waste sites.

Superfund is the name given to the environmental programme established to address abandoned hazardous waste sites. The Superfund programme is responsible for finding the parties that caused the contamination at a site, and in absence of any responsible party, with undertaking the soil remediation (USEPA, 2008). A remediation of contaminated soil is carried out, if the total contaminant concentration exceeds the 'trigger value', established based on health or land use risk.

2.1.3 Remediation

A myriad of technologies exists for contaminated land remediation/management, which can be divided into chemical (e.g. neutralization, oxidation/reduction, soil washing, soil vapour extraction), physical (e.g. vertical barriers), thermal (e.g. incineration, vitrification), stabilisation and biological (e.g. bioremediation, composting, phytoremediation). These techniques aim at dealing with one of the three key contamination linkage elements (source, pathway, receptor) and some examples are provided in Table 2.1.

Table 2.1 – Examples of techniques used for contaminated land treatment (modified from Barr *et al.*, 2003)

Method	**Description**	**Application**	**Contaminants**	**Linkage element affected**
Chemical				
Oxidation - reduction	Destructive treatments that use highly reactive reagents to convert the contaminants to less toxic end products	in situ	organics	source
Pump and treat	Removes free liquids containing the contaminants by pumping. The extracted contaminants undergo treatment.	ex situ	organics	source
Soil washing	Exploits differences in physical properties (such as size, related techniques shape, density, surface characteristics) to separate contaminants or contaminated soil particles from uncontaminated soil (Barr et al, 2003).	ex situ	metals, organics	source
Soil vapour extraction	An in situ method, where a vacuum is applied to the soil to remove volatile and semivolatile contaminants. The gas leaving the soil may be treated to recover or destroy the contaminants (FRTR, 2010).	in situ	organics	source
Thermal				
Thermal desorption	The soil is heated at low (<320C) or high temperature (<560C) to volatilise the contaminants. This method eliminates or destroys the contaminants leaving the soil clean and maintaining the original properties.	ex situ	volatile metals, organics	source
Vitrification	Uses high temperature to melt subsurface minerals. Organic contaminants are thermally destroyed and the inorganic contaminants are immobilised in a glassy residue (Rani *et al.*, 2008)	in situ/ex situ	metals	source
Incineration	Incineration is a destructive technique, which uses high temperatures (900-1200C) to breakdown a wide range of organic contaminants. Off gases and combustion residuals generally require treatment.	ex situ	organics	source

Table 2.1 – Examples of techniques used for contaminated land treatment (modified from Barr *et al.*, 2003) continuation

Method	Description	Application	Contaminants	Linkage element affected
Stabilisation				
Stabilisation/solidification	Involves mixing the contaminated soil with a hydraulic binder, which physically encapsulates and chemically stabilises the contaminants.	in situ/ex situ	metals, organics	source
Monitored natural attenuation	Relies on the nature to destroy contamination in soil by absorption, biodegradation, dilution.	in situ	metals, organics	pathway
Biological				
Windrows	Soil is typically placed in 2 m to 3 m thick layers or heaps, and materials such as wood chips, bark or compost are often added to improve the soil structure and increase aeration.	ex situ	organics	source
Biopiles	Excavated soil is placed in a static heap and nutrients are added to the contaminated soil. A network of internal galleries is created and air is circulated through to enhance biodegradation. The heaps are covered with an impermeable liner to minimize the risk of contamination of the soil outside the treatment area.	ex situ	organics	source
Physical				
Capping	The contaminated materials are left in the ground and the contact with them is prevented by installing an impermeable cap.	in situ	metals, organics	source
Other				
Dig and dump	Involves excavation of the soil and disposal to landfill. Expensive and unsustainable method of dealing with contaminated soil, but it featured high amongst the most popular method before 2005.	ex situ	metals, organics	source

3. Solidification/Stabilisation

Solidification/Stabilization (S/S) is a process which involves mixing waste or contaminated soils with a cementitious material to reduce the mobility of contaminants into the environment (Shi and Conner, 2004). This is achieved by the physical incorporation of contaminants within a hardened mass of low permeability (solidification), and the chemical conversion of contaminants into an insoluble form (stabilisation) (Environment Agency, 2004). If appropriately designed, the S/S soils should only allow gradual release of contaminants into the environment (Lange, 1996).

In the US, there are 57 priority wastes for which S/S is a best demonstrable technology (BAT) and a summary is shown in Table 2.2. The contamination was most likely created due to an industrial activity, therefore large quantities and vast areas are normally involved. The implementation of the S/S treatment is therefore dependent on site specific conditions. A summary of the delivery methods for S/S is presented in Section 3.1.

The chemistry of each contaminant is very different, and a single cementitious binder is not sufficient to treat all contaminants. A wide range of binders and special additives is utilised during S/S treatments, and this will be discussed in section 3.2. The mechanisms of contaminant immobilization by S/S vary with each type or class of contaminant, therefore an overview of characteristic reactions is presented in section 3.3.

Table 2.2 – Contaminants, for which S/S is BAT (from Conner, 1990)

Metals
- Antimony
- Arsenic
- Barium
- Beryllium
- Cadmium
- Chromium
- Copper
- Lead
- Mercury
- Nickel
- Selenium
- Silver
- Thallium
- Vanadium
- Zinc

Volatile compounds

Semi-volatile organic compounds

Inorganics other than metals
- Cyanide
- Fluoride
- Sulfide

Organochlorine pesticides
- Aldrin
- Alpha-BHC
- Beta-BHC
- Delta-BHC

3.1 Delivery methods of Stabilisation/Solidification

Stabilisation/Solidification can be delivered via an *ex situ* or *in situ* process. *Ex situ* treatment involves excavation of the contaminated material and processing prior to mixing it with an appropriate binder system. At the end of the remediation the treated material is backfilled into the original place or transported to a point of deposition.

In situ treatment is applied at the origin of the contamination, by directly adding the binder, in the form of slurry or as a powder, using a number of different pieces of equipment (Figure 2.2).

Figure 2.2 – Equipment used for the S/S implementation, *in situ* and *ex situ*: a) pug mill; b) rotavator; c) mixing auger; d) in drum mixer; e) *in situ* blender; f) backhoe

The depth of remediation for *in situ* applications varies from shallow depths (<0.5 m) to more than 5 m. A description of the equipment suitable for *in situ* and *ex situ* mixing and the advantages/limitations of each type of application are presented in Tables 2.3 and 2.4.

Table 2.3 – Equipment and types of *in situ* and *ex situ* mixing (modified from BCA, 2004)

S/S type	Depth of treatment	Equipment	Remarks
Ex situ	All depths	Pug mill, cement and mortar mixers	Can operate in continuous or batch mode. Limited to a prescribed capacity.
		In-drum mixers	The contaminated material is placed in a drum, which acts as a container for setting and hardening. The drum is disposed of with the treated material.
		Fixed or mobile plant	The mixing carried out with mechanical batch or continuous mixers.
In situ	Shallow (< 0.5 m)	Augers, backhoes, rotating head blenders, rotavators	Applies to powder additions
	Intermediate (0.5 – 5 m)	Modified excavation plant	
	Deep (> 5m)	Hollow stem augers, pressure injection	Mainly applications of slurries, but powder materials are also used. The depths up to 35 m are possible. The use is dependent on the economics.

Table 2.4 – Advantages and limitations of in situ and ex situ processes for the treatment of contaminated soils (modified from BCA, 2004)

	Ex situ	In situ
Advantages	Good quality control of the treatment. Treated materials can be inspected visually. High production rates. Requires shorter period of time. Tolerant of low bearing capacity and unstable soils	Large volumes of materials to be processed. Suitable for saturated ground conditions. Can be used where space is restricted. Appropriate for mixing at depths up to 25 metres. Little or no secondary waste generated.
Limitations	Transport cost to and from the treatment facility. Extra costs associated with excavation of soils prior to treatment. Need for large areas on site.	Not suitable for soils containing debris, buried obstacles. Uneven mixing and difficulty in assessing the treatment accuracy. The bearing capacity of soil must be sufficient to support the mixing equipment. Presence of underground services may complicate the process.

The choice of delivery depends on a wide range of factors, which include the nature of the soil, the contaminants, the expected properties of the material obtained, regulatory requirements, bearing capacity of soil, depth of contamination and the economics (CASSST, 2003; Al-Tabbaa and Perera, 2005). Out of the 69 S/S projects carried out in the UK between 2001 and 2007, sixty percent were applied *ex situ* (Stegemann, 2009). Table 2.4 gives the main advantages and disadvantages for implementing S/S, *ex situ* or *in situ*.

3.2. Binders and additives

The choice of binder is made according to i) compatibility between the cement and the contaminated soil; ii) chemical fixation of contaminants; iii) physical encapsulation of contaminants; iv) leachability of contaminants from treated soil; v) durability of treated contaminated soils and vi) cost effectiveness (Shi and Spence, 2005a).

Depending on the type of contamination and the design properties of the stabilised material, a combination of binders is used. Six generic binder systems seem to dominate the treatment by S/S and they are Portland cement, cement/fly ash, cement/soluble silicate, lime/fly ash, kiln dust and phosphate (Conner and Hoeffner, 1998). Other binders and additives can be used to stabilise the contaminants and a non exhaustive list is presented in Table 2.5.

Table 2.5 – Common binders used in Stabilisation/Solidification (modified from Spence and Shi, 2005b)

Primary binders	Additives	
	Inorganic	Organic
Portland cement	Activated carbon	Bitumen
Lime	Neutralising agents	Urea formaldehyde
Alkali-activated slag cement	Oxidising agents	Polybutadiene
Alkali-activated pozzolana cement	Phosphates Organophilic clays	Polyester Polyethylene
Sulphur polymer cement	Carbonates	
Kiln dust	Zeolites	Organic polymers
Calcium aluminate cement	Reducing agents	Rubber particulates
	Silica fume	
	Surfactants	
	Sulfides (inorganic, organic)	
	Gypsum	
	Pulverised Fly Ash	
	Iron slag	
	Soluble silicate	

3.2.1 Cement binders

According to BS EN 197:1 (British Standards, 2000), there are five specifications for cements, as shown in Table 2.6. The subdivision of these five types of cement depends on the total amount of clinker with/without additions of other materials such as pozzolana, blast furnace slag, silica fume, shale and limestone. Each cement has a particular application for general use and for stabilisation/solidification (Table 2.6).

Table 2.6 – Main types of cements available on the market according to BS EN 197-1

Type	Name
CEM I	Portland cement
CEM II	Portland slag cement Portland silica cement Portland pozzolanic cement Portland fly ash cement Portland burnt shale cement Portland limestone cement Portland composite cement
CEM III	Blastfurnace slag cement
CEM IV	Pozzolanic cement
CEM V	Composite cement

The most commonly used cement in the UK and US is CEM I. Other special cements such as sulfate resisting or calcium aluminate cements have been applied to contaminated soils and wastes (Johnson, 2005).

3.2.1.1 Portland Cement (PC)

Cement is composed of four main mineral phases, amounting to 95% by weight: $3CaO \cdot SiO_2$ (C_3S - tricalcium silicate), $2CaO \cdot SiO_2$ (C_2S - dicalcium silicate), $3CaO \cdot Al_2O_3$ (C_3A - tricalcium aluminate) and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ (C_4AF - tetracalcium aluminoferrite). Approximately 5% of gypsum ($CaSO_4 \cdot 2H_2O$) is added during the manufacture of the cement clinker to prevent the rapid reaction of the C_3A phase upon the addition of water resulting in an immediate hardening of cement paste called “flash setting” (Bye, 1999)

C_3A is extremely reactive and this is controlled by the addition of gypsum during the manufacture of the cement. Amongst the four cement phases C_3A is the first to react. This phase does not contribute to long-term strength development, but has a strong influence on the early strength. The principal contributors to the long-term strength are the calcium silicate phases (C_3S and C_2S). C_3S is most reactive of the silicates and makes an important contribution to concrete strength, particularly up to 28 days. C_2S reacts slower than the C_3S and contributes to strength development at ages more than one week (Bye, 1999). The C_4AF phase is often said to react slowly (in comparison to the other phases) and only contributes to the long-term properties of cements.

Cement hydration is the term used to describe the range of reactions between cement and water to produce a hardened product. These are complex reactions, which consist of four stage-overlapping reactions (eq. 2.1 – 2.5), occurring at different rates according to the nature of the mineral phase.

Hydration progresses inwards from the surface of the grain of cement, beginning with the aluminate phases. Taylor (1990) established that the rate of reaction for the cement phases is $C_3A > C_3S > C_4AF > C_2S$, where the C_3A phase generates the most heat.

$$\underset{\text{calcium aluminate}}{C_3A} + \underset{\text{gypsum}}{3C\overline{S}H_2} + \underset{\text{water}}{26\,H} \rightarrow \underset{\text{ettringite}}{C_6A\overline{S}_3H_{32}} \qquad (2.1)$$

$$\underset{\text{calcium aluminate}}{2C_3A} + \underset{\text{ettringite}}{C_6A\overline{S}_3H_{32}} + \underset{\text{water}}{4\,H} \rightarrow \underset{\text{monosulfate}}{3(C_4A\overline{S}H_{12})} \qquad (2.2)$$

$$\underset{\text{dicalcium silicate}}{2C_3S} + \underset{\text{water}}{6H} \rightarrow \underset{\text{calcium silicate hydrate}}{C_3S_2H_3} + \underset{\text{portlandite}}{3CH} \qquad (2.3)$$

$$\underset{\text{tricalcium silicate}}{2C_2S} + \underset{\text{water}}{4H} \rightarrow \underset{\text{calcium silicate hydrate}}{C_3S_2H_3} + \underset{\text{portlandite}}{CH} \qquad (2.4)$$

$$\underset{\text{tetracalcium aluminoferrate}}{C_4AF} + \underset{\text{portlandite}}{4CH} + \underset{\text{water}}{23H} \rightarrow \underset{\text{calcium aluminate hydrate}}{C_4AH_{14}} + \underset{\text{iron substituted calcium aluminate hydrate}}{C_4FH_{13}} \quad (2.5)$$

Ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) is the first hydrate to form within minutes, as a result of the reaction of the C_3A phase with water in the presence of gypsum (Gougar *et al.,* 1996). The maximum amount of ettringite formed is reached after one hour, which corresponds to the induction or the "dormant" period in the cement hydration. At this point the cement grains are coated with newly formed ettringite, which hinders the permeation of water and delays further hydration. After the dormant period, which lasts a few hours, the ettringite is converted to monosulfoaluminate (monosulfate) (eq. 2.2).

The hydration of Portland Cement continues with the reaction of calcium silicates (C_3S and C_2S), which form calcium silicate hydrate gel (C-S-H) and calcium hydroxide or portlandite (CH). C-S-H gel is the main hydration product of Portland Cement, comprising 50 mol % of most cement pastes (Gougar *et al.*, 1996). The gel has a variable composition, with an average of Ca/Si ratio between 1.7 – 1.8 (Bye, 1999).

3.2.1.2 Sulfate-resisting Portland cement (SRPC)

Sulfate-resisting Portland cement is a special Type of CEM I cement, which was specially designed to overcome concrete failure due to sulfate attack (Eglington, 2004). This failure process was noted for concrete placed in soils containing high concentrations of sulfates or in contact with sea water. The component in concrete found to be participating to the reaction with sulfates was the C_3A (Taylor, 1997). SRPC is produced by reducing the alumina content in the raw materials and keeping the calcium silicate content high through the increase of the silica content (Bye, 1999). In the UK, the maximum percentage of C_3A phase in SRPC is 3.5%, as specified in BS 4027:1996 (Bye, 1999). A typical composition of the SRPC by comparison with Portland cement is indicated in Table 2.7.

Table 2.7 – Typical phase composition of SRPC compared to PC in % wt

Cement Phase	SRPC	PC
C_3S	69.6	57.9
C_2S	3.8	13.4
C_3A	3.6	9.5
C_4AF	13.8	11.0

from Sahmaran (2007)

The hydration reactions for SRPC are similar to PC, as indicated in section 3.2.1.1. Although SRPC is widely used in concrete placed in sulfate soils, it has not reached the same acceptance for stabilisation/solidification of contaminated soils. SRPC is not believed to provide better durability over that obtained by using PC (Clear, 2005), hence its limited use. In addition, it has been shown that, in the case of soils, sulfate attack could also occur without the contribution of the C_3A phase (Environment Agency, 2004).

3.2.1.3 Pulverised Fuel Ash (PFA)

Pulverised fuel ash is a by-product of the energy production from coal. The exhaust gases from coal fired power stations carry fine dust particles produced by the boilers which are removed by electrostatic precipitators and represent the PFA. The properties of PFA depend on the type of coal used and can therefore vary in chemical composition. The ASTM literature identifies two types of PFA: i) Class F, a silica rich and lime low ash, obtained from bituminous coal and lignite and ii) Class C, a calcium rich ash from sub-bituminous coal (Bye, 1999).

Pulverised Fuel Ash is used in S/S alongside cement or lime, to improve the properties of the treated soil such as permeability, strength, and provide pH adjustment. By comparison with cement hydration, the PFA/cement system leads to similar hydration products. The difference with pozzolanic reactions is that they consume portlandite instead of producing it. This is of a particular importance in sulfate corrosion resistance and alkali aggregate reaction. Typical reactions in PFA/cement systems are presented in eq. 2.6 – 2.9 (Pollard *et al.*, 1991).

$$CH + S + H \rightarrow C_xS_yH_z \qquad \text{(C-S-H of varying stoichiometry)} \qquad (2.6)$$

$$CH + S + H \rightarrow C_xA_yH_z \qquad \text{(hexagonal/cubic aluminate hydrates)} \qquad (2.7)$$

$$CH + A + S + H \rightarrow C_xA_yS_zH_w \quad \text{(hydrogarnet)} \qquad (2.8)$$

$$CH + S + A + H \rightarrow C_xA_y(CS)_zH_w \quad \text{(ettringite and derivatives)} \qquad (2.9)$$

The replacement of portlandite with C-S-H following the pozzolanic reaction, described above, induces physical and chemical changes to the hardened cement. The space occupied by the clusters of portlandite is replaced with fine gel porosity of C-S-H, lowering the permeability, increasing strength and changing the pore size distribution (Bye, 1999). Permeability decrease has an important effect on transport mechanisms through the stabilised soil, hence improved resistance to damaging phenomena such as sulfate attack (Neville, 2004).

It was found that the use of PFA reduces the alkalinity of the system and therefore improves the immobilisation of amphoteric metals, like lead, zinc, chromium, cadmium compared to reference Portland cements (Dermatas and Meng, 2003).

3.2.1.4 Activated carbon

Activated carbon is a common additive used with cement or lime in S/S treatments for absorbing organic compounds and immobilising many heavy metals (Hebatpuria *et al.*, 1999). This is produced from solid carbonaceous materials like peat, wood, cocoshells or coal, by exposure to medium to high temperatures (Menendez-Diaz and Martin-Gullon, 2006). The properties of activated carbon include high microporosity and surface area, which are ideal for adsorption of contaminants. The adsorption of organics is a complex process that may involve dispersive interactions, hydrogen bonding, chemisorption, and surface polymerization (Hebatpuria *et al.,* 1999).

3.2.1.5 Limestone

Another additive used in S/S as a bulking agent or pH adjustment is limestone. This has been used to elevate the pH of strongly acidic wastes/soils prior to applying highly alkaline binders (Bates and Malott, 2005).

3.3. Contaminant immobilisation

Solidification/Stabilisation is performed to immobilise contaminants, which are posing a risk to human and environmental health. Depending on their stability, the contaminants can be encapsulated or take part in chemical reactions with the binder, i.e. precipitation reactions (Lange, 1996). Although discussed here separately, there is not a clear distinction between the two mechanisms. Moreover, other mechanisms such as chemisorption, adsorption, diadochy, ion exchange, pH and redox control, reprecipitation are also acting in S/S systems and could influence the contaminant immobilisation (Conner, 1990). A summary of the likelihood and implications of each mechanism on the contaminant retention is given in Table 2.8.

Table 2.8 – Mechanisms involved in contaminant immobilisation in S/S systems (modified from Conner, 1990)

Mechanism	Description
Sorption	Is a general term for describing the retention of contaminants by cohesive forces. Sorption of contaminants at the surface of hydration compounds and mineral is termed adsorption, within the solid matrix is sorption and chemisorption, for close range physical or chemical interactions between contaminant and the sorbent. The latter is not significantly different from absorption, however major differences relate to desorption of the contaminants (Lange, 1996). No single sorbent is suitable for removing all contaminants, therefore a number of sorbents are available such as activated carbon, clays, zeolites.
Diadochy	Takes place on the contaminant substitutes for another atom of similar size and charge in a crystalline lattice.
Ion exchange	Another process contributing to metal retention. Is a reversible process and can sometimes interfere with the normal setting of cement. Common ion exchangers are organic resins, zeolites, clays etc.
pH	Cement, lime and other alkaline materials are used for pH control. The alkaline conditions in cementitious systems cause the contaminants to become soluble, insoluble or amphoteric (soluble in both alkaline and acid conditions). The species which are not precipitatated are characteristic of the first class. The amphoteric class is relatively insoluble at near-neutral pH but become increasingly soluble as the pH increases.
Redox potential	Certain metals have higher solubility and toxicity depending on their valence state. Therefore often additives are used to reduce or oxidise the contaminants prior to the treatment by S/S. Moreover, the redox conditions created by the remediation formulation/binder can affect their chemical speciation and drastically change their solubility (Hoeffner *et al.*, 2005).

The prevalent factors affecting immobilisation of inorganic contaminants are different from those affecting the organic contaminants (Conner and Hoeffner, 1998). It was shown that pH, redox and chemical speciation influence inorganic contaminants, whilst the immobilisation of organics is based on processes such as destruction or alteration and physical encapsulation and absorption.

3.3.1 Encapsulation (physical immobilisation)

In S/S, the physical encapsulation of contaminants can be achieved at several levels: microencapsulation, macroencapsulation and embedment (Conner, 1990). Microencapsulation comprises the immobilisation of fine particles or contaminant/waste agglomerates into the cement matrix. Encapsulation of droplets of non miscible organic compounds had been observed (Stegemann, 2005). Physical immobilisation is characteristic to insoluble compounds, which include inorganic and organic compounds. Physical deterioration could therefore compromise the immobilisation, since this can lead to exposure of the contaminants.

Macroencapsulation is extensive containment of the S/S treated soil, by use of secondary encapsulation. In this type of encapsulation, the contaminated soil is, for example, cemented with polybutadiene binder and then encapsulated in a thick polyethylene jacket or the soil is placed in a thermoplastic container, after which the cover is permanently fused on.

Embedment refers to incorporation of distinct waste masses in large blocks or containers, prior to final disposal. This type of physical immobilisation has been employed for medical laboratory waste or hazardous waste at specialised disposal facilities.

3.3.2 Chemical reaction (precipitation)

Metal precipitation, as low solubility species, is by far the most important immobilisation mechanism in S/S systems (Conner, 1990). In Portland cement systems, metal hydroxides are the most common metal species, however sulfides, silicates, carbonates and phosphates are formed following the use of additives to control metal speciation. Sorbents, ion exchangers and complexing agents can be used where re-speciation is not effective (Conner and Hoffner, 1998).

3.3.2.1 Hydroxide precipitation

In Portland cement systems, the high alkalinity generated by cement hydration induces the precipitation of metals as hydroxides. Metal hydroxides are low-solubility species (Conner and Hoeffner, 1998) and therefore stable at the typical alkaline pH of cementitious systems, A number of metal hydroxides such as lead, chromium, cadmium, nickel, zinc are pH sensitive.

They exhibit a minimum solubility at pH in the alkaline range, but increases in solubility take place as the pH moves in either direction from that point.

3.3.2.2 Silicate precipitation

The silicate precipitation results from the reaction of Portland cement with a soluble silicate additive. This produces a highly stable matrix, which displays properties similar to soil like friability and rigidity (Conner, 1990). The silicate precipitation reactions are desired for polyvalent and amphoteric metals of environmental concern such as lead, chromium, arsenic, cadmium and zinc. The silicates formed are non-stoiechiometric and often non crystalline, therefore are still poorly understood. It was shown that if applied correctly, the silicate precipitation process can decrease heavy metal leaching to less than 0.1 mg/l, in most wastes (Conner, 1990).

3.3.2.3 Carbonate precipitation

Although not as common as hydroxide or silicate precipitation, carbonate precipitation may be responsible for metal immobilisation in S/S systems. This reaction takes place when carbon dioxide is available in the system, from the atmosphere or degradation of organic compounds, and reacts with a metal hydroxide to form a metal carbonate (eq. 2.10).

$$Me(OH)_2 + CO_2 + H_2O \rightarrow MeCO_3 + 2H_2O \qquad (2.10)$$

For some metals the carbonates are more stable than their hydroxide homologues, as in the case of barium, lead or cadmium. Conner (1990) reported that the immobilisation of zinc and nickel was dictated by the solubility of hydroxides, whilst that of lead and cadmium was linked to the carbonates precipitates.

3.3.2.4 Sulfide precipitation

Sulfide solubility is several orders of magnitude lower than that of hydroxides, throughout the pH range. Therefore sulfide precipitation is particularly effective for the immobilisation of highly toxic metals such as mercury (Conner, 1990).

3.3.2.5 Phosphate precipitation

Soluble phosphates are used for the treatment of contaminants in soils or wastes, due to the low solubility of the reaction products (Conner and Hoeffner, 1998). Phosphate precipitation does not change the physical characteristics of the soil, therefore cement is added, if a solid mass is necessary. Dermatas *et al.* (2006) successfully treated lead contamination using phosphates and cement. The reaction products exhibited very low solubility over a wide pH range (Hoeffner *et al.*, 2005).

3.3.3 Uptake by cement hydrates

Extensive investigations on the mechanisms of incorporation of heavy metals in the structure of C-S-H have found that four generalised mechanisms exist: a) additions (eq. 2.11); b) isomorphic substitution (eq. 2.12); c) formation of new compounds; d) multiple mechanisms acting at the same time.

$$\text{C-S-H} \quad + \quad \text{M} \quad \rightarrow \quad \text{MCSH} \qquad (2.11)$$

Calcium silicate hydrate — Metal — Metallic calcium silicate hydrate

The mechanism described by equation 2.11 is mostly characteristic of C-S-H gel with low Ca/Si ratio (Klich, 1997). By contrast, the substitution of the calcium ions in the C-S-H gel by the metallic ions was found to take place for high Ca/Si ratio C-S-H according to the equation (2.12). The limiting factor for the metal substitution in the C-S-H structure is the number of calcium ions which can be replaced (Klich, 1997)

$$\text{C-S-H} \quad + \quad \text{M} \quad \rightarrow \quad \text{MCSH} \quad + \quad \text{Ca}^{2+} \qquad (2.12)$$

Calcium silicate hydrate — Metal — Metallic calcium silicate hydrate

Ettringite has a large potential for ion substitution due to its columnar structure and substitution centres which can be either the cations Ca^{2+}, Al^{3+} or the anions SO_4^{2-}, OH^-; the stoichiometry of ettringite produced in concretes shows an excess or deficiency of certain compounds (Gougar *et al.*, 1996).

There is experimental evidence that indicates the substitution of SO_4^{2-} ions with oxyanions produced at high pH of cement hydration from amphoteric metals (Klemm, 1998). All amphoteric metals are susceptible to leaching because of their ability to react with acid and bases to form soluble products. Substitution in the crystal lattice of ettringite changes this behaviour. Generally, substituted ettringite has very low solubility (Klemm, 1998), and metal leaching from newly formed structures no longer poses a risk. Divalent cations can replace Ca^{2+} ions in the structure of ettringite (Gougar *et al.,* 1996), while some trivalent cations can replace Al^{3+} (Klemm, 1998).

As shown in Table 2.8, the mechanisms of immobilisation of contaminants vary according to the nature of the contaminant. A description of metal specific reactions is described in the next sections (3.3.3.1 to 3.3.3.4).

3.3.3.1 Lead

In S/S treated soils, X-ray Photoelectron Spectroscopy (XPS) investigations showed that lead was present as sulfate or carbonate, precipitated on the outer surfaces of cement clinker (Trussell and Spence, 1994). This represents a relatively weak immobilisation, as fluctuations in pore water pH can dissolve the precipitated salts making the metal available for leaching (Gougar *et al.,* 1996). The pH dependency of lead has been proven by a number of authors. Jing *et al.* (2004) argued that there are three bands of pH related leaching behaviour:

- at slightly acidic pH (below 6), the predominant species seems to be $PbOH^-$;
- between 6 – 12, minimal Pb leaching occurs due to the formation of hydroxide precipitates ($Pb(OH)_2$), which are incorporated in the calcium hydrates;
- at high alkaline pH (>12), soluble hydroxide anion complexes ($Pb(OH)_3^-$) form.

Since lead is an amphoteric metal with minimum solubility in a narrow range of pH between 8-10 (Conner, 1990), a rapid increase in metal leaching was observed for pH values above or below this range.

Glasser (1997) suggested that divalent Pb ions can generally replace calcium ions in the structure of the cement hydrates, forming insoluble solid solutions. The mechanisms of immobilisation of Pb are described in equations 2.13-2.15 (Environment Agency, 2004).

$$\text{C-S-H} + \text{Pb} \rightarrow \text{Pb-C-S-H} \qquad \text{chemisorption} \qquad (2.13)$$

$$\text{C-S-H} + \text{Pb} \rightarrow \text{Pb-S-H} + \text{Ca} \qquad \text{substitution} \qquad (2.14)$$

$$\text{Pb} + \text{OH} + \text{SO}_4 \rightarrow \text{mixed salt} \qquad \text{precipitation} \qquad (2.15)$$

Another possible Pb compound silicate was described by Conner (1990), relating the release of Pb to the dissolution of silicon.

3.3.3.2 Zinc

Zinc is non-toxic and in the United States is not regulated under the Resource Conservation and Recovery Act, which stipulates the maximum acceptable limits for metals which might pose a risk to human health or the environment.

This metal was found to interfere with cement hydration at concentrations greater than 20 wt % (Conner, 1990). Among the interferences are: retardation of cement hydration, decrease in the strength of the concrete and an increase in permeability through promotion of ettringite formation (Trussell and Spence, 1994). The same authors report that the increase in cement permeability has no implications for the immobilisation of Zn, suggesting that it is chemically bound in the S/S system.

At the high pH generated by the addition of cement in S/S systems, Zn forms hydroxides which are amphoteric in nature and therefore capable of reacting with both acids and bases. The equilibrium is described in equation 2.16 (Li *et al.,* 2001).

$$Zn^{2+} + OH^{-} \rightarrow Zn(OH)_2 \rightarrow 2H^{+} + Zn(OH)_2^{2-} \qquad (2.16)$$

Hydroxy complexes such as $Zn(OH)_4^{2-}$ and $Zn(OH)_5^{3-}$ formed at very high pH can be adsorbed onto the C-S-H or react to give rise to zinc complex hydrated compounds (Li *et al.,* 2001).

3.3.3.3 Copper

Although copper does not have known human toxicity, it is often found in contaminated soils and is treated by S/S. Cu is an amphoteric metal, which forms hydroxides stable at high pH. Komarneni *et al.* (1988) showed that Cu could substitute for Ca in C-S-H, but was more likely to be present as hydroxy-carbonates or incorporated into sulfoaluminate phases.

Lim *et al.* (2006) analysed a series of cement treated sewage sludges and observed, through a series of leaching tests, that the release of Cu was related to the DOC (dissolved organic carbon). A reasonable linear relationship between the DOC and the Cu leaching was recorded. DOC was assumed to be associated with the soluble humic substances in the sludge, which are known to form stable complexes with heavy metals. At the same time, their dissolution could be related to the high leaching of Cu.

3.3.3.4 Arsenic

Arsenic is a highly toxic element, which combines with most metals to form arsenides. Because of its wide commercial uses e.g. in the production of pesticides, in the glass industry, manufacture of alloys and electronics, arsenic is a common element in contaminated soils/wastes (Conner, 1990). The existence of numerous valencies, anionic and cationic species, inorganic and organic compounds make the chemistry of arsenic very complex. The organic-arsenic compounds require pre-treatment for breakdown of the complex before treatment by S/S.

Phenrat *et al.* (2005) identified three main mechanisms of arsenic immobilisation in S/S systems: sorption on C-S-H gel, substitution for sulfate ions in the structure of ettringite or formation of calcium-arsenic compounds. The latter was reported to be the most efficient mechanism of immobilisation of arsenic and represent the solubility limiting phases.

3.3.3.5 Organic contaminants

The traditional methods for treatment of organic compounds are incineration, thermal desorption, biodegradation, oxidation or dechlorination. These methods destroy the contaminants, and thus eliminate long-term effects (Conner, 1990). However, low levels of organics in a contaminated soil make these specific methods expensive and inefficient; therefore other techniques like S/S are employed for the contaminant treatment.

The immobilisation of organics in S/S systems is largely based on physical encapsulation, but hydrolysis, oxidation, salt formation and reduction may occur during the S/S treatment (Conner, 1990). The efficiency of organic contaminant treatment by S/S can be improved by using suitable adsorbents prior to the treatment, or mixing with the cementitious binder.

3.3.3.5.1 Polyaromatic hydrocarbons (PAH)

Polyaromatic hydrocarbons are formed during incomplete combustion of coal, oil and gas, but are also present in crude oil, creosote and asphalt. Certain PAHs (high molecular weight) are known human carcinogens and also affect animals and aquatic organisms (Health Protection Agency, 2010; Kulkarni *et al.*, 2008). PAHs are not water soluble and break down slowly in the environment (Environment Agency, 2010a).

Remediation of PAH contaminated soils using S/S has been employed in US on 17 sites, over 13 years (USEPA, 2007). PAHs do not interact with the inorganic S/S binder, therefore their stabilisation is mainly reliant on physical encapsulation. The treatment with Portland cement alone was not found to be efficient in immobilising PAHs (Mulder *et al.*, 2001; Conner, 1990), therefore additives or absorbents capable interacting with the PAHs are commonly employed prior to the cement treatment. The absorbents used most often are organophillic clays, activated carbon, zeolites (Hebatpuria *et al.,* 1999; Leonard and Stegemann, 2010).

3.3.3.5.2 Polychlorinated byphenyls (PCBs) and dioxins

Polychlorinated biphenyls are aromatic organic compounds, widely used in the past as lubricants and insulators in transformers. These compounds have high stability and toxicity, therefore are considered persistent organic compounds (Environment Agency, 2010b). The high thermal and chemical resistance of PCBs means they do not readily break down when exposed to heat or chemical treatment, which makes their destruction extremely difficult. Another problem associated with PCBs is the risk of generating extremely toxic dibenzodioxins and dibenzofurans through partial oxidation.

Dioxins are polyhalogenated aromatic hydrocarbons that result non-intentionally from incomplete combustion during industrial processes (Kulkarni *et al.,* 2008). Dioxins are highly toxic and persist in the environment over long periods of time (> 30 years) (Haglund, 2007). The toxicity of dioxins is expressed as toxic equivalent quantities (TEQs), where the most toxic congener 2, 3, 7, 8- tetrachlorodibenzodioxin (TCDD) is rated as 1.0 and the less toxic congeners as fractions of this.

Similarly to PCBs, dioxins are resistant to most common acids, bases, oxidizing agents, and reducing agents at ambient temperatures, and are also temperature stable (Haglund, 2007). In addition, dioxins bind to fine fractions of soil, therefore making the treatment of dioxin contaminated soils complicated.

Remediation formulations consisting of Portland cement were found to be effective for the treatment of PCBs (Pollard *et al.,* 1991). PCBs are practically insoluble in water, therefore tend to be well immobilised in the cement matrix (Conner, 1990). The efficacy of the S/S treatment of dioxins has not been fully demonstrated, however activated carbon was shown to improve the immobilization of dioxins.

3.3.3.5.3 Total petroleum hydrocarbons (TPHs)

Total petroleum hydrocarbons are complex mixtures made up of several hundred aliphatic and aromatic hydrocarbons. Their composition varies depending on the crude oil refined to generate the product, the type of product, the season of the year, and any performance additives. Common sources of TPHs are petrol stations, underground storage tanks, home and commercial heating oil storage tanks, refineries, crude oil production sites and accidental spills.

High concentrations of organics pose a major concern for S/S since they have a retarding effect on the reaction of cement (Pollard *et al.* 1991), and may be mobilised after the curing of the solidified mix (Vipulanandan, 1995). This is due to the reliance of TPH immobilisation on physical encapsulation in voids formed in the cement matrix and sorption on cement hydrates (Karamalidis and Voudrias, 2007; Leonard and Stegemann, 2010). Therefore, absorbents are generally used to encapsulate the organic compounds prior to cement treatment (Hebatpuria *et al.*, 1999; Conner, 1990).

3.4. Durability of S/S soils

This section reviews the durability of S/S soils and the supporting information regarding the long term performance of those systems.

Durability is the ability of concrete to withstand physical and chemical changes, whilst maintaining its design properties, when exposed to its intended service environment (Mehta and Monteriro, 2006). Depending on the exposure conditions and the properties desired, the concrete requires different degrees of durability. This is achieved by using appropriate ingredients, methods of placement and the place of installation. In a similar way, S/S soils have to conform to the above and this will be discussed in 3.4.1-3.4.5.

As far as the durability is concerned, the S/S soil must meet design targets related to physical and chemical integrity. An example of targets in the UK and the USA is indicated in Table 2.9.

It is necessary to look at the intrinsic and extrinsic factors affecting durability in concrete to establish the baseline for the study of S/S real samples. A series of internal and external factors contribute to the durability of the concrete. The internal degradation of a concrete is produced by deleterious compounds incorporated into the mix and normally affects largely the texture of the concrete. An example of an intrinsic attack is the alkali aggregate reaction which will be described in more detail later in this chapter. Extrinsic or external attack takes place from agents located outside the concrete and is limited to the exposed surfaces.

Table 2.9 – National recommended target values for S/S soils (from Al-Tabbaa and Perera, 2005a)

Property	USA	UK
Permeability (m/s)	$<10^{-9}$	$<10^{-9}$
UCS (kPa)[1]	350	600
Freeze/thaw	Pass[2]	NA
Leaching	TCLP limits	Drinking water quality

[1] unconfined compressive strength
[2] ASTM 1988 and 1990

Two types of degradation can take place in cementitious systems and they are chemical or physical in nature. Chemical attack occurs as a result of a reaction of a chemical agent with the cement paste, which leads to deterioration. This includes sulfate attack, carbonation, but also alkali silica reaction (see sections 3.4.1 – 3.4.3). Physical deterioration comprises the effects caused by freeze/thaw and cyclic wetting/drying and will be described further in sections 3.4.4 – 3.4.5.

3.4.1 Sulfate attack

Sulfate attack can occur as a result of the reaction of sulfates (calcium and magnesium) from the environment (external sulfate attack) or from the cement (internal sulfate attack). The term "sulfate attack" is often erroneously used to encompass a variety of reactions, of which only one or two are true sulfate-attack mechanisms that specifically involve the chemical effects of sulfate ions (Hime and Mather, 1999).

3.4.1.1 Ettringite

Ettringite is a crystalline mineral that occurs naturally, but is also formed during the hydration of cement and in small quantities, depending on the conditions, after the cement has set. This type is called secondary or delayed ettringite and requires specific conditions to form. At typical temperatures (25°C) the pH must be above 10, and a source of water has to supply as much as 26 moles. Additionally, a source of aluminum, sulfur and calcium is also required (Harris *et al.,* 2004).

In hardened cement, ettringite often exists as spherical clusters or parallel needles of different sizes. If ettringite crystallizes without obstruction, e.g. in the pore space, it has the typical needle-shaped crystal habit. The length-thickness ratio of synthesized ettringite crystals is closely related to the pH of the reaction solution; long, fiber-shaped crystals are formed at pH values between 10 and 12, but microcrystalline ettringite was present at pH values above 13.0 (Harris *et al.*, 2004).

Ettringite is hardly detectable in concretes stored in dry climates, but can be observed in the void space after a short time (6 months) when exposed to alternating cycles of wetting and drying. However, there is no evidence of any serious impairment of the properties of the solid concrete (St John *et al.*, 1998).

Many papers have been published on delayed ettringite formation and its impact on concretes and cement stabilized soils (Cody *et al.*, 2004; Casanova *et al.,* 1997). Some authors argue that its presence indicates a risk to the concretes due to its expansive nature (Lee *et al.,* 2005a). Nevertheless, the occurrence of ettringite in voids or cracks is very common in concretes and is not always associated with damage, although a high quantity of ettringite may have a deleterious effect (French, 1998).

3.4.1.2 Gypsum

Gypsum is the primary product of sulfate attack at high sulfate ion concentrations (Santhanam *et al.,* 2001). To date, no clear documentation on the disruption caused by the presence of gypsum exists. Nevertheless, some authors reported that gypsum has a deleterious effect on the durability of cementitious systems (Klich *et al.,* 1999; Lee *et al.,* 2005a). Two aspects of gypsum related deterioration need to be addressed; concrete surface softening and expansion. This effect is produced as a result of the conversion of portlandite to gypsum or of the reaction of gypsum with the hydrated calcium aluminate to form ettringite (Environment Agency, 2004), followed by a volume increase.

3.4.1.3 Thaumasite

The formation of another phase called thaumasite ($Ca_3Si(CO_3)(SO_4)(OH)_6 \cdot 12(H_2O)$), or non-binding calcium carbonate silicate sulphate hydrate, occurs as a result of the reaction between C-S-H gel, SO_4^{2-}, CO_2 or CO_3^{2-} and water, in high humidity and low temperature conditions (<15°C) (Collett *et al*, 2004).

The Thaumasite Expert Group has identified two distinct ways in which thaumasite can precipitate as a reaction product, in concrete, leading to distinct effects on its structure (Crammond, 2002). These are thaumasite form of sulfate attack (TSA) and thaumasite formation (TF). TSA is associated with significant damage to the matrix of a concrete or mortar due to the replacement of cement hydrates by thaumasite, whilst TF refers to cases where thaumasite can be found in pre-existing voids and cracks without necessarily causing deterioration (Crammond, 2002).

3.4.2 Carbonation

Carbonation is the reaction of atmospheric carbon dioxide with the S/S treated materials, which influences these materials chemically and structurally in several ways. The changes induced by the carbonation reaction can be observed in the microstructure, but also in the leaching behaviour of the contaminants. Carbon dioxide reacts with the products of cement hydration with their conversion into calcium carbonate according to the equations 2.17 – 2.19.

$$CH_{(s)} + CO_{2\,(g)} \rightarrow CaCO_{3\,(s)} + H_{(l)} \qquad (2.17)$$

$$C-S-H_{(s)} + CO_{2\,(g)} \rightarrow CaCO_{3\,(s)} + SiO_2nH_2O + H \qquad (2.18)$$

$$C_3A\overline{S}_3H_{32} + 3CO_2 \rightarrow 3CaCO_3 + 3C\overline{S}H_2 + AH_x + (26-x)H \qquad (2.19)$$

Carbonation requires the presence of water to act as a solvent for CO_2, but pore saturation can hinder the CO_2 transport, preventing the carbonation from occurring (St. John *et al.*, 1997). In the same way, the absence of water in the pores will not allow the carbonation to take place (Lange, 1996).

The C-S-H gel is one of the most important hydration products in an S/S system and is recognised as important for contaminant immobilisation. Malviya and Chaudhary (2006) reported that carbonation has a detrimental effect upon the properties of the material due to consumption of the Ca ions from its structure to form calcite (eq. 2.18). This process takes place without an obvious change of the morphology. However, accelerating the hydration process by curing in a carbon dioxide atmosphere (modified S/S-accelerated carbonation process) has a positive effect on the mechanical and chemical properties of the waste-forms (Lange, 1996).

The conversion of ettringite to calcite is due to a direct reaction with the CO_2 (eq. 2.19) and results in volume increase which infills the pore spaces. The structure formed has a higher density and improved structural integrity (Malviya and Chaudhary, 2006).

3.4.3 Alkali aggregate reaction

Alkali aggregate reaction (AAR) is a general term to describe any reactions between alkalis present in the pore solution of a concrete and the minerals in aggregates. The main alkali-aggregate reactions are alkali-silica reaction (ASR), alkali-silicate reaction and alkali-carbonate reaction (ACR). Alkali-silica reaction is an expansive reaction between sodium and potassium hydroxides in the pore solution and a siliceous component of an aggregate. This produces a gel that forms in the aggregate pores or at its margins. The gel can incorporate water and swell, exerting a pressure on the surrounding material, causing cracking and disruption of the hydrated cement paste (Neville 2004). The formation of the gel can take from a few months to a few years and this depends on three main conditions: the alkalinity of the pore fluid surrounding the particle is sufficiently high; the moisture content is not less than 85% in the pore structure and the presence of a reactive mineral in the aggregate (St. John *et al.,* 1998)

3.4.4 Freeze-thaw cycles

This process involves cycles of freezing/thawing of the water found in the pores of the material. This takes place in the micropores, as the large voids are normally filled with air. According to Taylor (1997), the damage is directly associated with the volume expansion when the water freezes inside the pores as the available space is insufficient for accommodating the extra volume created. Alternative theories propose that frost damage could be due to the formation of ice crystals and the pressure exerted by them in the capillaries (Taylor, 1997). There are five factors that contribute to the damage: the amount of water in the pores, the exposure conditions, pore size, rate of absorption and the degree of saturation (Perera *et al.*, 2005b).The most severe degradation occurs when the surface exposed to the weather is large and is maintained wet for long periods of time (Eglington, 1998).

3.4.5 Wet/dry cycles

This process occurs when the material is subjected to wetting and drying cycles. It can be caused by fluctuation in the water table level or penetration of rainwater or floodwater into the S/S soil. The disruption of paste and aggregate can eventually cause expansion and cracking, scaling, and crumbling of the concrete. The damage occurs as a consequence of the swelling of the cement gels and other absorbing materials in the S/S soils, when water is absorbed (Perera *et al.*, 2005b).

Although the concretes exposed to the environment suffer from degradation to a certain extent, in S/S this can be prevented by additional protection measures. Effective cover systems exist, and are applied based upon the environmental and the site specific conditions. They have the role of isolating the treated material from the atmosphere, rainwater, and water table to reduce the risk of degradation according to the mechanisms described in this chapter.

3.5 Long-term performance of stabilised/solidified soils

The long term performance of S/S soils is closely linked to both the physical and chemical properties developed, after binder addition, and at the exposure to the field conditions. To date, most studies relating to the longevity of S/S soils focused on understanding their chemical performance by applying a number of accelerated short-term leaching tests (van Zomeren *et al.*, 2003; van der Sloot, 2000) and very limited attention was given to real-life S/S materials (Klich, 1996; EPRI, 2005; Al-Tabbaa and Perera, 2005). The general consensus is that although these tests offer an insight into the behavior of the S/S soils, they have important short-comings i.e. do not fully reproduce the conditions in real-exposure environments (Perera *et al.,* 2005b; Klich, 1996; Glasser, 1997).

Studies of S/S soil up to five years after small scale technology demonstrations have been undertaken (Al-Tabbaa and Perrera, 2005). These studies included a number of leaching tests, physical tests (UCS, permeability) and in some cases SEM and XRD examinations. The results have shown that the S/S soils were performing as intended, and the metal leaching was gradual and within their site specific limits.

The only systematic study on S/S soils to date was however carried out by Klich (1996). The samples used in this study were obtained from four full scale soil remediation projects and two demonstration sites, up to 6 years old. The conclusions of her study were that S/S systems are metastable and slight to moderate degradation was observed. From the mineralogical point of view the S/S systems were similar to concrete; moreover, the phases found in weathered S/S soils were the same with those developed in environmentally exposed cement-based materials and concretes.

4. Conclusions

This chapter reviewed the legislation and practices applicable to contaminated soils, in the UK and the USA.

- The environmental awareness, the pressure to redevelop contaminated land and the landfill tax regulations have created an incentive to develop methods of soil remediation rather than relying upon landfilling.

- Stabilisation/Solidification (S/S) is used to improve the chemical and physical properties of the soil and allow the land to be reused. This technology uses cement binders or a mixture of cement and additives to immobilise certain inorganic and organic contaminants in soils and other hazardous materials.

- The durability of soils treated by S/S is not well understood, despite its use as a technique for many years. The lack of confidence in the technology is due the absence of field performance data.

In this study full-scale remediated sites of different ages, binder systems, and environmental loads affecting degradation mechanisms were sampled, and studied for their behaviour with time. The next chapter describes the main materials and methods used to investigate the properties and performance with time these S/S soils.

Chapter 3 Materials and Methods

1. Introduction

The previous chapter is a literature review of the contaminated land and the treatment methods used for the treatment of contaminated soils with focus on stabilization/solidification. This review offered an insight in the mechanisms of contaminant immobilisation and the processes influencing the durability of the S/S soils, and identified a gap in the knowledge regarding the S/S soil performance with time.

Chapter 3 describes the materials and methods used in this work to address the gap in the knowledge, identified in the previous chapter. Many different tests can be used to assess the S/S soil performance; some are imposed by the regulators, others are performed to give more assurance that the S/S treatment was successful. A combination of these tests will be used in this work and will be presented here, for more clarity, in three sections: basic characterisation, compliance testing and performance testing. The basic characterisation tests aim to determine the initial properties of the S/S soil, whilst the compliance tests to assess the performance of S/S soil against their site specific performance criteria. The performance testing provides a comprehensive evaluation of the physical and chemical properties of the aged S/S soils.

2. Materials

Soil samples were obtained from seven full-scale remedial operations and one technology demonstration via a number of methods. A summary of the sites sampled is presented in Table 3.1.

The sampling planning and collection, for the Superfund sites was coordinated by the USEPA and carried out by a specialist contractor. Georgia Power, the owner of the two sites in Georgia, US collected and distributed the samples, according to the same protocol. In the UK, the Caerphilly site was sampled by Celtic Technology Ltd using a random sampling strategy. The Astra Pyrotechnics site was sampled by the University of Greenwich and the Royal Engineers, whilst the Halton site was sampled by an external contractor selected by the site owner, supervised by the University of Greenwich. Details of the types of samples recovered, sampling equipment and the description of the individual sites are presented and discussed in Chapter 4.

Table 3.1 – Overview of the location and ownership of the S/S sites

Site	Location of site	Type of remediation	Site owner	Source of samples
American Creosote	Arkansas, US	Full scale	Superfund	USEPA
Astra Pyrotechnics	Kent, UK	Demonstration	University of Greenwich	University of Greenwich
Caerphilly	Wales	Full scale	Not known	Celtic Technologies
Columbus MGP	Georgia, US	Full scale	Georgia Power	Georgia Power
Halton	Cheshire, UK	Full scale	Halton Borough Council	University of Greenwich
Pepper Steel	Florida, US	Full scale	Superfund	USEPA
Quarry Dump	Georgia, US	Full scale	Georgia Power	Georgia Power
South 8th Street	Tennessee, US	Full scale	Superfund	USEPA

Testing

Previous studies of S/S soils have indicated that their properties are on a continuum between soils and concretes (Klich, 1997, Conner and Hoeffner, 1998) and the prevalence of any one of these extremes will be dependent on the proposed end use of the soil. In the research and practice, some tests which have been designed for concrete investigation have also been applied to S/S soils, but others such as chemical (mainly leaching) and geotechnical (grading, plasticity, particle density) have been used as an assessment of soil performance (Perera and Al-Tabbaa, 2005a). Due to the complexity of these materials, a combination of the above tests will be employed to gain insights into the S/S soil behaviour over time and these are described in the next sections.

3. Basic characterisation of soils

The basic characterisation of the S/S soils consisted of pH and moisture content and total metal content, which will be described in the sections 3.1 and 3.2.

3.1. pH and moisture content

3.1.1. Background

The pH was routinely measured in this work to support mineralogical, microstructural and leaching results and to indicate whether neutralisation has occurred by, for example, weathering.

3.1.2. Method

pH and moisture content were determined in triplicate on "as received" soils, following screening and homogenization. A 10 mm sieve was used to remove large stones and other debris. The larger fragments of soil were crushed to below 10 mm, re-sieved and homogenized using a riffle splitter. Portions of this soil were retrieved and prepared for pH and moisture content determination, according to BS1377: Part 3: 1990 (British Standards, 1990).

3.2. Acid digestion

3.2.1. Background

Acid digestion is a non-selective method of solubilisation of analytes from a solid material using repeated additions of a strong acid or a mixture of strong acids and oxidising agents. The most frequently used acids are nitric and hydrofluoric acids, nitric and hydrochloric acids (aqua regia).

Digestion with acids was used in this work to determine the heavy metal contents of the treated and untreated soils, at one of the eight sites investigated. The procedure used was the USEPA 3050B (USEPA, 1996). Although this acid digestion method does not provide the total metal content of the sample analysed (Chen and Ma, 1998), it was performed for comparison with the historic data available from the time of remediation at the Astra Pyrotechnics site.

3.2.2. Method

Three 1g replicate samples from each S/S soil were oven dried at 40°C, crushed to <10 mm and then digested. Replicate blanks were also prepared to ensure that no contamination had occurred. The accuracy of the procedure was checked against certified reference material (CRM023-050, lot# DG023 from RTC). Three samples were prepared from the soil reference material and digested following the same procedure as above.

The solutions obtained after the filtration of the digestates were analysed by ICP-OES (section 5.2). The metals recovery rates for the certified material are given in Table 3.2.

All reagents used were of analytical grade, from BDH Chemicals. All dilutions were done with high purity water obtained with PURELAB Option-R 7/15 system (Vivendi Water Systems Ltd).

Table 3.2 - Results from digestion of certified reference material (CRM)

Element	Reference value (mg/kg)	Confidence interval (mg/kg)	Prediction interval (mg/kg)	Average measured ± standard error (mg/kg)*	% recovery
Zn	93.8	88.0-99.5	63.9-123.6	89.1 ± 8.2	94.9
Pb	213.5	204.6-222.4	170.0-257.0	170.7 ± 34.5	79.9
Cu	8.9	8.3-9.6	5.7-12.2	8.2 ± 5.1	92.0
Cr	31.0	28.3-33.8	17.2-44.9	27.4 ± 12.8	88.4

*values represent the average of three replicates

3.3. X-ray Fluorescence Spectroscopy (XRF)

3.3.1. Background

X-ray fluorescence spectrometry is a non-destructive analytical technique used to identify and determine the concentrations of elements present in solid, powder and liquid samples. XRF is capable of measuring elements from beryllium to uranium at trace levels often below 1 mg/kg (PANanalytical, 2010).

XRF was used in this work to determine the bulk oxide composition of the S/S soils, as described in the next section.

3.3.2. Method

Bulk chemical analyses of the cement-stabilized soils were carried by the Materials and Engineering Research Institute, Sheffield Hallam University. The oxide composition (major elements) was determined on glass beads, whilst the minor elements were measured on pressed pellets. The instrument used to carry out the analyses was a Philips PW2440 Wavelength Dispersive Spectrometer.

4. Compliance testing

Standard tests for physical and chemical performance, including unconfined compressive strength, permeability and pass/fail leaching tests were applied to the S/S soils. This approach aimed at assessing soils current properties against their site specific performance criteria, established at the time of remediation.

Since the sites are located in the UK and USA, different tests were performed to comply with the local legislation or site specific requirements. To facilitate the understanding of the following sections and the correspondence between the method presented and the S/S soils to which it was applied, a testing matrix was compiled (see Table 3.3).

Table 3.3 – Testing matrix for the S/S soils

Test	American Creosote	Astra Pyrotechnics	Caerphilly	Columbus MGP	Halton	Pepper Steel	Quarry Dump	South 8th Street
PERM	●	●	●	●	●	●	●	●
UCS	●	●	●	●	●	●	●	●
TCLP		●						
DIN		●						
NRA					●			
SPLP	●			●		●	●	●
NEN			●					

PERM – permeability; UCS – unconfined compressive strength; TCLP – toxicity characteristic leaching test; DIN – German water leaching test; NRA – National Rivers Authority leaching test; SPLP – synthetic precipitation leaching test; NEN – Dutch tank leaching test

4.1. Physical testing

4.1.1. Background

Unconfined compressive strength (UCS) is a measure of the monolithic S/S soils' ability to resist mechanical stresses, which may be acting in the soils' environment of service (Perera and Al-Tabbaa, 2005a).

Another important property of the S/S soils is the permeability or hydraulic conductivity. This represents the rate at which water can flow through a material and is key transport property, since it influences the durability of treated wastes by preventing external agents from entering the S/S soils.

4.1.2. Method

The UCS of the S/S soils was carried out by an external laboratory in the USA, according to the ASTM D1633 method, whilst the permeability was measured according to ASTM D5084 method.

4.2. Chemical testing (leaching)

Leaching is a process through which a hazardous constituent from a waste-form is transferred into the environment via a solution called a leachate (Conner, 1990). Leaching tests are accelerated tests aimed at determining the rate of constituent leaching from the waste-form and this is expressed as the concentration of a constituent in the leachate. Leaching tests are used to (i) screen wastes, to classify them as hazardous and non hazardous in nature; (ii) mimic field leaching or (iii) determine the intrinsic properties of wastes (Garrabants and Kosson, 2005).

Leaching tests used for regulatory purposes are pass/fail. The results obtained from the test are compared with set limits, which must not be exceeded. Examples of this type of test include the Toxicity Characteristic Leaching Test (TCLP), German water leaching test (DIN 38414) and the National Rivers Authority test (NRA).

4.2.1. Toxicity Characteristic Leaching Procedure

4.2.1.1. Background

The Toxicity Characteristic Leaching Test (TCLP) (USEPA, 1980) was developed in the United States by the Environmental Protection Agency and is used for regulatory purposes. This test simulates the contaminant leaching in a municipal landfill, where industrial solid wastes and municipal wastes are co-disposed, and generating acidic liquors, representing the "worst case" management of unregulated waste. The TCLP was used for classifying wastes, but also for determining the effectiveness of treatment at remediated sites. The principle of the test involves the extraction of the contaminants from the waste using an acid leachant, to mimic the landfill conditions.

4.2.1.2. Method

The leaching test was carried out according to the USEPA 1311 method, although, due to the limited capacity available on the end-over-end rotator, a reduced amount of soil was used for leaching compared with the stated method. The liquid to solid ratio, the rotation speed and the contact time were kept unchanged. A summary of the TCLP method parameters is presented in Table 3.4.

A preliminary evaluation was carried out on a small portion of soil, to determine the appropriate extraction fluid, as required by the standard method. Following this evaluation, two different extraction fluids were used in the same test, due to the difference of alkalinity between the untreated and the S/S soils. The untreated soil had a slightly acidic pH, and the USEPA Fluid 1 was employed, whilst the S/S soil had an alkaline pH and USEPA Fluid 2 was chosen. The composition of the two extraction fluids is given in Table 3.4.

Table 3.4 – Characteristic parameters and conditions used for various leaching tests

Parameter	TCLP 1311	DIN 38414-S4	NRA	SPLP 1312
Grain size	< 10 mm	< 9.5 mm	< 5 mm	< 1 cm
L/S ratio	20:1	10:1	10:1	20:1
Leachant	Fluid 1 Sodium acetate pH = 4.93 ± 0.05 Fluid 2 Acetic acid pH = 2.88 ± 0.05	Deionised water	Deionised water	Fluid 1 H_2SO_4/HNO_3 pH = 4.2 ± 0.05 Fluid 2 H_2SO_4/HNO_3 pH = 5.0 ± 0.05 Fluid 3 water
Leachant renewal	0	0	0	0
Contact time	18 h	24 h	24 h	18 h
Rotation speed	30 rpm	N/A	N/A	30 rpm

10 g of soil was weighed and mixed with the appropriate leaching fluid in a PTFE bottle. Each soil sample and the procedural blanks were prepared in triplicate, and placed on an end-over-end rotator, for 18 h. At the end of the agitation period, the solid was separated from the solution by vacuum filtration, through Millipore AP 40 fibre glass filters and discarded. The solutions collected were acidified with concentrated 69 % v/v HNO_3 to a pH < 2, and analysed by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) (section 5.2).

The reagents used during the TCLP test were: a) glacial acetic acid; b) sodium hydroxide solid (99-100%); c) nitric acid (69% v/v); d) hydrochloric acid (37.5% v/v). The extraction fluids were prepared according to the standard TCLP method, from concentrated analytical grade reagents (a and b), supplied by VWR. All dilutions were done with high purity water obtained with PURELAB Option-R7/15 system (Vivendi Water Systems Ltd).

4.2.2. DIN 38414-S4 leaching test

4.2.2.1. Background

The DIN 38414-S4 test (DIN-NORMEN, 1984) is a regulatory batch leaching test, developed for compliance purposes in Germany, and widely used throughout Europe. The only contaminants mobilised during the DIN leaching test are those present in water soluble form. While this is a valuable testing procedure, it is unfortunately open to criticism as some waste types may contain water insoluble contaminant compounds. Thus additional extraction procedures, utilising more aggressive leachants e.g. TCLP are sometimes performed.

The DIN test was superseded for regulatory purposes by the EN 12457 leaching test, which came into effect in 2003. However, for the evaluation of waste-forms treated by S/S before this date, the DIN 38414-S4 may be used for comparison purposes.

4.2.2.2 Method

The water leaching test was performed using a non-cooled Gallenkamp shaker. 10 g of soil was weighed and mixed with high purity water. Triplicate samples were prepared, together with procedural blanks. The bottles were sealed and shaken. The parameters used are described in Table 3.4. Prior to filtration, the bottles were centrifuged for 5 minutes at 2500 rpm (non-cooled Sanyo bench centrifuge, model Mistral 3000E) and the solution filtered through cellulose nitrate membrane filters 0.45 μm from Whatman®. The solution obtained was acidified with concentrated HNO_3 to a $pH < 2$ and stored at 4°C prior to the analysis by ICP-OES (section 5.2).

All reagents used in the leaching test were of analytical grade. High purity water was obtained from PURELAB Option-R 7/15 system (Vivendi Water Systems Ltd). Analytical grade nitric acid (69% (v/v)) supplied by VWR was used for leachate acidification prior to storage.

4.2.3. National Rivers Authority (NRA)

4.2.3.1. Background

The NRA leaching test (Lewin *et al.*, 2004) is a standard single batch compliance test, which was developed for assessing the leachability of mainly inorganic compounds from contaminated soils, and simulates the behaviour of soils coming into contact with acid rain. The NRA test was superseded in 2003, by the European leaching test EN 12457.

4.2.3.2. Method

Leaching was carried out in triplicate on 10 g of soil homogenized by cone and quartering. Prior to leaching, the samples were ground to < 5 mm in size and mixed in PTFE bottles with deionised water at a liquid:solid ratio of 10:1. The bottles were left to stand on a shelf for 24 h and the solution filtered through cellulose nitrate membrane filters 0.45 μm from Whatman®. The resultant solution was acidified with 2% v/v HNO_3 and analysed for the elements of interest using an ICP-OES (section 5.2).

4.2.4. Synthetic Precipitation Leaching Test

4.2.4.1. Background

The Synthetic Precipitation Leaching Procedure (SPLP) (USEPA, 1994) is designed to evaluate the impact of contaminated soils on groundwater, when exposed to acid rain.

4.2.4.2. Method

The SPLP test was carried out by the Resource Laboratory, LLC in Portsmouth, USA. Leaching was performed on cone and quartered samples of granular material obtained from American Creosote, Pepper Steel, Quarry Dump, Columbus MGP and South 8th Street sites.

The extraction fluid consisted of a mixture of 60/40 H_2SO_4/HNO_3 (Fluid 1 or 2) or reagent water (Fluid 3), as stated in the standard method (USEPA, 1994). The samples were mixed with the Fluids 1-3 and rotated end-over-end for 18 h, at 30 rpm. At the end of the leaching test, the samples were filtered and analysed by ICP-OES.

4.2.5. NEN 7375 tank test

4.2.5.1. Background

The tank test is designed for quantifying the long-term diffusive leaching of contaminants from a monolithic S/S waste or soil (Environment Agency, 2005).

4.2.5.2.Method

This test was carried out by Severn Trent Laboratories Ltd, according to the EA NEN 7375:2004. The tank test consisted of 8 stages, carried out for 64 days, under no agitation, using unbuffered deionised water as leachant. The leachates obtained from each stage were analysed by GC/MS, in the same laboratory.

5. Performance testing

Although the compliance testing gives, in many cases, a useful indication of the S/S soil evolution with time, it cannot explain the changes observed. For this reason, performance testing consisting of a series of leaching, mineralogy and microstructure tests were carried out and are described in sections 5.1 – 5.4.

5.1. pH dependent leaching test and neutralisation capacity

5.1.1. Background

The metal contaminant immobilisation following treatment by S/S depends, to great extent, on the pH of the system (Conner, 1990). pH dependence leaching test provides information on the acid neutralization capacity of the S/S soils and identifies the sensitivity of metal leaching to pH changes as a result of external stresses e.g. soil acidification (Cappuyns and Swennen, 2008). By combining a pH dependent leaching test with a geochemical model such as MINTEQA2, the solubility limiting phases during metal leaching can also be identified, leading to a better understanding of the phenomena governing metal immobilization in S/S soils.

5.1.2. Method

The pH dependent leaching test was carried out according to the prCEN/TS 15364 (2005) standard procedure. The test consisted of two stages: 1) the pre-treatment of the soil with solutions of nitric acid and sodium hydroxide and 2) the pH dependent leaching test. The first stage is required to determine the amount of acid to be added to the sample to increase or decrease the leachate pH to 4.

Since the buffering capacity of each sample varied, the amount and the concentration of the acid/alkali additions required a sample by sample assessment. This was done by adding increasing amounts of nitric acid/sodium hydroxide to the S/S soil and measuring the pH, after each addition. The experiment continued until the pH reached the value of 4 and 13, respectively. The typical acid concentration used was 0.5 M and that of the alkali was 0.1 M; however deviations from these values were required for a small number of samples.

Bottles containing 10 g of S/S soil were prepared and the solution of acid/alkali of known concentration, determined in the first step, was added to a liquid to solid ratio L/S = 10 (l/kg). The bottles were placed on an end-over-end rotator for 48 h, and the pH was measured at 4, 44 and 48 h after the start of the experiment. The solutions were filtered after 48 h and analysed by ICP-OES (section 5.2).

5.2. Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES)

5.2.1. Background

ICP-OES is used for performing quantitative and qualitative analysis of major, minor and trace elements in solution. The sample to be analysed is introduced into hot argon gas (plasma), where all chemical bonds are dissociated and the atoms and ions excited. Following excitation in the plasma, the atoms and ions emit characteristic light as discrete lines, which are separated according to their wavelengths by an optical system and used for identification and quantification of individual elements (Nolte, 2001). The working range of an ICP extends over six orders of magnitude, from μg/l to g/l.

This technique was used in this work to analyse the concentration of heavy metals in leachates or digestates of S/S soils.

5.2.2. Method

A PerkinElmer Optima 4300DV simultaneous ICP was used to determine the concentration of a number of metal contaminants in solution, for the UK sites.

5.2.2.1 Instrument performance

The instrument performance was verified at the beginning of the analysis using a certified solution (BDH Spectrosol). The elements analysed were As, Ca, Co, Cu, K, P, Pb, Se, Tl at concentrations of 10 mg/l and Ba, Cd, Mg, Mn, Zn with concentrations of 1 mg/l. Relative standard deviations within the range 0.5 – 3% were considered acceptable and therefore the performance of the instrument good (Nölte, 2003).

5.2.2.2. Instrument calibration

The calibration blank and standards were prepared in 2% v/v HNO_3. The calibration standard was prepared from a combination of single element stock solutions (SpectrosoL®, BDH Laboratory Suppliers). A five point calibration curve, including a calibration blank was constructed for each analyte.

5.2.2.3 Detection limits

The limit of quantitation (LOQ) for each analyte was determined using reagent blank solution acidified with 2% v/v HNO_3. The reagent blank was analysed ten consecutive times, performing a routine rinsing procedure between each analysis. At the end of the analysis, the standard deviation for each analyte was displayed by the instrument, which was used to calculate the LOQ via the following equation (3.1).

$$\mathrm{LOQ} = s \cdot \sigma \qquad (3.1)$$

where s is the standard deviation of the concentrations of each element

σ is the degree of confidence and is equal to 10, for quantitative analysis

A summary of the detection limits for the quantitative analysis of the analytes of interest is presented in Table 3.5.

Table 3.5 – ICP-OES limit of quantitation

Element	LOQ (mg/l)
Pb (220.353)	0.080
Cr (267.716)	0.020
Cu (324.752)	0.010
Zn (213.857)	0.010

5.2.2.4 Quality control

To check for accuracy and precision of measurements, a quality control programme was established containing: i) initial calibration verification (ICV) and ii) continuing calibration verification (CCV) solutions. The ICV was prepared from single element solutions in 2% v/v HNO_3 (see section 5.2.2), and was run after the initial calibration and at the end of the analysis to verify the validity of the calibration standards.

One of the calibration standards was used as CCV, which was run every 10 samples. This ensured that the calibration remain valid throughout the analysis.

5.3. X-ray, optical and microscopic methods of analysis

Optical and X-ray methods were used to examine the microstructure of aged S/S soils and to identify the mineral phases developed over time in the S/S soils. Certain mineral phases have been shown to play an important role in the durability of these materials and their identification gives a valuable insight into the material performance over time, due to intrinsic and extrinsic loads.

5.3.1. Scanning electron microscopy (SEM)

5.3.1.2. Background

Scanning electron microscopy (SEM) is a powerful imaging and microanalysis method used extensively for investigating cementitious materials and soils (Ouki and Hills, 2002; Stutzman, 2004; Scrivener, 2004). The electron microscope has a depth of field 100 times higher than an optical microscope and can be used to a magnification between x50 and x50,000. Two modes of operation are available on an SEM: imaging with two kinds of signals (secondary and backscattered electrons) and composition with characteristic X-rays. Electron micrographs are greyscale images and the contrast of an individual phase is determined by its average atomic number. This allows the observation of the spatial distribution of the phases, very important for studies of the durability of cementitious materials. On the other hand, the X-ray analysis capability provides quantitative information on features observed in the electron micrographs by determining the elemental composition. For the purposes of the analysis, these features can be used alone or in combination.

5.3.2.2. Sample preparation (resin blocks)

The specimens were prepared from intact cores recovered from the S/S soils. The SEM sample preparation was based on that for concrete (Crumbie, 2001; Kjellsen *et al.*, 2003). Due to the poorly indurated nature of the soils, this method was modified to suit the current samples. A summary of the steps followed during the preparation is indicated below.

Fragments freshly cut from the cores, with dimensions of approximately 30 x 30 mm, were cast into epoxy resin (Epoxy 301 by Struers). The resin blocks were ground by hand to expose the surfaces to be analysed, using successive SiC paper with decreasing grit sizes (30, 15 and 10 μm). Absolute ethanol supplied by VWR was used to clean the resin blocks between stages. The use of non water based cleaning fluid was chosen to prevent the hydration of cement phases and preserve the appearance of the soils at the time of sampling.

The resin blocks were polished on an Engis polishing machine, with progressively decreasing grit size diamond pastes (3, 1 and 0.25 μm), supplied by Struers. Between each stage, the resin blocks were sonicated in absolute ethanol to remove the polishing agent. Prior to the SEM analysis a thin layer of carbon was applied to the highly polished blocks to provide a conductive pathway for electrons. An Edwards carbon coater was used, under vacuum conditions of approximately $10^{-4} - 10^{-5}$ torr.

The resin blocks were analysed with a Jeol JSM-5310LV electronic microscope (JEOL Inc., Japan) with LaB_6 filament at an accelerating voltage of 20kV. The SEM was equipped with an Energy Dispersive Spectrometer (EDS).

5.3.2. Transmitted Light Microscopy

5.3.2.1. Background

Optical microscopy can be used for micron level investigations. Polarising light microscopy, utilising reflected and transmitted light was used in the present work. Transmitted light microscopy is suitable for identification of transparent minerals and has been used for identification of rock forming minerals, but also extended to artificial mineral materials i.e. cements or concretes. Applications of this technique for the study of concrete include identification of potentially deleterious compounds, porosity, microcracking and reactive aggregates.

The theoretical limit of observation for optical microscopes is 1 μm; however the practical limit is somewhere between 5 - 10 μm (St. John *et al.*, 1998). The analysis under a transmitted light microscope requires preparation of thin slices of the sample and mounting them on a glass slide. In the identification of a certain mineral, the thickness plays an important role. The thickness of thin sections is typically 30 μm and most optical data for natural minerals are based on this. Nevertheless, in the study of concrete, 20-25 μm thick samples are optimal for the examination of microstructure.

The interpretation of the information obtained from a transmitted light microscope is based on the optical properties of minerals e.g. pleochroism, colour, relief, birefringence, twinning, but also the shape and size of the feature of interest. The examination of a sample can be done in two 'modes' each one revealing certain optical properties of the mineral:

- plane polarized light (shape, cleavage, relief, colour);
- and cross-polarised light (interference, extinction, twinning, birefringence)

5.3.2.2 Sample preparation (thin sections)

Replicate thin sections were prepared from the extracted cores, in a specialised laboratory in Denmark, according to the procedure described in Jakobsen *et al.* (2000) and stored under a stream of nitrogen (5 ml/min) to prevent surface carbonation. The thin sections were analysed by Transmitted Light Microscopy and SEM/EDS. The optical microscope used was a Nikon transmitted light microscope, Model Optiphot-Pol, Nikon Equipments Inc. equipped with digital camera (Kontron Progres 3012, manufactured by Kontron Electronik GmbH, Munich, Germany).

5.3.3. X-ray Diffractometry (XRD)

5.3.3.1 Background

X-ray diffraction is an analytical method capable of providing qualitative and quantitative data of crystalline compounds in a solid sample (Skoog and Leary, 1992).

This method was employed to characterise the S/S treated soils containing clay minerals from the soil, hydration products formed with the S/S treatment or alteration products resulting from the exposure to the environment.

5.3.3.2 Method

5.3.3.2.1 Bulk x-ray diffraction

A Siemens D500 diffractometer was used to perform X-ray diffraction analyses. The source of radiation used was CuKα with the tube running 40 kV and 30 mA. The powders were scanned from 5° to 65° 2θ, step size 0.02° and step time 1.2s. The interpretation of the X-ray diffractogram was carried out using DIFFRAC^{plus} EVA software by Bruker AXS.

Qualitative XRD was carried out on the S/S soils recovered from the pilot and full-scale applications. Oven-dried samples were crushed to < 1 μm and pressed powder mounts were prepared. The phases at low diffraction angles were difficult to identify in pressed powder form, therefore an additional preparation was necessary and this is described below.

5.3.3.2.2 Clay separation

A 5 g measure of soil was mixed well in a 250 ml PFTE bottle with 100 ml of high purity water, dispersed in an ultrasonic bath for 5-10 minutes and left to further disaggregate overnight. The suspension obtained was transferred into a centrifuge tube and spun in a non-cooled Sanyo bench centrifuge model Mistral 3000E, at two different speeds. The first centrifugation step (750 rpm) was applied to separate the silty from the clay-sized fraction.

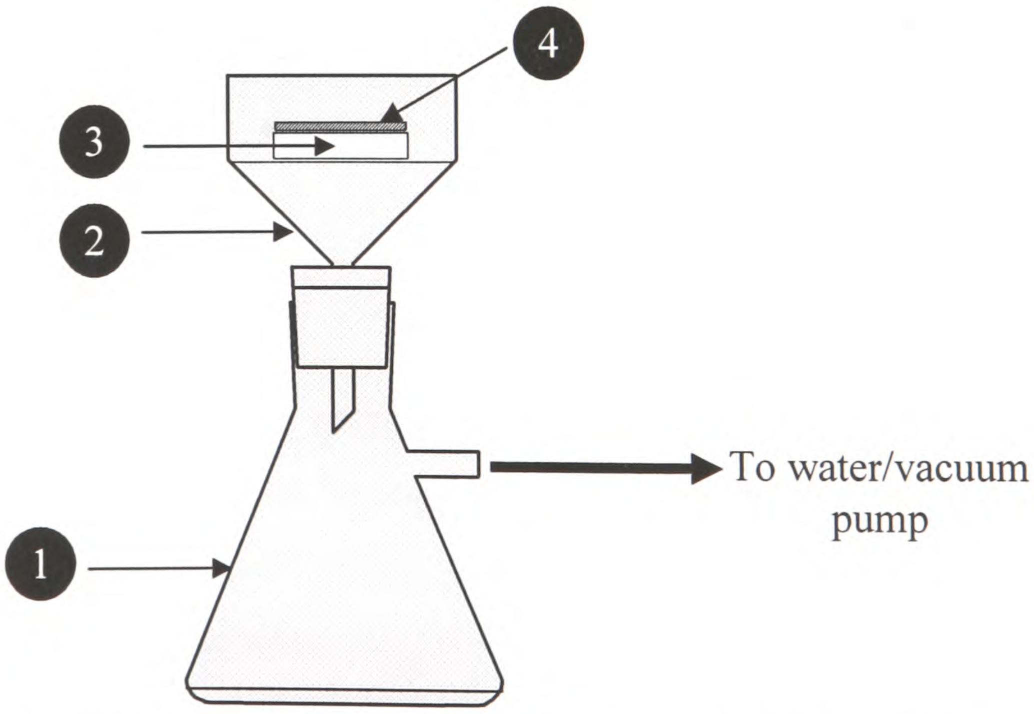


Figure 3.2 – Preparation of oriented mounts for clay mineral identification (1) filter flask; (2) Büchner funnel; (3) ceramic tile; (4) deposited clay layer

Due to the low rotation speed, the silty fraction deposited, whilst the clays remained suspended in solution. The solution was decanted into another centrifuge tube and spun at 2000 rpm. The sediment was retained and the liquid discarded, less one or two drops to facilitate the solid transfer onto a ceramic tile. Before mounting the clay suspension the ceramic tiles were heated on a hot plate set at 90°C. The hot clay tile was placed inside a filtration device illustrated in Figure 3.2. Using a Pasteur pipette, the clay suspension was deposited as a thin layer on the ceramic tile, under vacuum. The tiles were left to dry overnight at room temperature in a desiccator.

To differentiate between members of a clay mineral group, a series of chemical and thermal treatments were necessary. The chemical treatment using glycerol causes the clay minerals to expand and give characteristic diffraction patterns that can be more easily associated with a specific clay mineral. If a thermal treatment, which causes the collapse of certain peaks at higher temperature, is applied, the mineral identification can be completed (Moore and Reynolds, 1997). Consequently, XRD analyses were performed on the ceramic tiles as follows:

a) untreated;
b) glycerol treated;
c) heated at 550°C.

The analysis of the clay was performed using the same instrument as the bulk XRD (see section 6.3.2.1). The scanned angles were 2-30 degrees 2θ, step size 0.02° and step time 2.4 s.

5.4. Thermal analysis (TA)

5.4.1. Background

Thermal analysis measures a physical property of a compound as a function of temperature, when subjected to controlled heating or cooling. According to the property measured, the thermogravimetric methods can be classified as: thermogravimetry or TG (weight loss), differential thermal analysis or DTA (energy changes) and differential scanning calorimetry or DSC (heat evolution) (Dodd and Tonge, 1987).

For over two decades, thermal analysis has been used in the cement industry as an important analytical tool, capable of providing information on the mineralogy and minor changes in chemical composition of raw materials. Other applications include qualitative, but also quantitative determination of cement hydration or degradation products etc (Bhatty and Miller, 2004).

5.4.2. Method

5.4.2.1. Sample preparation

The soils from each site were freeze-dried (at 10^{-3} mbar) to eliminate the unbound water and then ground to a fine powder using a ball mill (Fritsch Pulverisette, Germany). To avoid cross contamination, a small amount of sample was ground and discarded, before the collection of the sample used for the TG analysis. The time of grinding was kept constant (3 minutes).

5.4.2.2 Method

The thermal analysis was carried out in the laboratories of the Environmental Research Group at the University of New Hampshire, USA. The soil samples were analysed using a simultaneous DSC/TGA, model SDT Q600 V8.0 Build 95 (TA Equipments, USA) between 30-1000°C at 20°C/min, in nitrogen atmosphere (100 ml/min). The TGA was performed on 10 – 15 mg of finely ground sample (~1 μm), packed into alumina crucible by tapping ten times. The qualitative interpretation of results was performed using the published literature.

6. Conclusions

This chapter introduced the methods used to characterise the S/S soils and test their performance over time. The methods employed for sample preparation prior to examination and testing by various analytical techniques are also described.

The following chapter provides a detailed description of the S/S sites, through the construction of conceptual models for each site. The specific loads to which the S/S soils are exposed to in their service environment are presented in the conceptual models and are examined, to gain insights into the potential factors affecting the S/S soil durability.

Chapter 4 Site descriptions and sampling methods

1. Introduction

In the previous chapter, the materials and methods used in this work were presented. Physical and chemical tests were chosen to carry out the basic characterisation of the S/S soils, the compliance testing and the performance evaluation of the S/S soils.

Chapter 4 introduces the eight S/S sites studied in the current work. The site remediation strategies are described, along with the methods of obtaining the samples for study. The history of each site is traced in the literature to provide an understanding of the source and extent of contamination, and the environmental loads to which the soils are exposed to. These loads are used to create conceptual models for the prediction of likely impacts on the S/S soils.

2. Sites

A number of sites in the UK and the USA were studied and the full description of each of them is given in the following sections (2.1 to 2.8).

2.1. Astra Pyrotechnics, UK (AP)

2.1.1 Site description

The Astra Pyrotechnics site is located in Dartford, UK, and covers an area of approximately 8.5 hectares. The site is located close to the confluence of the Rivers Darent and Thames on reclaimed salt marsh. This site had become contaminated with a range of heavy metals from the manufacture of low-grade military explosives and fireworks over a period of 100 years (Blue Circle, 2000).

The main contaminants identified were copper, zinc, lead and chromium, which were concentrated in several hotspots. One of the most contaminated areas, covering 20m x 10m to a depth of 0.6 m, contained 96,000 mg/kg of copper, 81,000 mg/kg of zinc, 750 mg/kg of lead and 71 mg/kg of chromium. This area was treated with cement as part of a remediation demonstration in 2000 (Blue Circle, 2001). Two technologies were applied: stabilisation/solidification and accelerated carbonation.

Figure 4.1 – Remediation at Astra Pyrotechnics site (a) excavation of soil, (b) site preparation, lining and drainage construction; (c) soil screening; (d) treated soil backfilling from Blue Circle (2000)

The soils were excavated to 0.45 m, above the water table situated at 0.9 m, stockpiled adjacent to the site of excavation, screened and shredded. Four engineered cells were constructed in the excavation and completely lined with impermeable high density polyethylene (HDPE) (see Figure 4.1a-d). For each cell an integral drainage system and an inspection chamber were installed to enable controlled sampling of leachate and the evaluation of metals release with time (Blue Circle, 2000).

The soil was quartered and separately mixed with different binders in a modified cement mixer, as shown in Figure 4.2. One cell was left untreated (1), whilst the rest were treated with 20% Portland cement (2), 20% EnvirOceM cement (3, 4). The soil from cell 4 was deliberately carbonated prior to infilling the engineered cell. All cells were backfilled and left un-compacted and uncovered, to promote weathering.

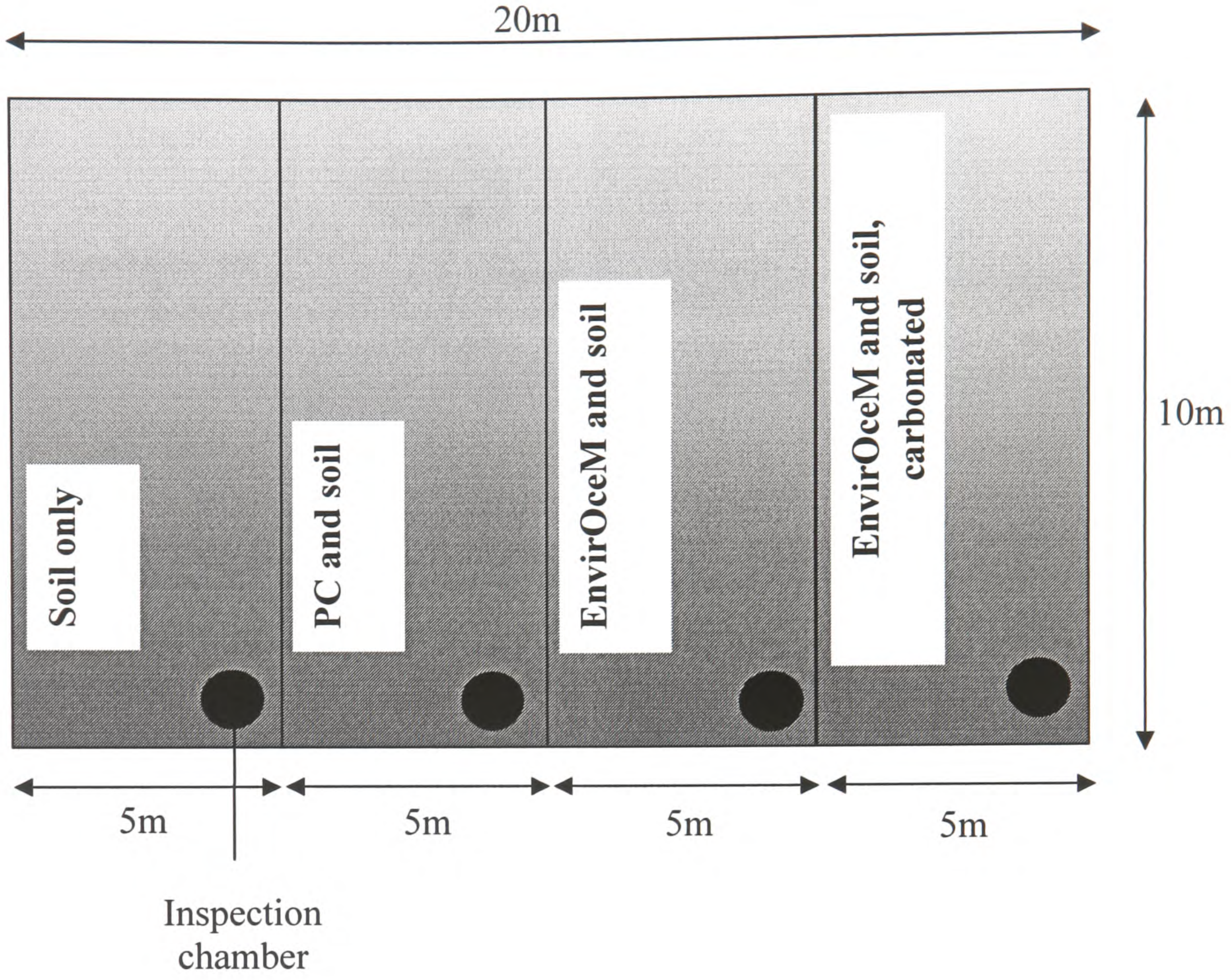


Figure 4.2 – Diagram of the treated soil layout at Astra Pyrotechnics site, UK

The leaching of metals from the soil was established at the time of remediation as the performance criterion. The high water table meant that the main risk was its contamination by downward leaching of metals. Therefore, the leaching required compliance with the UK Drinking Water Inspectorate limits (DWI, 2000). A summary of the limits is given in Table 4.1.

Table 4.1 – Drinking Water Quality limits for selected elements

Element	Limit (mg/l)
Copper	5
Zinc	5
Lead	0.05
Chromium	0.1

2.1.2. Conceptual model

The knowledge of the conditions on site has a key importance in understanding the S/S soil behaviour with time. For this reason a conceptual model of the site is presented in Figure 4.3.

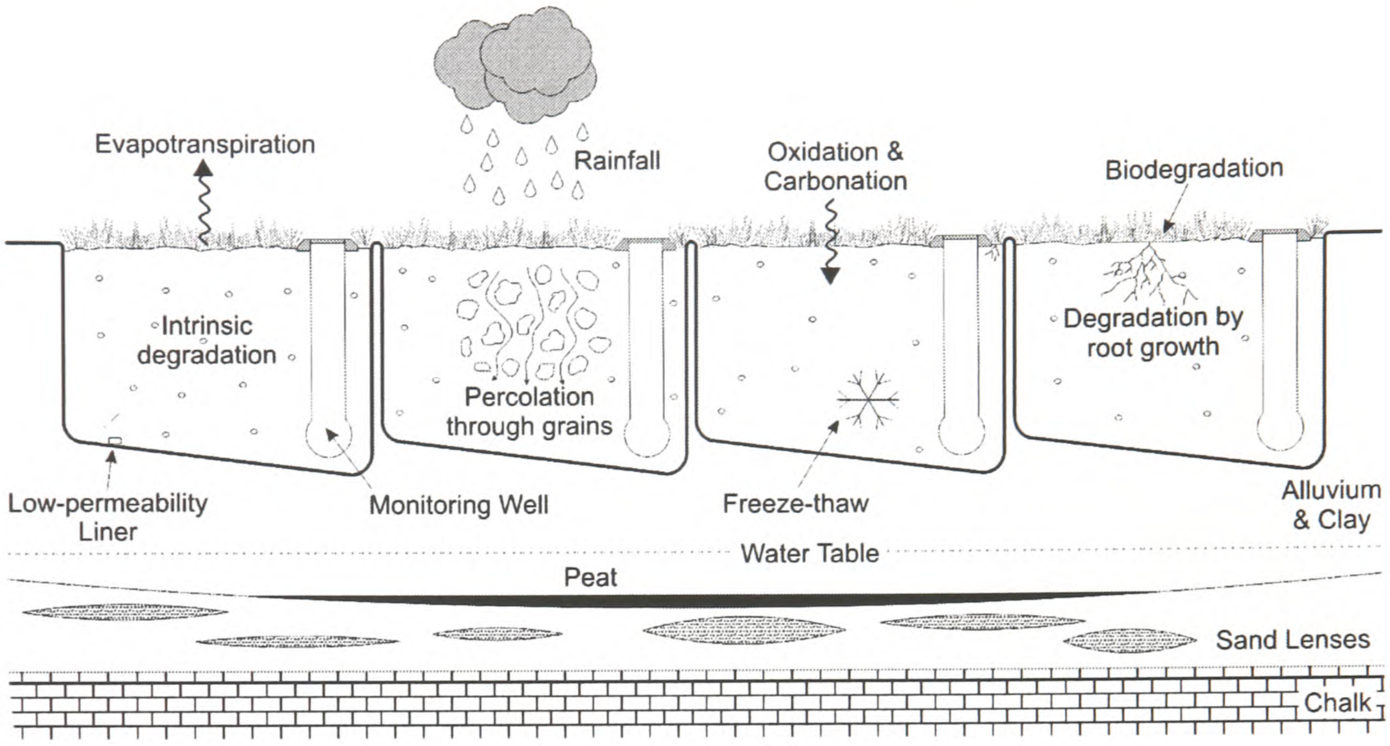


Figure 4.3 – Conceptual model for the Astra Pyrotechnics site, UK

The soils at Astra Pyrotechnics were shallow, uncompacted and open to the atmosphere. Therefore it was subjected to numerous processes such as carbonation, oxidation, erosion, water percolation, freeze/thaw and biodegradation, summarised and discussed in Table 4.10.

2.1.3 Sampling

The sampling of cement-treated soils was carried out by the Royal Engineers, under the supervision of University of Greenwich, four years following remediation. Samples were excavated from pits measuring 0.5 m x 1 m to the full depth of 0.6 m, in approximately 10 cm increments. Intact cores were difficult to obtain due to the granular nature of the soil. However, a number of cores were extracted from the first 20 cm of each treated soil. Due to the shallowness of the treated material and the risk of piercing the bottom cell liner, a hand driven core cutter was used. No cores were obtained from the untreated soil, which had insufficient strength for them to be removed intact.

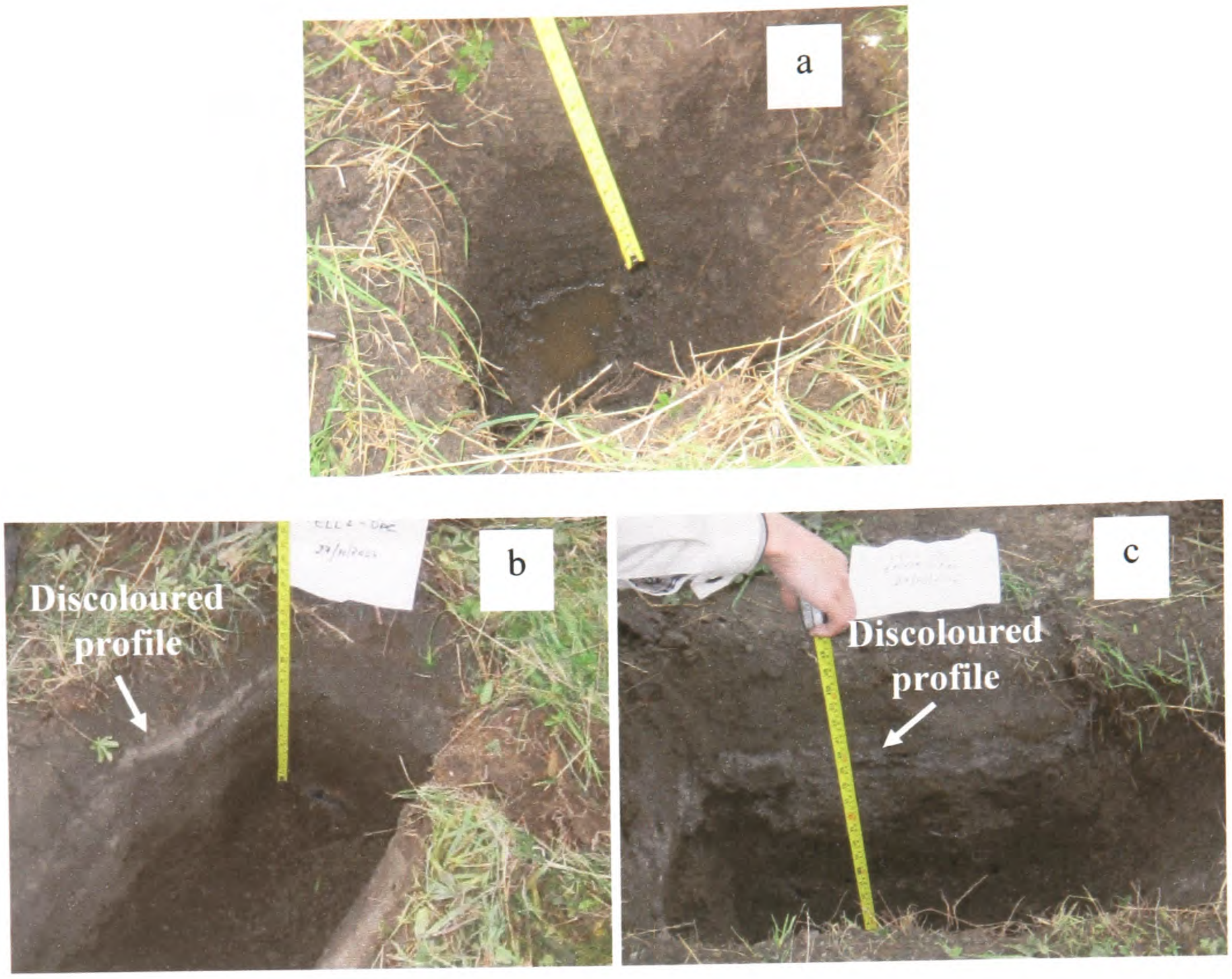


Figure 4.4 – Sampling excavation area at the Astra Pyrotechnics site, UK showing water ponding on the bottom layer in the untreated soil (a) and 'weathering' profiles in the Portland Cement soil (b); EnvirOceM soil (c)

2.2. Pepper Steel

2.2.1. Site description

Pepper Steel is a Superfund site located in Medley, Florida, approximately 15 km northwest of Miami (USEPA, 1986). The site occupies approximately 12 hectares. Numerous industrial activities have taken place on site since the mid-1960s, including battery manufacture, fibreglass boat manufacture, metal scraping and construction of precast concrete. The legacy of the intense industrial activity is soil and water contamination with metals and metalloids (lead, arsenic, cadmium, zinc, mercury, chromium, copper and antimony) and polychlorinated byphenyls (PCBs). Of these contaminants, lead, arsenic and PCBs were identified in concentration which could pose a risk for human health and the environment. The risk was through their migration into the groundwater and the underlying Biscayne Aquifer and the nearby Miami Canal. The Biscayne Aquifer provides drinking water for over 3 million people living in Southwest Florida (USEPA, 2007).

Figure 4.5 – Pepper Steel, USA (a) aerial photograph of the site after remediation; (b) the contamination at the site before remediation and (c) photograph showing the surface of the treated monolith few years after remediation (photographs courtesy of Ed Bates)

In 1987, soil remediation was initiated to prevent contamination of the Biscayne Aquifer. The operation started by the removal of all surface debris present from previous construction activities, followed by ex situ S/S treatment of the soil, to a maximum depth of 3.6 m. During this process, the contaminated soils were excavated and stockpiled outside the site. Fractions were screened to separate the material not suitable for processing (e.g. steel, concrete) and soil highly contaminated with organics, which were transported to landfill. The concentration of contaminants left in the soils was equal to or higher than 1 mg/kg of PCBs, 1000 mg/kg of lead and 5 mg/kg of arsenic (USEPA, 1986). This was mixed with the binder (20% by weight fly ash/cement mix) and backfilled in the excavation without compaction. The S/S soil was capped with a 30 cm layer of crushed limestone, to match the underlying geology on the site and to restrict the infiltration of water into the S/S soil. An image of the finished monolith is shown in Figure 4.5.

Table 4.2 – Pepper Steel remediation targets (from Gardner, 2005)

Property	Target value
UCS (MPa)	>0.1
Permeability (m/s)	$<10^{-6}$
Leaching (µg/l)*	
Lead	15
Arsenic	10

* 2007 performance values in groundwater

A number of physical performance criteria were established for the S/S soils and the values are indicated in Table 4.2. There were no enforceable limits for chemical performance, but guideline values to compare the metal leaching from the S/S soils. The guideline values for lead and arsenic at the time of remediation, in 1987, were equal to the drinking water quality limits of 50 µg/l (USEPA, 1994). However, in 2007 these limits were lowered to 15 µg/l for lead, and 10 µg/l for arsenic (USEPA, 2007).

As reported by the USEPA, Pepper Steel was vacant after remediation, and became overgrown with vegetation, and subject to extensive dumping of debris until 2005 (USEPA, 2007). Since then, a trucking company, as well as a facility that provides storage for land-sea containers and a pre-cast concrete facility have been operational at the site.

2.2.2. Conceptual model

Figure 4.6 indicates the factors likely to impact upon the durability of the Pepper Steel S/S soil, which are described in more detail in Table 4.10. Notably, the blockage of drainage ditches by organic material, and silt resulting from the erosion of the limestone cover was reported during the five-year review of site performance (USEPA, 2002). The engineering of the S/S soil increased the inclination of the surface, therefore during episodes of heavy rain significant runoff was generated eroding loose particles from the limestone cover. In addition, the growth of the pine tree root systems, had loosened the limestone cover and had also resulted in a heavy surface mat of needles, which likely slowed surface runoff velocities. The result was more infiltration through the limestone cover to the monolith followed by horizontal transport along its surface to the drainage collar (USEPA, 2002). These events are likely to cause exposure of the S/S monolith to rainwater and carbonation.

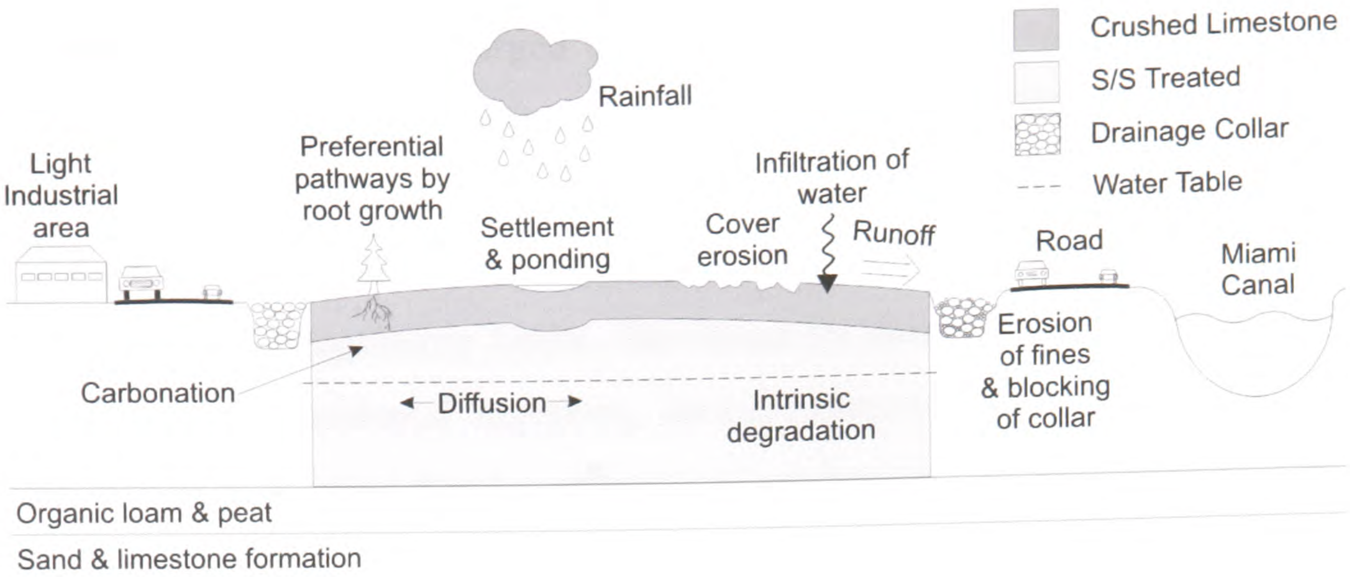


Figure 4.6 – Conceptual model for the Pepper Steel site, USA

2.2.3. Sampling

Sampling at Pepper Steel was carried out by the USEPA, using a random sampling pattern. Cores were extracted with a truck auger fitted with a core barrel and using water as lubricant. Intact cores could not be obtained for the full depth of soil, but cores between 5 to 25 cm long were recovered.

The cores were well indurated, containing numerous white inclusions (Figure 4.7). Macropores of up to half a centimetre were frequently observed at the surface of the extracted core. There were no visible cracks at the surface of the core, but they were observed in cross section, after impregnation with fluorescent dye. Fine intersecting cracks, skirting the edge of an aggregate and joining a porous area in the matrix were noted.

Figure 4.7 – Fragment of core recovered from Pepper Steel, USA

2.3. American Creosote (AC)

2.3.1. Site description

The American Creosote site is a Superfund site. The 24 hectare former wood preservation site is located in Jackson, Tennessee, USA (USEPA, 2004a). For over forty years, until

1973, the plant routinely discharged untreated process water, which polluted the Forked Deer River, located at the southern boundary of the site. Contamination with creosote and pentachlorophenol (PCP) was found in the soil, surface water, sludge and shallow subsurface water. In addition, metals and metalloids like lead and arsenic have been identified above the regulatory limits. The threat for human health was thought to occur through accidental incidental ingestion, dermal contact with contaminated soil, and/or inhalation of contaminated dust by unprotected workers at the site. However, the transport of contaminants via groundwater was also of concern (USEPA, 2004a).

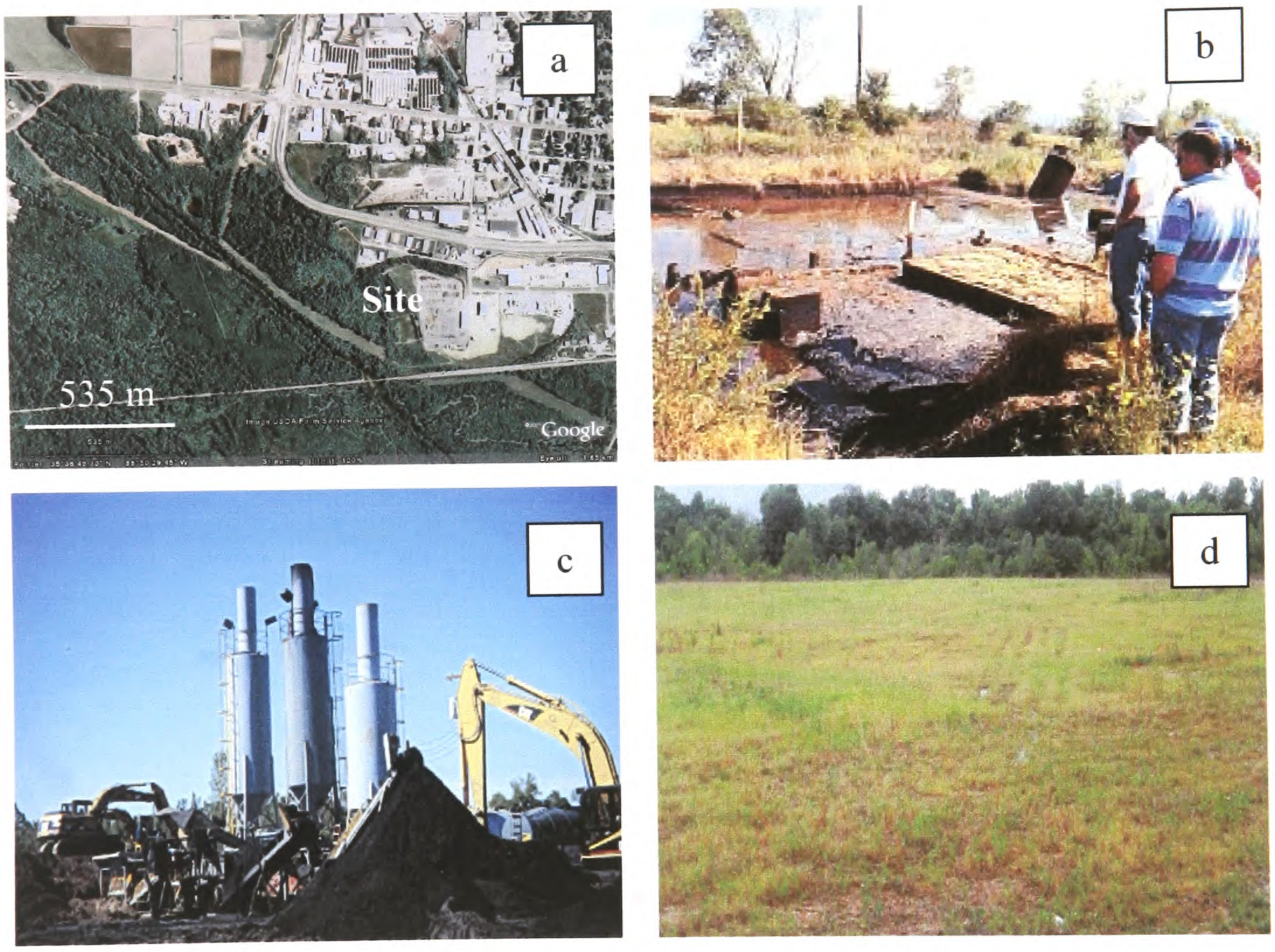


Figure 4.8 – American Creosote site, USA; aerial photograph of the site (a) (*Source: Google Earth*^{TM} *mapping service; created 26 April 2009);* site before remediation (b); ex-situ pugmill treatment of the soils (c) and site after remediation (d) (courtesy of Ed Bates)

In the United States, the 'polluter pays' policy is applicable. In the case of the American Creosote site, the soil contamination problem was not identified before the site operator went into liquidation in the 1980s. Consequently, the USEPA conducted the site assessment and its subsequent remedial operation, which took place in 1999, after the removal of the excess water and creosote from the site. The remaining contaminated soil was treated by ex situ S/S to a depth of 1.5m, using a formulation of 5 % Portland cement, 4.5 % fly ash and 1.3 % powdered activated carbon (percentage by weight of untreated soil) (Bates *et al.*, 2002). The treated soils were compacted and covered with a geosynthetic clay liner (GCL), capped with 0.6 m of clean fill and 0.12 m of topsoil (Bates *et al.*, 2002). The last stage of the remedial operation was seeding with grass, to improve the water drainage, and the installation of protective fencing to restrict the access to the site. The potential risk associated with the contamination on site limited its reuse to light industrial activities (USEPA, 2004a).

At the time of remediation, goals for contaminant leaching from the monolith were established with the view of reuse in industrial activities (Table 4.3). These values were calculated to achieve the cancer risk protection level for future workers on site.

Table 4.3 – American Creosote remediation targets (from Gardner, 2005)

Property	Target value
UCS (MPa)	>0.7
Permeability (m/s)	$10^{-8} - 10^{-7}$
Leaching (μg/l)	
Arsenic	< 50
PAH	<10
Dioxins	$< 30 \times 10^{-3}$
PCP	< 200

The site was purchased by a local company, Jackson Energy Authority and is currently used for equipment storage (USEPA, 2004a).

2.3.2. Conceptual model

The American Creosote site was treated by S/S, and following completion, placed under capping. This is a succession of impermeable geosynthetic clay liner (GCL), subsoil, topsoil and vegetation (Figure 4.9).

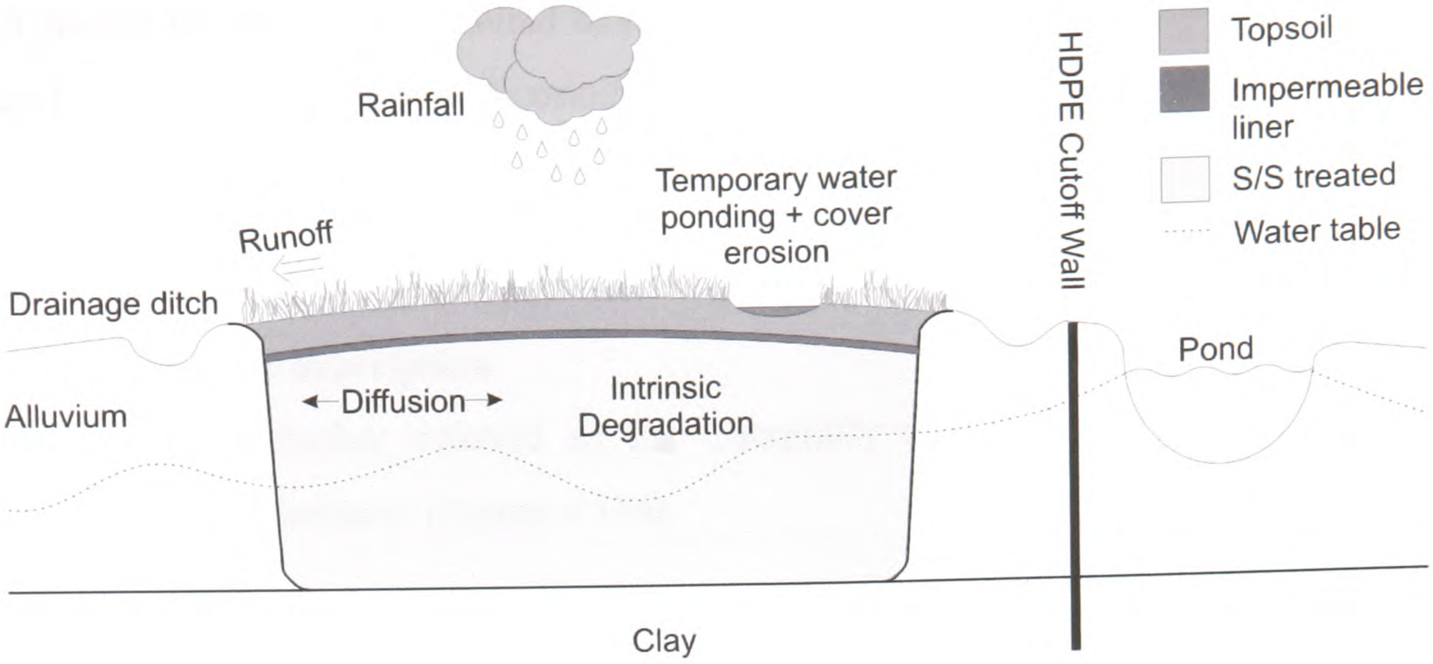


Figure 4.9 – Conceptual model for the American Creosote site, USA

The bottom of the monolith was also impermeable due to the presence of a natural clay layer. As a consequence, only limited mass transport is expected to take place. Issues were reported over time and these included settling of the cap and vegetation growth on capping (USEPA, 2004a). Moreover, several flooding events were recorded in the first five years of service and due to poor flood protection, as reported in the five year report, non-aqueous phase liquid was found in a number of monitoring wells, which required pumping and off-site disposal (USEPA, 2004a).

2.3.3. Sampling

The American Creosote site was sampled three years after the remedial operation, using a random sampling strategy. A diamond core barrel was used and dry and wet drilling methods were applied. The cores extracted were well indurated and did not contain visible cracks. An example a core recovered is shown in Figure 4.10.

Figure 4.10 – Fragment of core extracted from the American Creosote, USA

It should be noted that a limited amount of intact material was obtained even using water and slow coring. The failed coring generated granular material, which was retained for chemical tests.

2.4. Caerphilly, Wales (CA)

2.4.1. Site description

Castle Mews, further referred as the Caerphilly site, is located in South Wales and comprises 0.27 hectares (Figure 4.11a).

Figure 4.11 – The site in Caerphilly, Wales - aerial photograph of the site (a) (*Source: Google Earth*^{TM} *mapping service; created 17 April 2007)*; tarry soils at before remediation (b) and in situ treatment of soils (c) (courtesy of Celtic Technologies Ltd); finished site (d); recent site re-development as residential area (e, f)

This contained a variety of metals such as arsenic, cadmium, lead, mercury and organics (polyaromatic hydrocarbons-PAH and petroleum hydrocarbons-TPH), resulting from unregulated waste disposal (Figure 4.11b). Generally, the levels of metal contamination were below the acceptable limits (ICRCL 59/83), while the organics exceeded the thresholds.

The site was remediated by in situ cement stabilisation/solidification in 2006, to a depth of 1.5 m (Figure 4.11c). EvoCem, a proprietary mix formulation developed by Celtic Technologies Ltd, was used at 12% by weight of soil. The S/S soil was covered by 0.5 m of made ground; the finished site is presented in Figure 4.11d. Since the treatment by S/S, the site was reused for construction of residential homes (Figure 4.11 e,f).

2.4.2. Conceptual model

The Caerphilly site was covered with permeable material. Therefore, it is likely that the S/S soil will be subjected to a number of environmental loads, as described in Figure 4.12. These include rain infiltration, carbonation and oxidation. The effect of these environmental loads on the long-term performance of the S/S soil is discussed in more detail in Table 4.10. Since 2008, the site has been largely covered by building slabs, tarmac access road and car park, for a newly built area with low rise apartments. Therefore, only minimal exposure of the soil to the environment is expected to occur.

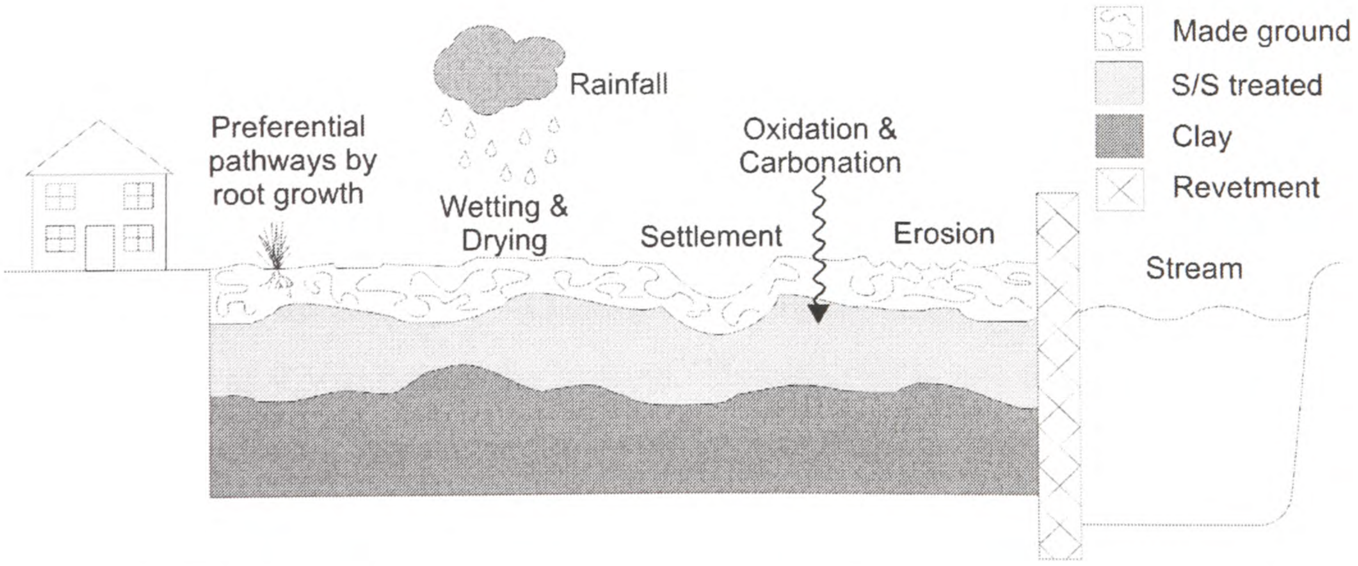


Figure 4.12 – Conceptual model for the Caerphilly site, Wales, in the first two years after remediation

2.4.3. Sampling

The Caerphilly site was sampled by the remediation contractors, 6 months after treatment, using a random sampling technique. A truck auger was used to retrieve two consecutive 1.5 m cores, from the surface of the soil to the full depth of the treated soil. During sampling it became obvious that the Caerphilly soils were granular rather than monolithic in nature. The sampling of intact cores by both wet and dry coring was difficult, and finally only wet coring was employed. All cores extracted had visible cracks at various points along their length, and were poorly indurated (Figure 4.13). Therefore, it is likely that the cracking observed was most likely caused by friction during sampling and not by in situ degradation.

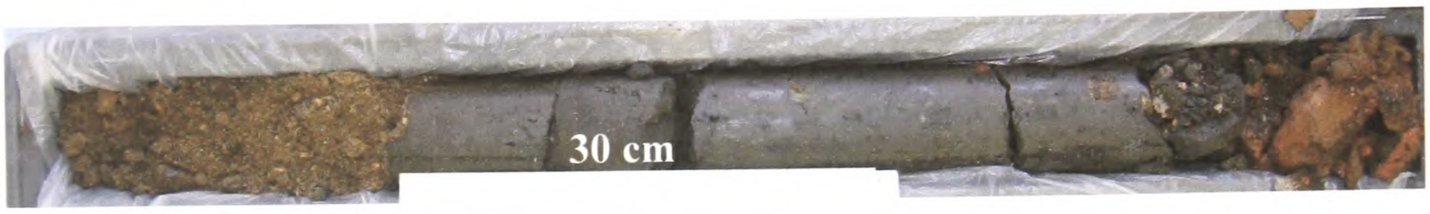


Figure 4.13 - Core recovered from Caerphilly, Wales

2.5. South 8th Street, USA (S8)

2.5.1. Site description

The South 8th Street is a Superfund Site situated on the flood plain of the Mississippi River in West Memphis, Arkansas (USEPA, 2004b). Previously a quarry, South 8th Street was used as a disposal site for industrial and municipal waste. An area of approximately 6.5 hectares was specifically reserved for the disposal of the oily sludge from an oil refinery, between 1960 and 1970. The contamination caused by the sludge was mostly with petroleum hydrocarbons and sulfuric acid, but high concentrations of lead were also identified. Lead was the contaminant of concern at 22,000 mg/kg, which could be released at the low pH on site (pH <1), into the groundwater. The groundwater table is located between 1.5 to 9.1 m below the ground. This aquifer is not supplying drinking water, but is used for regulating the water levels in adjacent lakes. Therefore the South 8th Street was not considered to represent a high threat. Nevertheless, risk to human health was possible through accidental contact exposure to the highly corrosive sludge or inhalation of toxic gases (sulfur dioxide and hydrogen sulfide) given off by the sludge.

Stabilization of the oily sludge pit began in 1999 and was finished in 2000. The remedial works took place in two stages: pre-treatment of the acid sludge and a second stage involving the actual treatment reagents (Figure 4.14).

Figure 4.14 – South 8th Street, USA- aerial photograph of the site (a) (*Source: Google Earth^{TM} mapping service; created 17 April 2007*); the contaminated soils before remediation (b); in situ remediation (c); finished S/S soil (d) (courtesy of Ed Bates)

Both stages utilised a 2.4 m diameter in-situ auger. The pre-treatment involved the addition of 25 percent by weight of crushed limestone, needed to raise the pH from zero to approximately 4.5, to prevent release of acid gases through excessive heating from subsequent reagents (Bates and Malott, 2005).

The second stage treatment involved mixing the untreated sludge with 20% Portland Cement and 10% coal fly ash by weight of sludge. The treated monolith was then covered with a geosynthetic clay liner to reduce possible water infiltration, which was in turn protected by a 0.6 m soil cap.

The target criteria of the remediation are presented in Table 4.4. Unlike the other sites studied in this work, an allowance for the range of performance criteria was made by the USEPA (Bates and Malott, 2005). This was necessary due to the substantial variability of the waste and the small sample size analysed at the time of the remediation design.

Table 4.4 – South 8th Street site characteristics of the treated soils and remediation targets (from Bates and Malott, 2005)

Property	Target value
UCS (MPa)	> 0.28 for any sample and 0.3 average of all samples @28 days
Permeability (m/s)	$<10^{-7}$ for any sample and 10^{-8} average of all samples@28 days
Leaching (µg/l)	
Lead	< 75 for any sample and 15 average of all samples

South 8th Street is now privately owned and is currently undergoing redevelopment as a barge terminal on the Mississippi River (USEPA, 2009).

2.5.2. Conceptual model

South 8th Street has been subjected to a number of environmental loads, described in Figure 4.15. Frequent flooding events were reported yearly between November and June up to a depth of 4.5 m (USEPA, 1998). The likely impact of this on the soundness of the S/S soil is described in more detail in Table 4.10.

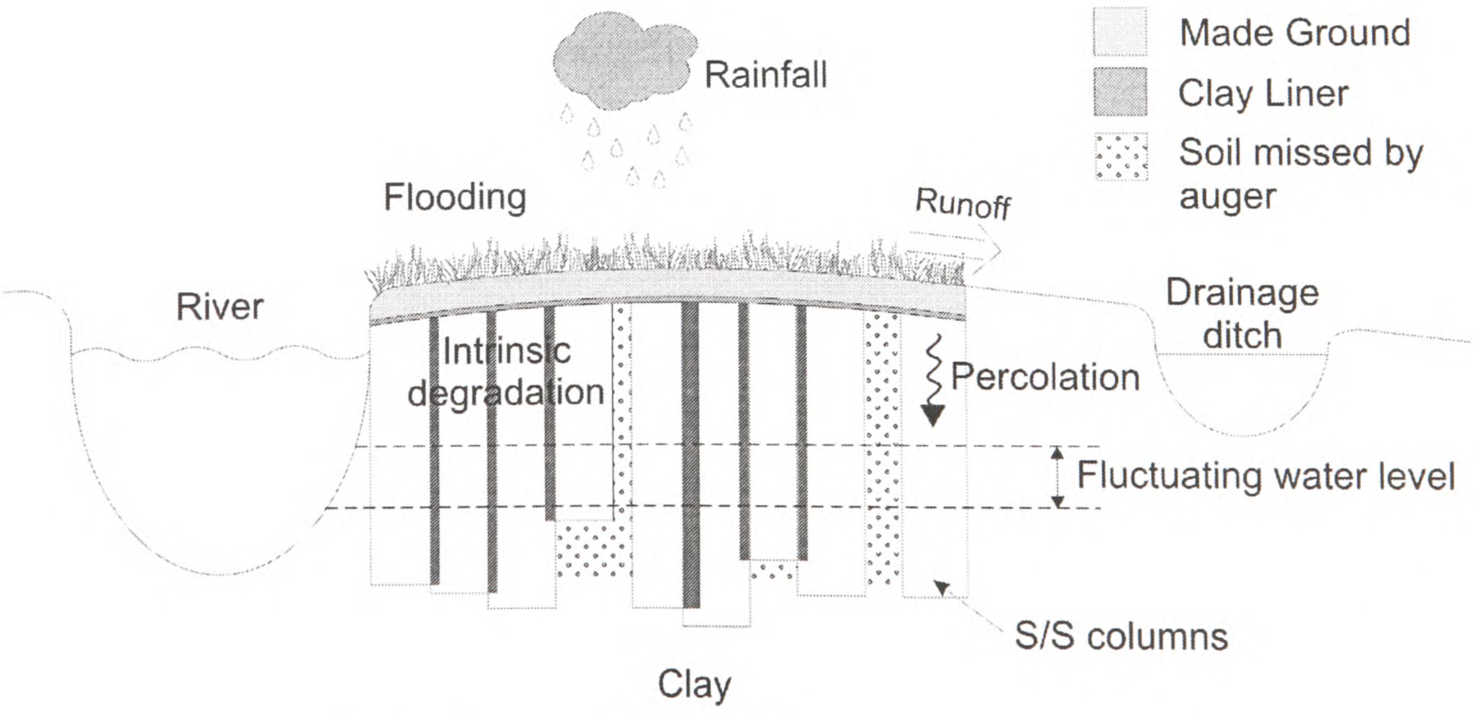


Figure 4.15 – Conceptual model for the South 8th Street site, USA

2.5.3. Sampling

South 8th Street site was sampled by the USEPA and University of New Hampshire, four years after the S/S treatment using rotosonic drilling equipment. Following unsuccessful attempts to recover intact material by both wet and dry coring, one intact sample was finally obtained. An image of a core fragment is shown in Figure 4.16. Granular material from the failed coring was retained for further tests.

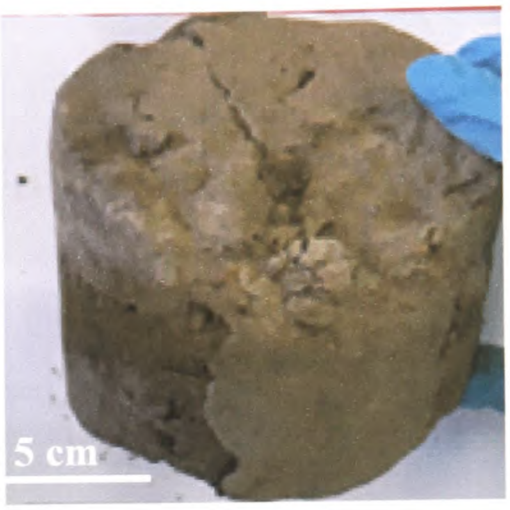


Figure 4.16 – Core sample recovered from South 8th Street, USA

2.6. Halton, UK (HA)

2.6.1. Site description

The Hutchinson Street site, further referred as the Halton site is located in Cheshire in north-west England (Curtis and Holt, 2004). This site was heavily contaminated as a result of industrial activity since the 1880s. The primary activity operating in this area was the production of soap, using the Le Blanc process. The residue obtained from this process was a highly alkaline toothpaste-like material, locally known as "Galligu", which was found at up to 4 m depth (Figure 4.17). Other contaminants like arsenic, lead, zinc, cadmium, copper, nickel and chromium were also identified in some areas. The pH of the contaminated soil varied greatly, from 2.6 to 12.2, with the lowest pH being measured within the first 1 – 2 m depth (Curtis and Holt, 2004). Contamination of controlled waters with heavy metals was the main risk identified, which led to the soil remediation. Due to the considerable amount of contaminated soil needing treatment (87,000 m^3), the contractor undertaking the remedial operation decided to create an impermeable cap by treating the surface of the contaminated soil by in situ S/S. A formulation containing 6% Portland Cement and 0.5% proprietary additive (Powercem 2) was used to treat the contaminated soil, in situ. Shallow mixing was carried out using a rotovator type-plant, on the first 35 cm of the soil, which was left to harden. A layer of 20 cm of reclaimed railway ballast, followed by Terram geotextile and 10 cm of sand and topsoil were added to the treated monolith (Figure 4.17).

Figure 4.17 – The Halton site, UK; aerial photograph of the site (a) (*Source: Google Earth^{TM} mapping service; created 17 April 2007*; soil contaminated with Galligu before (b) and in situ remediation (c); finished site (d)

To complete the remediation, grass was sown to prevent erosion and surface infiltration. The remedial targets established for the soil remediation are given in Table 4.5.

Table 4.5 – Remedial targets for the Halton site (from Curtis and Holt, 2004)

Property	Target value		Target value
CBR (%)	>15		
Permeability (m/s)	$<10^{-8}$		
Leaching (µg/l)*			
Lead	<25	Copper	2000
Cadmium	<5	Selenium	<10
Arsenic	<10	Nickel	<20
Chromium	<50	Zinc	Not available

* Water Supply (Water Quality) Regulations 2000

It should be noted that the Water Supply (Water Quality) Regulations 2000 are not strictly enforceable limits, but are used for comparison with the metal leaching (Curtis and Holt, 2004).

2.6.2. Conceptual model

Figure 4.18 shows the factors likely to influence the performance with time of the S/S at Halton site.

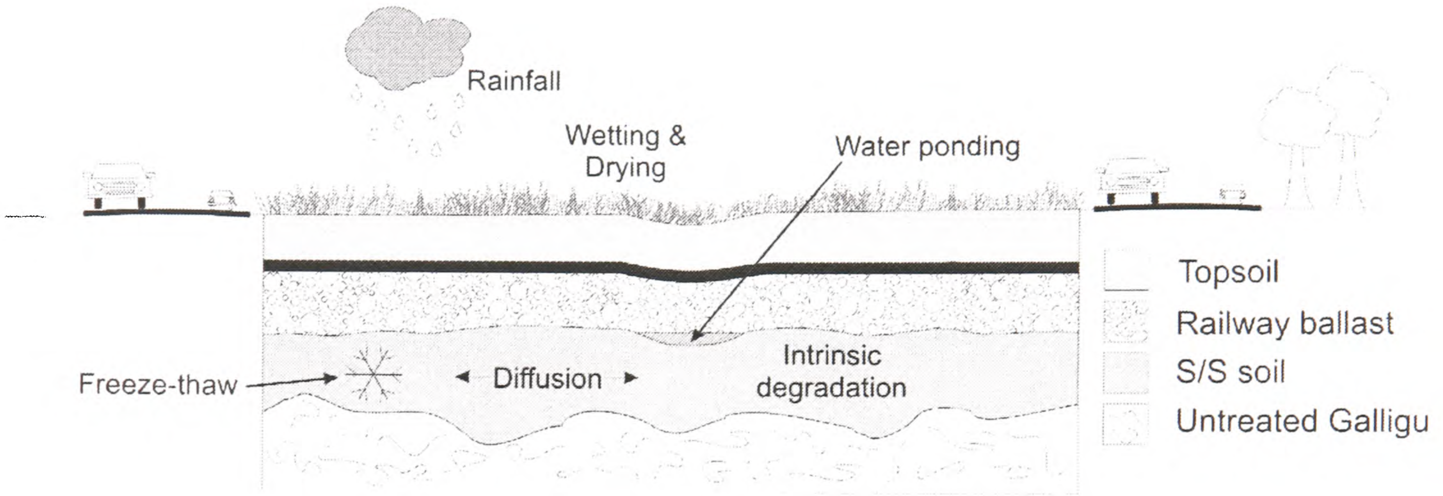


Figure 4.18 – Conceptual model for the Halton site, UK

It should be noted that, at the time of sampling, water ponding on the monolith was observed. This is generally an indication of poor drainage or settlement of the monolith. The latter is likely since the S/S soil sits on untreated Galligu, which is geotechnically unstable and moves under loading. The impact of water ponding on the S/S on the durability is discussed further in section 3.

2.6.3. Sampling

The sampling at Halton was carried out five years after remediation by a private contractor, under the supervision of the University of Greenwich. Before coring, the grass, topsoil, gravel and geotextile were removed to expose the top of the monolith (Figure 4.19). The material was recovered using a 15 cm core barrel and water to avoid overheating. Intact cores of 30 cm length and 98 mm diameter were obtained from a number of locations on site. An image of typical core extracted is shown in Figure 4.20. The cores were well indurated, but displayed mottling effects which could be attributed to carbonation. However, this observation required confirmation of this phenomenon by analytical methods.

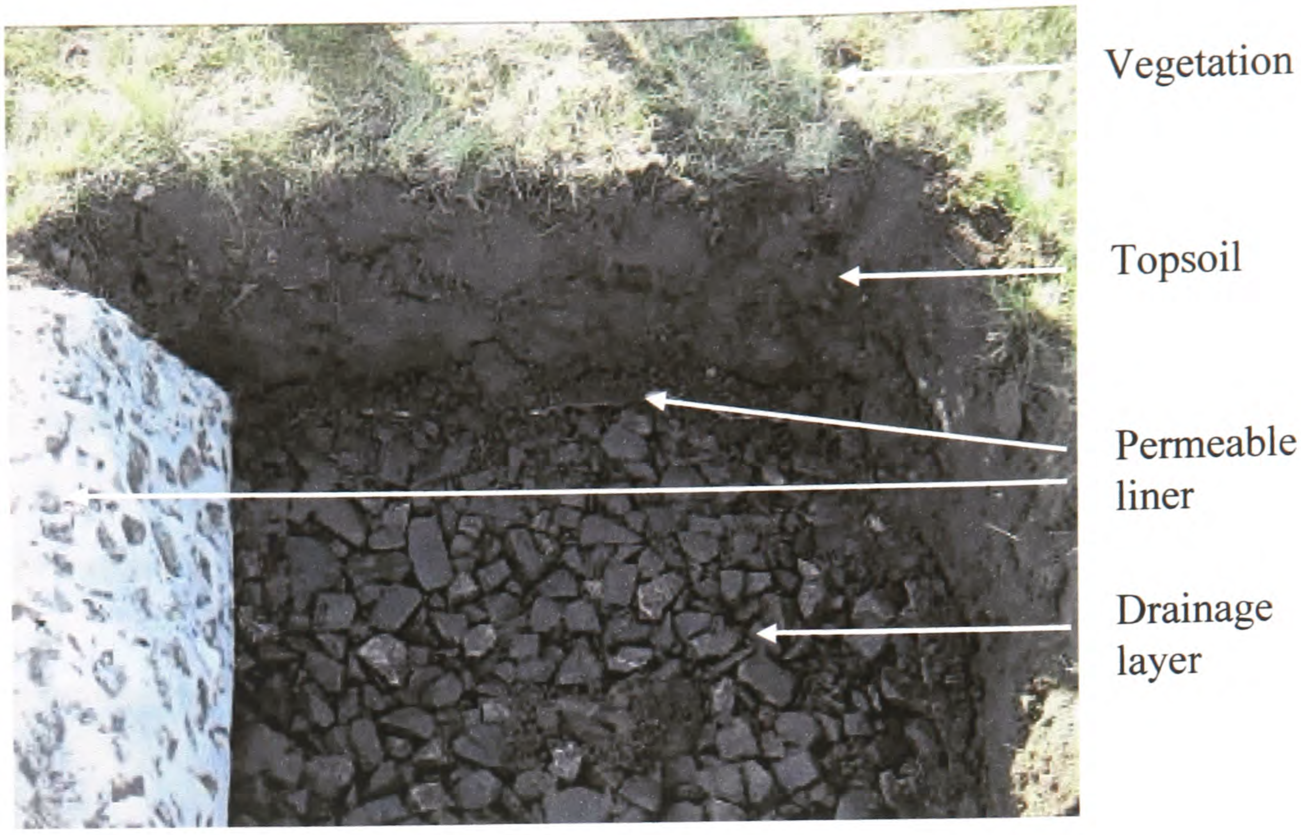


Figure 4.19 – Layers of the cap, above the S/S monolith at Halton

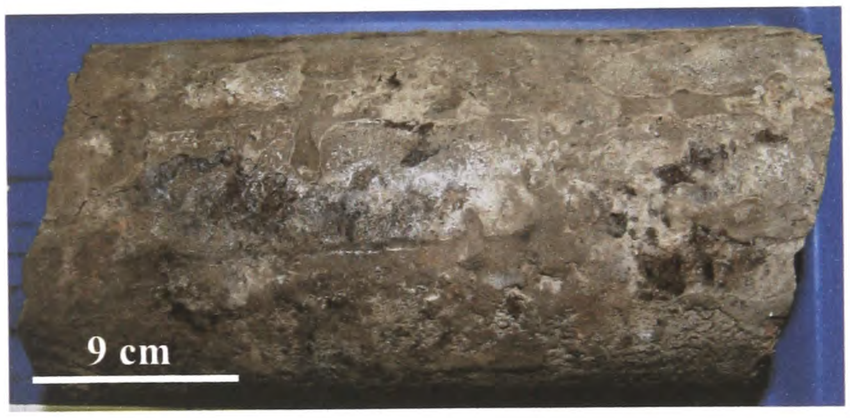


Figure 4.20 - Core sample extracted from Halton, UK

2.7. Columbus MGP, USA (MGP)

2.7.1. Site description

The Columbus MGP site comprises 1.6 hectares and is located on the bank of Chattahoochee River, in Georgia, southern United States (Figure 4.21a). The site was used for gas manufacturing between the 1850s and 1931, leaving a legacy of soil contamination. The main contamination identified was with PAH, BTEX and cyanide.

The site was remediated as part of a riverside redevelopment in 1992. The S/S treatment was applied to the area adjacent to the river using hollow-stem augers (Figure 4.21b, c). In total 70,000 cubic metres were treated and 1,800 overlapping columns were constructed. A wall of overlapping S/S treated soil columns was constructed along the river bank using

25% Portland cement. The zone in contact with the river was sealed with sprayed Shotcrete (Fleri and Whetstone, 2007). Approximately 65,000 cubic meters of soil, between the river and the boundary wall were excavated and segregated into "affected" and "non-affected", based on the level of contamination (Fleri and Whetstone, 2007). The "affected" soils were returned to the site and stabilized by in situ deep mixing to a maximum depth of 11 m. The stabilized area was subjected to surface profiling to ensure adequate drainage and then covered with a 6 cm high density polyethylene (HDPE) liner and 30 cm of "non-affected" soils, previously excavated from the site.

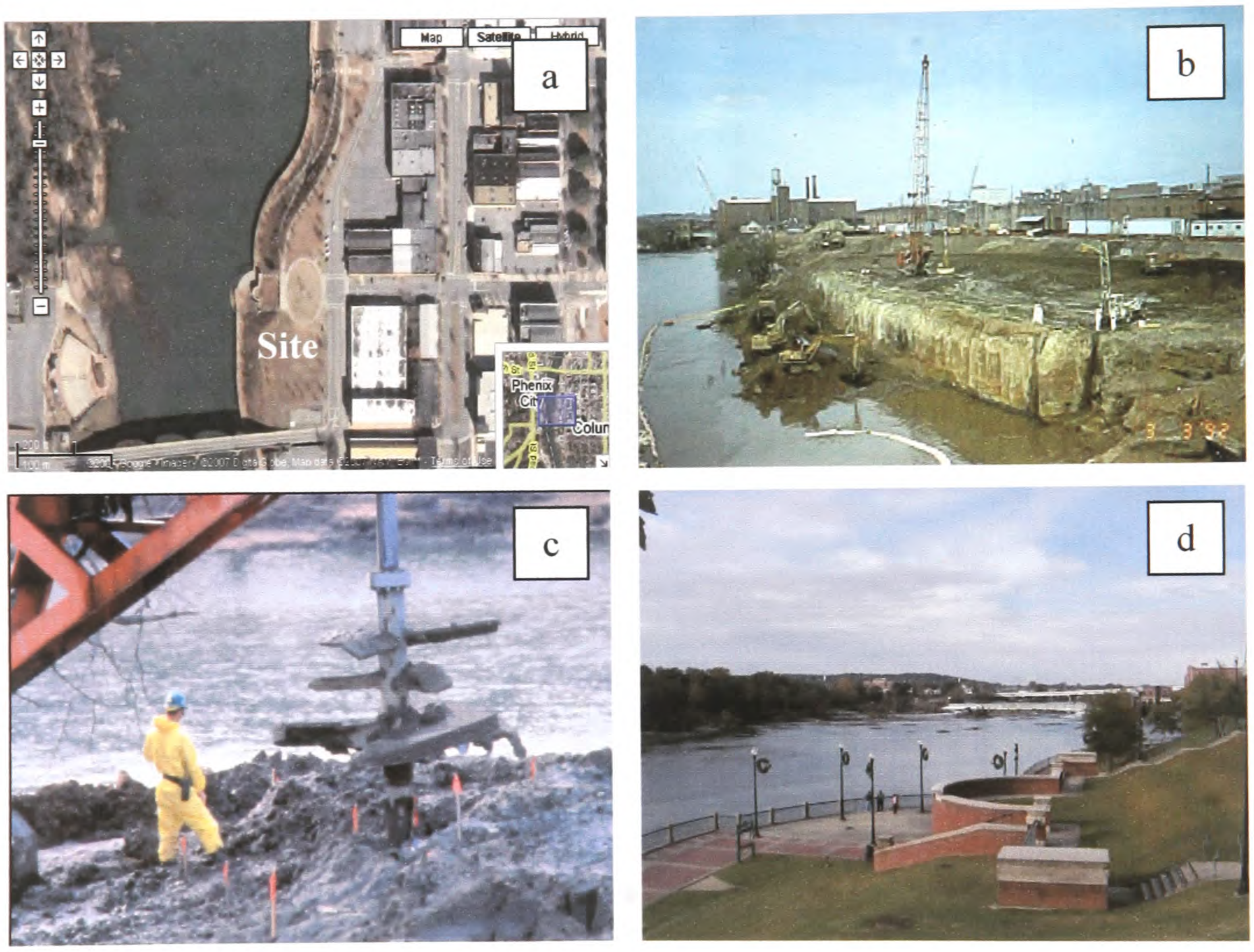


Figure 4.21 – The Columbus MGP site, USA; aerial photograph of the site (a) (*Source: Google Earth^{TM} mapping service; created 17 April 2007*); site before remediation (b), during and after remediation (c); finished site now a river park (d) (courtesy of Kevin Gardner)

The site remedial targets were established at the time of treatment and are given in Table 4.6.

Table 4.6 – Columbus MGP remediation targets (from Gardner, 2005)

Property	Target value
UCS (MPa)	>0.4
Permeability (m/s)	$<10^{-7}$
Leaching (µg/l)	
Cyanide	<200
PAH	Not defined

2.7.2. Conceptual model

The disposal scenario and the external and internal factors likely to impact on the long term performance of the Columbus MGP soils, are summarized in Figure 4.21 and detailed in Table 4.10.

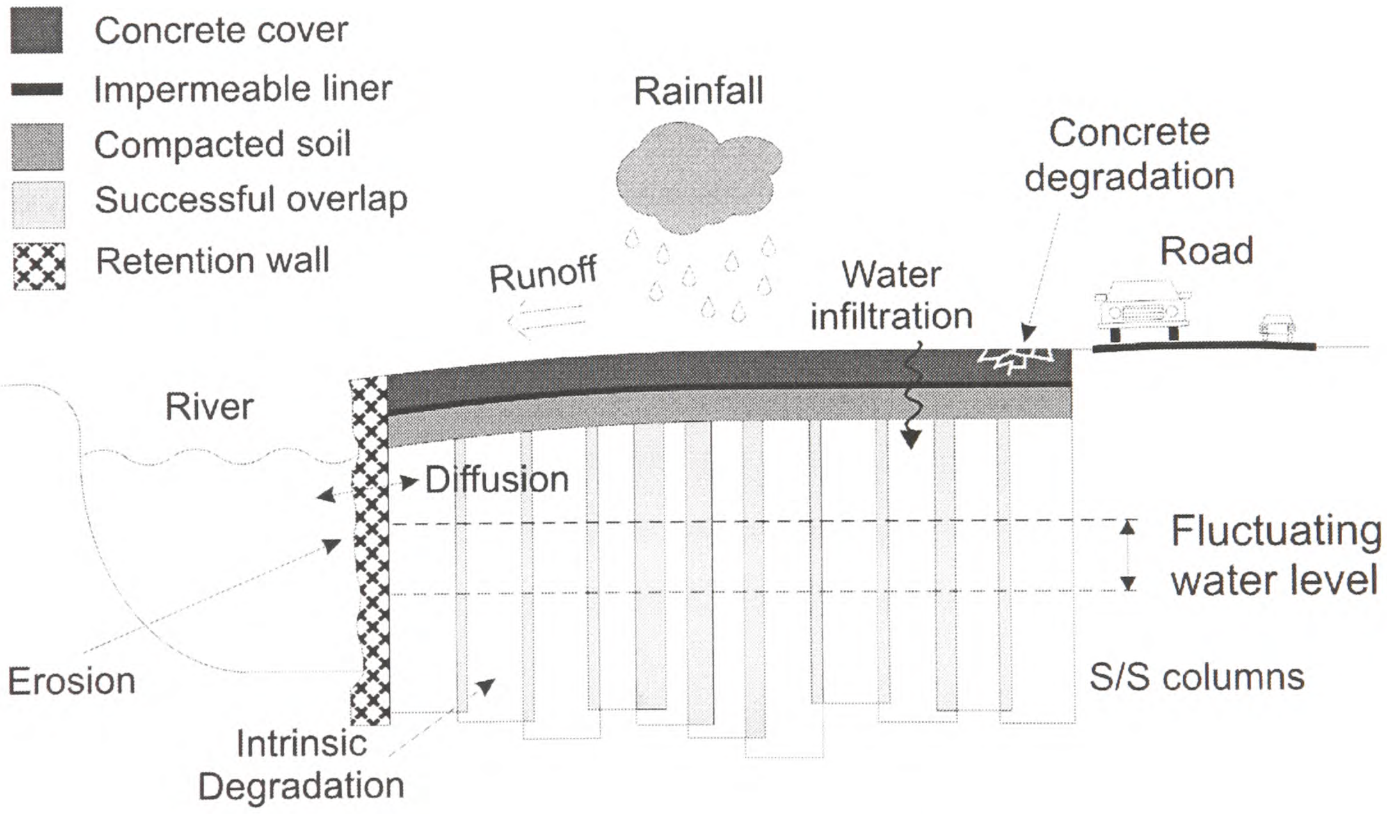


Figure 4.22 – Conceptual model for the Columbus MGP site, USA

2.7.3. Sampling

The Columbus MGP site was sampled by the owner of the site twelve years after the S/S treatment. During coring, only one intact sample was extracted without water being used as a lubricant. The remaining material was collected using wet coring and samples of approximately 5 cm in diameter were successfully recovered. The cores were well indurated and did not show any signs of alteration. Figure 4.22 shows an example of a typical sample extracted.

Figure 4.23 – Fragment of sample extracted by wet coring from the Columbus MGP, USA

2.8. Quarry Dump, USA (QD)

2.8.1. Site description

The Quarry Dump was a working quarry in the 1800s. Following a change in ownership the quarry pit was used for water storage as a cooling pond/reservoir related to steam generation for part of the period 1890-1926. Prior to 1965, "inert materials" were periodically disposed of in the cooling pond (Gardner, 2005) and construction debris such as excavated soil, rock, and cobblestone were also recorded.

The primary contaminants on this site were total petroleum hydrocarbons (TPH), lead, PCBs and PAHs. The site underwent S/S treatment in 1994. The upper 4.5 m of soil was excavated and disposed of to landfill, whilst the remaining soil was solidified with 25 % Portland Cement by application of shallow soil mixing and jet grouting. The treated soils were covered with a layer of concrete as indicated in Figure 4.24.

The remediation targets for this site are presented in Table 4.7. The primary goal was physical improvement of the soil i.e. UCS and permeability. No chemical targets were reported for this S/S soil (Gardner, 2005).

Table 4.7 – Quarry Dump remedial targets (from Gardner, 2005)

Property	Target value
UCS (MPa)	>0.4
Permeability (m/s)	$<10^{-7}$

Figure 4.24 – The Quarry Dump site, USA; aerial photograph (*Source: Google Earth^{TM} mapping service; created 17 April 2007)*

2.8.2. Conceptual model

The durability of the S/S soils is likely to be influenced by a series of factors, described in Figure 4.25. A more detailed discussion of each factor is given in Table 4.11.

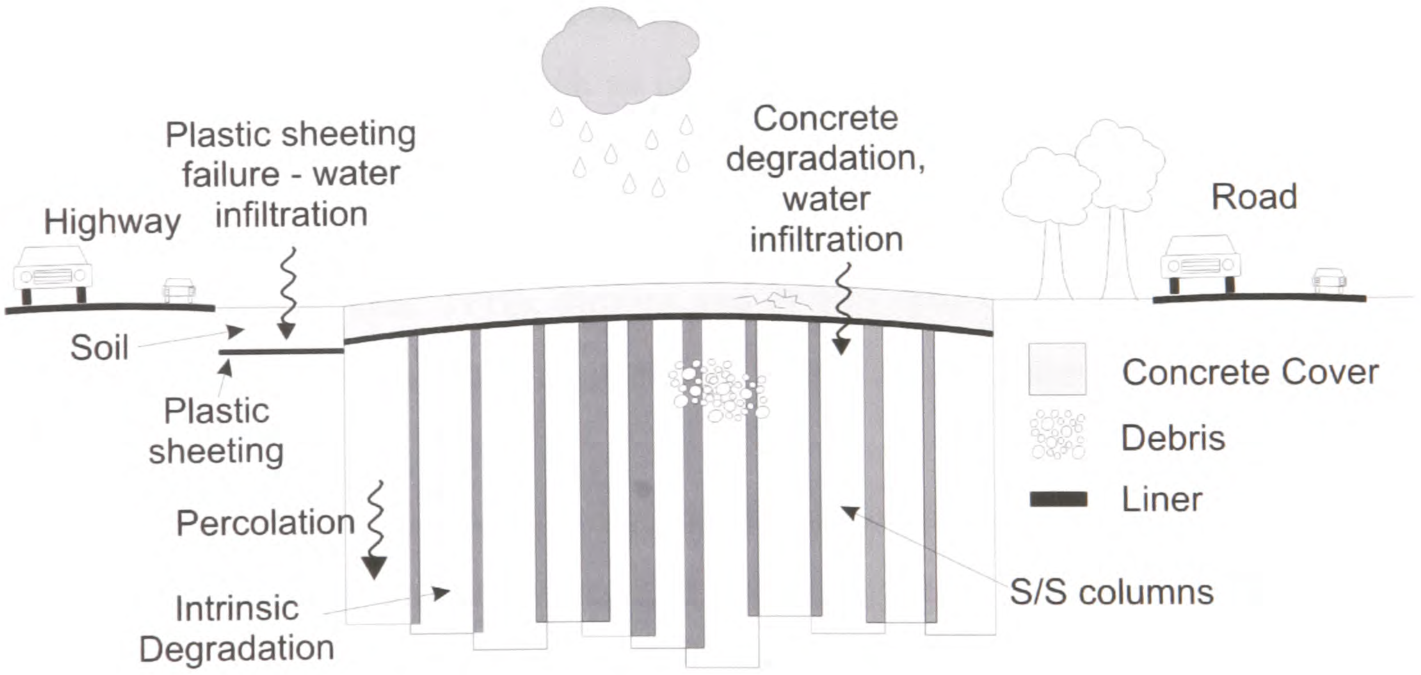


Figure 4.25 – Conceptual model for the Quarry Dump site, USA

2.8.3. Sampling

The Quarry Dump site was sampled by the owner of the site, ten years after the S/S treatment. A number of core samples of approximately 5 cm in diameter were recovered by wet coring, since no intact dry samples could be recovered. Figure 4.26 shows an example of the material obtained. The material recovered was poorly indurated, relatively uniform and contained a large amount of mica.

Figure 4.26 – Core sample extracted from Quarry Dump, USA

3. Discussion

The S/S soils were remediated using Portland cement based formulations, but proprietary additives and secondary materials such as coal fly ash and activated carbon were used to achieve the site specific physical and chemical design criteria. Amongst the contaminants found in the S/S soils feature heavy metals and metalloids (lead, chromium, zinc, copper, arsenic) and organics (PAHs, TPHs, dioxins and PCBs). The suitability of each binder for the treatment of soils was described in detail in Chapter 2 – Literature review.

The long term durability of S/S soils cannot be evaluated without investigation of a number of sites of different ages. In this work, eight sites remediated up to 16 years ago were sampled and analysed. Each site was characterised by distinct soil and containment types, binder systems and contaminants, and was located in various climates and environmental settings. The environmental conditions, in which the S/S soils were placed, depended on the initial location of contamination. In many cases, these soils were bordered or situated by major rivers and subjected to frequent flooding events and fluctuating water table (Figures 4.15, 4.22).

Table 4.8 indicates the factors likely to influence the durability of the S/S soils, depending on their service environment. A number of phenomena were observed and reported in the regular reviews carried out by the site owners, particularly in the USA; these are further indicated in Table 4.8 *as certain.* Other potential influences on the S/S soil (*possible and likely*) were inferred from the site specific conditions (USEPA, 2004a; USEPA, 2004b; USEPA, 2002; Fleri and Whetstone, 2007; USEPA, 1998; Celtic, 2006; Curtis and Holt, 2004).

The factors leading to degradation of the S/S soils can be chemical or physical in nature. In some cases they originate within the S/S soil (intrinsic), in other cases, they are external (extrinsic).

Intrinsic processes include alkali silica reaction, sulfate attack, carbonation as a result of biodegradation; however some of those mentioned can also be extrinsic i.e. sulfate attack or carbonation. Most chemical or physical degradation processes have been shown to either be favoured or caused by external factors such as the aggressive ions or water ingress (Neville, 2001).

Table 4.8 – Factors likely to influence the durability of S/S soils at each site

	PS	AC	MGP	AP	HA	S8	QD	CA
Cover/wall/soil erosion	●●●	●●	●●	●●		●●		●●
Flooding						●●●		
Fluctuating water table			●●●			●●●		
Water percolation				●●		●●	●●	●●
Wetting and drying				●●●	●●●			●●●
Freeze thaw				●●	●●			
Settlement					●●●			●
Carbonation	●			●●	●●	●		●●
Oxidation				●●	●●			●●
Intrinsic degradation	●	●	●	●●	●●	●●	●●	●●
Biodegradation				●●				
Vegetation growth	●●●			●●●				
Engineering failure	●●●	●●●	●		●●		●	

● possible; ●● likely; ●●● certain

Without aiming to give an exhaustive account of the degradation mechanisms in S/S soils, the most likely processes in the soils studied will be discussed in the next sections.

Cyclic wetting and drying of the S/S soil from either fluctuating water table, rainfall or flood water penetration may cause cracking and chemical alteration. According to the Environment Agency (2004) the level of ambient relative humidity determines the severity of degradation. This applies to monolithic materials, which are constrained by the physical properties and may not be relevant for granular materials. The degradation due to water ingress/percolation can be prevented through exclusion of water by installing impermeable capping or designing low permeability S/S soils (Environment Agency, 2004). All sites located in the US were covered by a geosynthetic clay liner, whilst in the UK sites were either exposed to the atmosphere, or separated by layers of topsoil and/or permeable liners.

Table 4.9 – Influence of humidity on deterioration of concrete (from Environment Agency, 2004)

Ambient relative humidity	Relative severity of deterioration process		
	Carbonation	Frost attack	Chemical attack
Very low (<40%)	slight	insignificant	insignificant
Low (40-60%)	high	insignificant	insignificant
Medium (60-80%)	medium	insignificant	insignificant
High (80-90%)	slight	medium	slight
Saturated (>90%)	insignificant	high	high

As indicated in Table 4.9, frost attack occurs in S/S soils exposed to high humidity, in saturated conditions, and when placed within the depth of frost penetration. Since the environmental setting of the S/S soils sampled varied from savana to humid subtropical climate, in the US and to humid temperate climate in the UK, frost attack was only a concern for some sites (see Table 4.10). Moreover, as reported by Bates (2009), all S/S sites in the US were placed below the depth of frost, in each State. The typical depth of frost in the UK is 450 mm (Perera *et al.*, 2005a), whilst in the US (the Southern States) is up to 250 mm (Sounding footings, 2010).

Damage due to vegetation growth on the S/S soils was identified from the literature (Sarsby, 2000). Although vegetation was not a major concern at most S/S sites investigated, one site could have been impacted by it. This site was Astra Pyrotechnics, which lacked secondary containment or capping and had a number of species of grass populating the treated soils. The effect of vegetation growth is two-fold: it decreases the water infiltration into the soil, by promoting evapotranspiration, but it can cause loosening of the S/S soils surface and create preferential pathways for external agents to penetrate into deeper soil layers. Plant roots produce carbonic acid when alive and organic acids when decaying (Conner, 1990); therefore vegetation can induce changes in pH and redox conditions, and promote dissolution of the S/S soil, and subsequently affect metal immobilization (Perera and Al-Tabbaa, 2005a).

Chemical attack can take place in S/S soils and can be either intrinsic or extrinsic. This includes sulfate attack and carbonation (Environment Agency, 2004). A description of various chemical attacks and their potential effects on the durability of S/S soils from the literature is given in Table 4.10 and was discussed in detail in Chapter 2.

The biodegradation and biological weathering can occur in S/S soils containing organic compounds or high content of organic matter. The biological induced degradation is due to the presence of microorganisms, which generate energy by metabolizing organic carbon and produce strong mineral acids (Knight *et al.*, 2002) This phenomenon is mostly seen at the surface of S/S soils and can lead to matrix dissolution and metal release (Rogers *et al.*, 2003).

Oxidation is an extrinsic process which takes place when atmospheric oxygen penetrates into the S/S soil. The rate of oxygen ingress is different depending on whether the soil is uncovered or covered or the cover is intact or broken, or is it placed in a saturated or unsaturated environment (Bozkurt *et al.*, 2000). This reaction is not expected at the S/S sites protected by secondary containment, but may be active at those uncompacted, uncapped and granular (see Table 4.10). Oxidation can increase the leaching of a number of metal contaminants (Conner, 1990) and generate acidic conditions by conversion of sulfides to sulfuric acid. The oxidation of organic compounds and organic matter can induce carbonation of the S/S soils resulting in the alteration of soil (Bozkurt *et al.*, 2000).

Engineering failure such as blockage of drains or promotion of cap erosion due to the inappropriate surface profiling was observed at a number of S/S sites (USEPA, 1994; USEPA, 2004a). This can expose the S/S soil to standing water or rainfall leading to degradation, as described in the sections above.

4. Conclusions

This chapter described the history of the S/S sites, the remediation methods, and the sampling strategies employed. The site specific environmental conditions were identified from the site documentation supplied by the site owners or the remedial contractors and the following conclusions can be drawn:

- The types of contaminants found in the S/S soils, the age of the treated soils and the remediation formulation employed at each site were different. The treatment binders for all sites incorporated Portland cement, although additives were used in some cases.

- Each site was subjected to different environmental loads, depending on their location and these were graphically presented as conceptual models. Extrinsic factors, primarily precipitation and exposure to groundwater or flooding, were likely to affect the S/S soils. However, some intrinsic processes, e.g. sulfate attack, were also identified as likely issues.

- Some factors have been already observed, including engineering failure and cover erosion. Further interpretation of the results will bear this in mind.

- The sampling showed that not all S/S soils were monolithic, as previously believed. This fact was not related to the binder content of the S/S soils.

- Despite the use of sampling techniques, which were adapted to the site conditions, the retrieval of intact cores was not always possible. Damage to the S/S material sampled was inevitable and this fact should be accounted for when interpreting the laboratory results.

- The majority of sites had site specific target criteria created as part of the remediation strategy. However, others were only compared to regulatory guideline values.

The sampling of actual sites was constrained by the ability to gain access and permission. To preserve the material collected from the seven full scale S/S soils, the samples from the pilot scale demonstration (Astra Pyrotechnics) were used initially to establish an effective testing strategy. In the next chapter, the chemical and physical behaviour of the samples extracted from a pilot scale site will be tested and the potential risk indicators for the durability of S/S soils identified.

Table 4.10 – Factors likely to influence the S/S sites during their service life

Factor	Effect on the S/S soil	Remarks
Vegetation growth	Reduction of infiltration, erosion Promotion of evapotranspiration Favours biological weathering	The vegetation growing directly on the stabilized soil can cause damage due to growth of plant roots (Environment Agency, 2004). The S/S soils should be placed below the plant rooting zone.
Evapotranspiration	Reduction of S/S soil moisture during rain events Salt crystallisation in pores leading to cracking	
Carbonation	Change of chemistry and microstructure. Strength reduction	The extent of carbonation depends on the permeability of the concrete and the concentration of carbon dioxide in the air (Fernandez-Bertos *et al.*, 2004). In hot climates with high humidity conditions the carbonation depths can reach several mm within days (Walker, 2002). In temperate climates, carbonation proceeds at rates between 0.05 mm and 1.0 mm per year (Environment Agency, 2004).
Oxidation	Change in solubility of inorganic and organic species Generation of acidic conditions	Sulphides in soil can be transformed into sulphates, forming acidic conditions, as well as the soil organic matter. Acidic conditions can further release metal contaminants present in a soluble form (EA, 2004). Oxygen penetration is favoured by cyclic wetting and drying conditions (Eglington, 1998).
Percolation	Development of preferential pathways, promoting contaminant leaching from the S/S soil. High surface area for reactions Advanced carbonation	Occurs in granular material.
Diffusion	Determines the transport mechanisms within S/S soil	Characteristic to low permeability monolithic materials. Depends on the permeability of the S/S soils and the surrounding geological material, and the rate of infiltration (Environment Agency, 2004). The controlling factors in the degradation of S/S soils in this scenario will be the temperature, the time the material is wetted and the degree of water saturation, particularly if there is a fluctuating water table (Kosson *et al.*, 1996)
Flooding, cyclic wetting/drying, fluctuating water table	Alteration of cement phases due to volume changes during wetting and drying leading to cracking. Leaching generation Favours carbonation	Can be prevented by exclusion of water (using barriers) or design of low permeability stabilized soil. Placement of S/S soils below the water table must be avoided, where possible (Environment Agency, 2004). The lower the liquid to solid ratio, the lower the contaminant leaching (Environment Agency, 2004)

Table 4.10 – Factors likely to influence the S/S sites to during their service life (continuation)

Factor	Effect on the S/S soil	Remarks
Intrinsic degradation - sulfate attack - alkali aggregate reaction - carbonation - biodegradation/biological weathering	Increased porosity, permeability Loss of strength Cracking and spalling Contaminant release from stabilised soil	Change of local chemistry and expansion with subsequent cracking of the S/S soil (Collepardi, 2003; St. John *et al.*, 1998). This can be prevented/minimised by use of pozzolanas to reduce the available alkalinity (Neville, 2004). Oxidation of organic matter and organic compounds by atmospheric oxygen generates carbon dioxide and water and can induce carbonation of the S/S soils (Bozkurt *et al.*, 2000). The acid production during the degradation of organic matter can mobilize metals from the stabilized soil (Rogers *et al.*, 2003).
Erosion	Development of preferential pathways Increase possibility of other types of attacks on the S/S soil	Can be prevented by adequately designing the inclination of the S/S soil.
Engineering failure - Blockage of drainage ditches - Slope inclination	- Water ponding or flooding of the S/S soil (USEPA, 2002) - Generation of runoff leading to transport of contaminants to adjacent areas	See flooding, wetting and drying, fluctuating water table See erosion

Chapter 5 Performance of pilot-scale cement-stabilised soils

1. Introduction

In the previous chapter, the S/S sites investigated in this work were described. Each site was subjected to different environmental loads, which were presented in conceptual models. The potential impact of the environmental loads on the S/S soils performance with time was also described. A review of the historical data on the sites revealed that they were of different ages, the types of contaminants varied, and that they were sampled using a range of techniques. Despite these differences, all the sites used a Portland cement-based binder system, sometimes in conjunction with other additives and fillers.

The availability of full scale soil samples is constrained due to a variety of factors including permission from owners to access the sites, liability for disturbance of the S/S soils and cost of sampling. Therefore it was necessary to establish the testing approach prior to examining the full scale samples. This chapter presents the findings from the characterisation and the performance assessment of a site used for pilot scale treatment trials. Free access and unrestricted sampling of the site was permitted, and full documentation on the site conditions and treatment method was available. The site was located in an aggressive environment, representing a worst-case scenario of exposure. These factors combined, the site made an ideal model for the design of an effective testing strategy for the other sites.

2. Choice of analytical approach

The soil treatment and the environmental loads acting at Astra Pyrotechnics site were described in Chapter 4. The visual observations during soil sampling indicated that weathering profiles were present in the Portland cement and EnvirOceM soils; therefore these soil profiles were investigated by a number of tests such as pH, XRD and total metal content. A description of each test and the sampling method are given in Chapter 3 (sections 3.1, 3.2, 5.3.3) and Chapter 4 (section 2.1.3). The test results are presented in the next sections.

2.1. pH variation

Typical pH values of S/S soils range between 12.5 and 13.5, depending on the content of alkalis present (Shi, 2005). In the absence of supplementary materials (e.g. pozzolana), which decrease the pH, any changes in the pH observed could be due to degradation caused by environmental exposure. Figure 5.1 shows the pH variation with depth of the untreated and treated soils, determined on three replicate samples. Four years after treatment the pH was near neutral for the untreated soil and moderately to highly alkaline for the treated soils (pH 9-12).

The pH of the untreated soil remained unchanged with depth, whilst that of the treated soils showed a variation, particularly for the Portland cement soil. The uppermost 5 cm had significantly lower pH compared with the profiles below 10 cm.

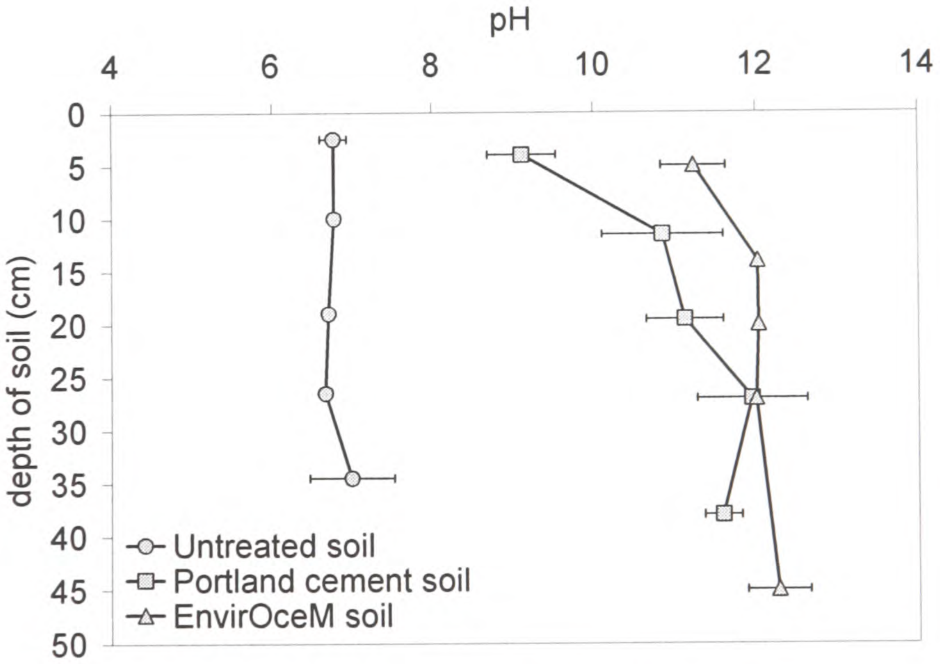


Figure 5.1 – The pH variation with depth in the untreated, Portland cement and EnvirOceM soils (error bars represent standard error)

2.2. Moisture content

The moisture content was measured on three replicate samples from each soil profile, according to BS 1377: Part3: 1990 method, described in detail in Chapter 3 (section 3.1). The results showed that the moisture of the untreated and treated soils varied with depth, but no trends were identified. Although the soils were exposed to identical environmental conditions, the moisture contents of the untreated and S/S soils were different. The values recorded by wet weight were up to 11% for the untreated soil and 25% for the S/S soils. A dip in the moisture content of the S/S soils was noted at 20 cm below the soil surface, which may explain the discolouration of the soil profile observed at sampling and shown in Chapter 4 (Figure 4.4).

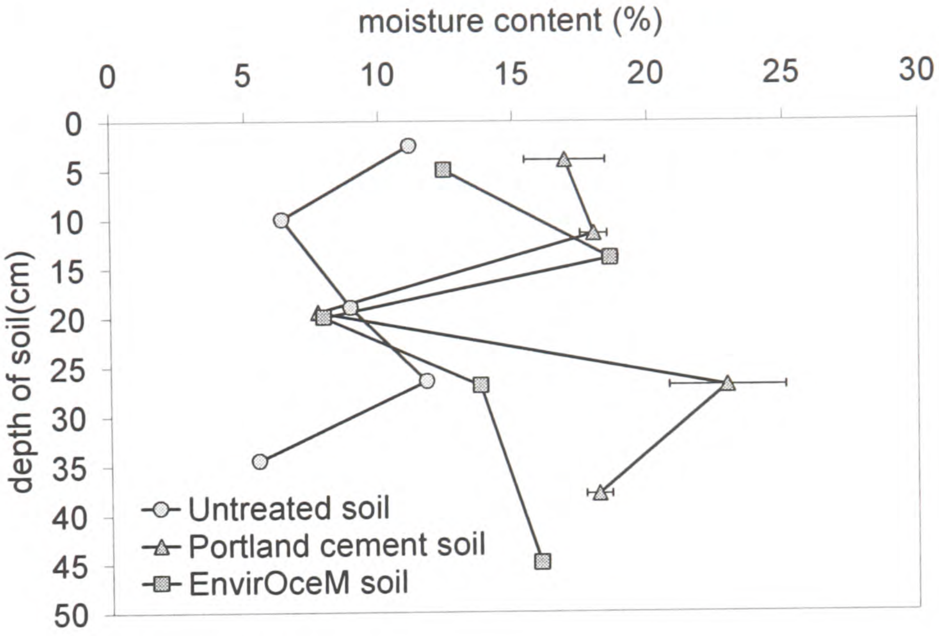


Figure 5.2 – Variation of soil moisture content with depth in the untreated and S/S soils (error bars represent standard error)

2.3. XRD

X-ray Diffraction was carried out to determine the mineral phases present in the soil profiles. Figures 5.3 – 5.5 show the phase distribution in the untreated and treated soils.

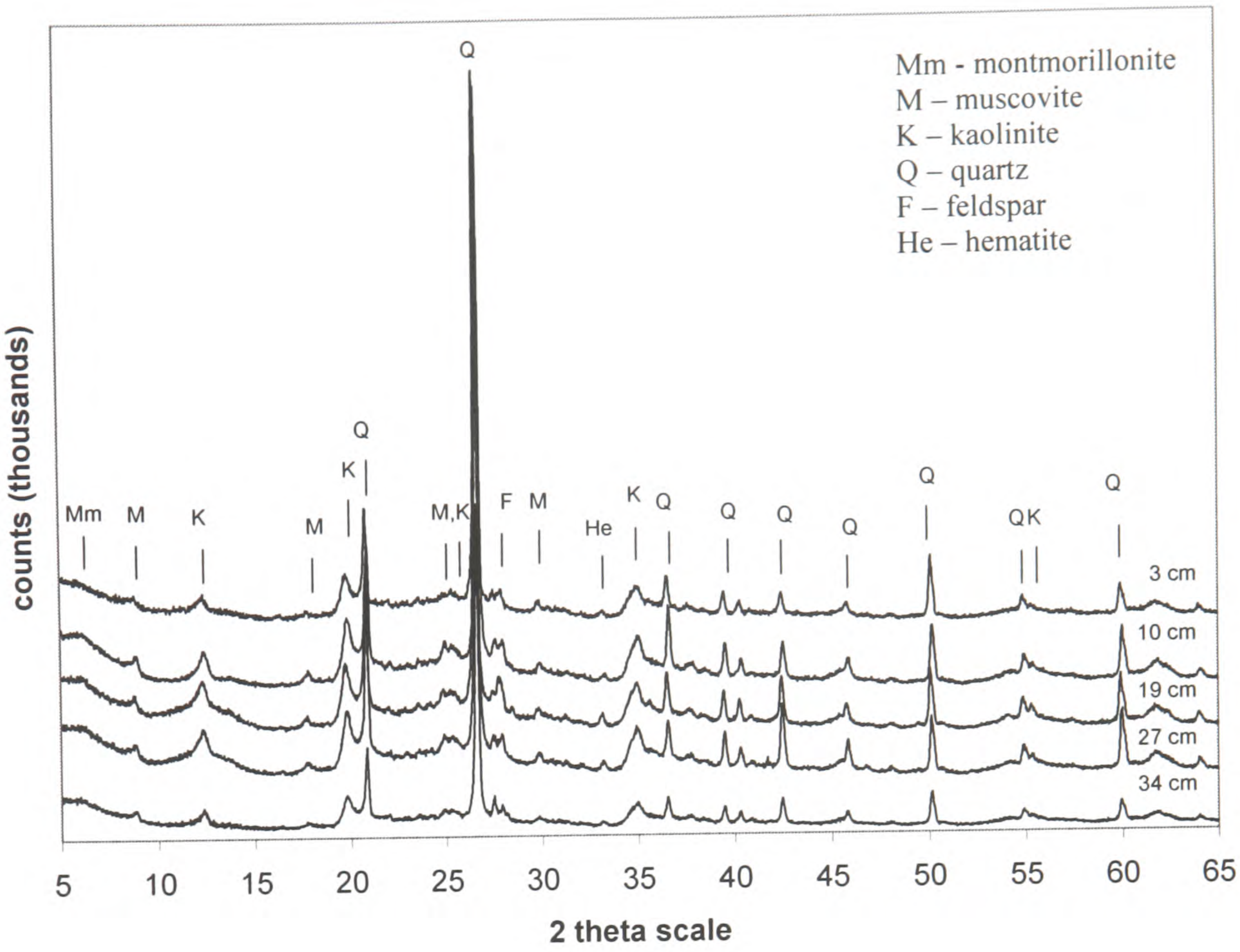


Figure 5.3 – The variation with depth of mineral phases in the untreated soil

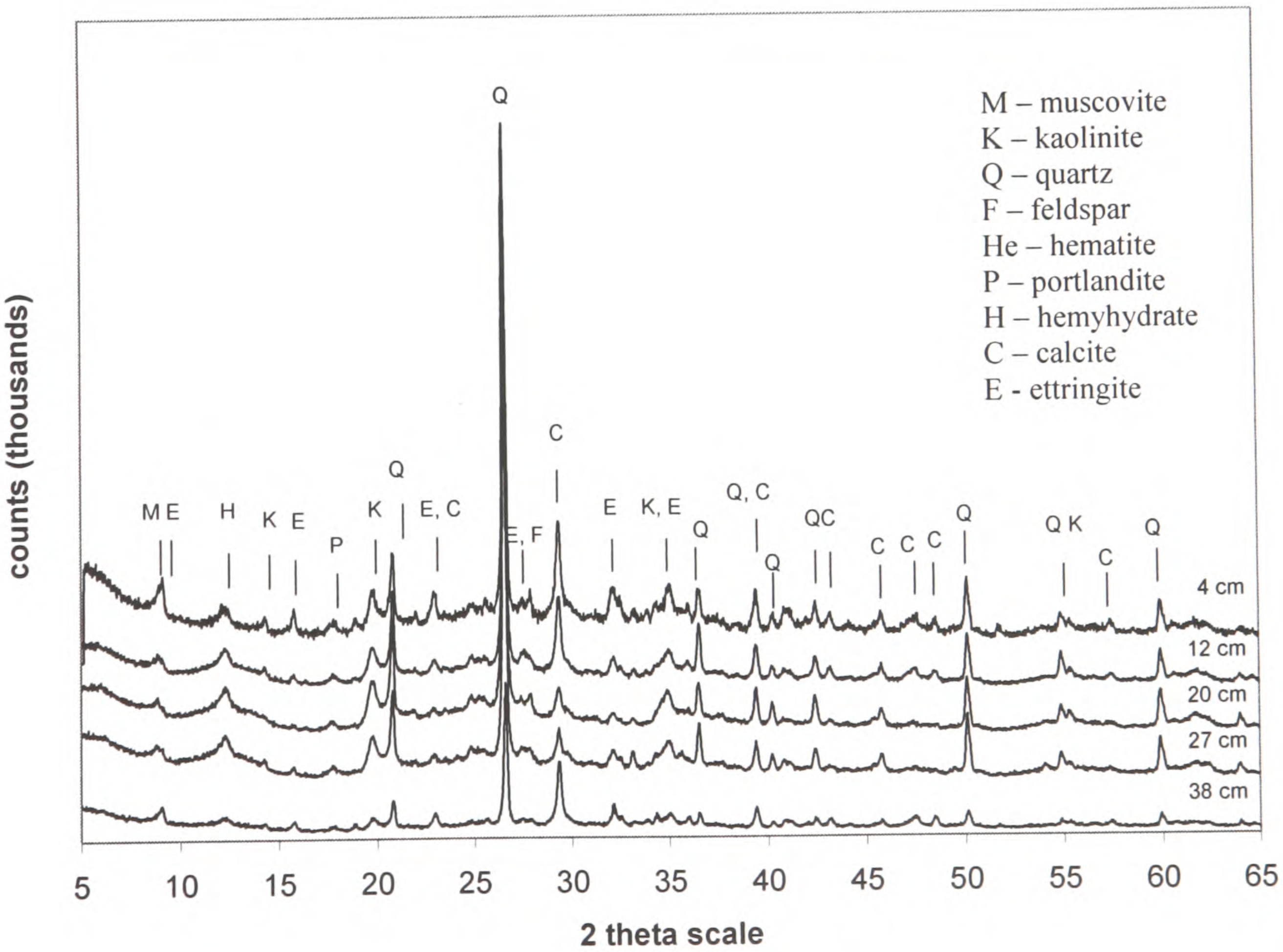


Figure 5.4 - The variation with depth of mineral phases in the Portland cement soil

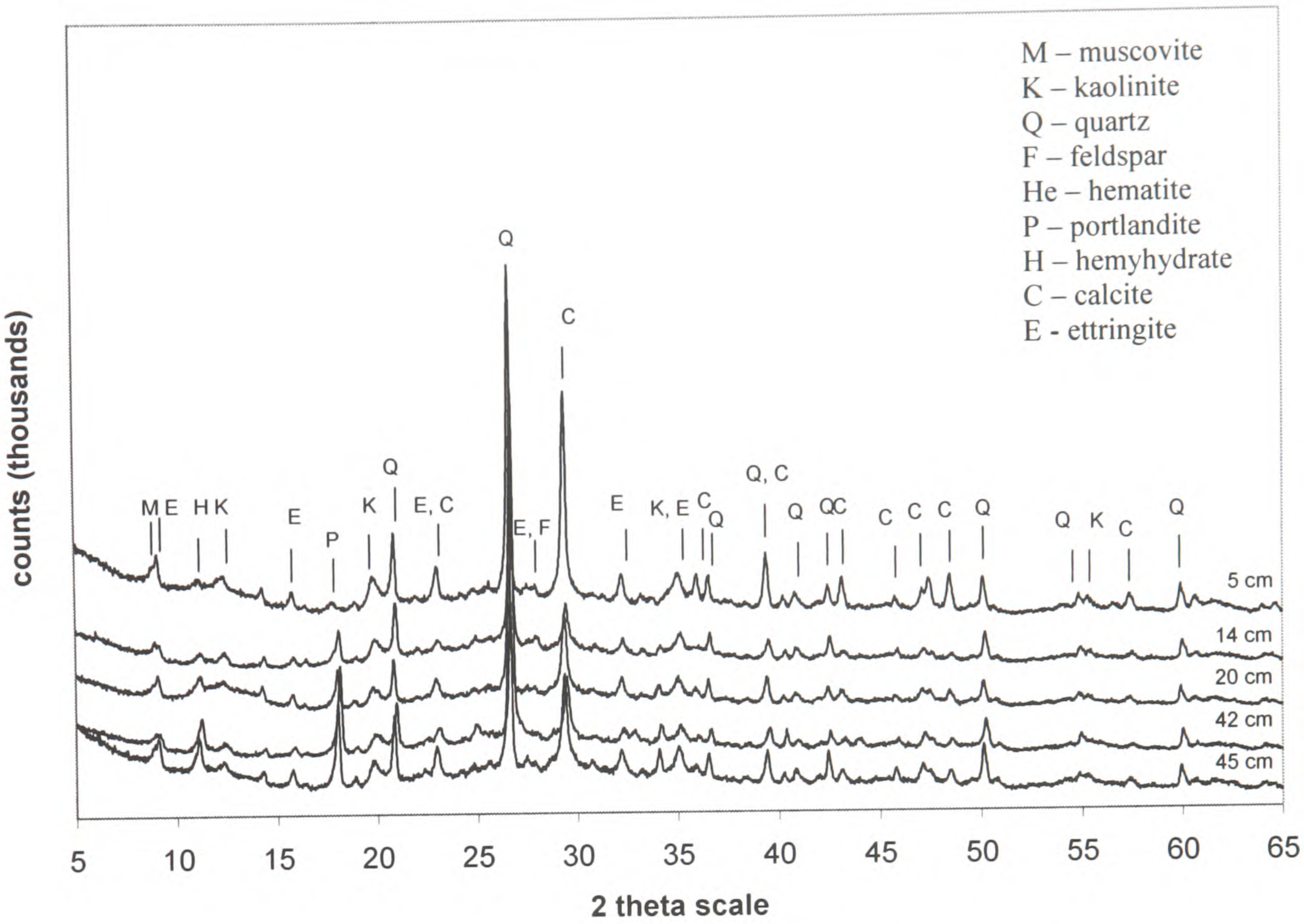


Figure 5.5 - The variation with depth of mineral phases in the EnvirOcem soil

The results indicated a lack of significant variation of the mineral phases throughout the depth, in good accordance with the pH measurements, except for the surface and bottom layers of the EnvirOceM treated soil. In this soil, the portlandite was more pronounced at the surface than at depth (Figure 5.5).

2.4 Summary

The variation of soil properties with depth was characterized using pH, moisture content and XRD. The results have shown that the untreated soils were uniform, whilst the S/S soils displayed variations with depth. The XRD analysis indicated that the same minerals were present throughout the S/S soil profiles, but their relative proportion varied. However, this variation was not sufficient to justify the detailed examination and testing of each individual sample within the profile, in the next sections. Therefore, composite samples obtained from all profiles from untreated and similarly from each of the S/S soils were studied further.

3. Characterisation of soils

The soil characteristics such as the colour and appearance are presented in Table 5.1.

Table 5.1 – Characteristics of the soils extracted from Astra Pyrotechnics

	Untreated soil	Portland cement soil	EnvirOceM soil
Colour	Greyish brown (10YR5/2)	Grey (10YR6/1)	Light brownish grey (10YR6/2)
Appearance	granular	granular	granular

3.1. Mineralogy

X-ray Diffraction was used to determine the mineral composition of the soils prior and post remediation. Figures 5.3-5.5 show the mineralogy of the Astra soils, which comprised quartz (SiO_2), montmorillonite ($(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2{\cdot}nH_2O$), kaolinite ($Al_2Si_2O_5(OH)_4$), illite ($(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$), feldspars, pyrite ($FeS_2$), hematite ($Fe_2O_3$), portlandite ($Ca(OH)_2$), ettringite ($Ca_6Al_2(SO_4)(OH)_{12}{\cdot}26H_2O$), calcite ($CaCO_3$) and bassanite ($CaSO_4{\cdot}1/2H_2O$).

Table 5.2 – Mineral composition of Astra soils at different ages, up to 4 years

Sample	Age (month)	Quartz	Kaolinite	Montmorillonite[b]	Muscovite	Pyrite	Hematite	Calcite	C_2S	C_3S	Aragonite	Portlandite	Bassanite	Ettringite	Anhydrite	Gypsum
Untreated soil	0[a]	●	●	●	●	●										
	16[a]	●	●	●	●	●										
	48	●	●	●	●											
Portland cement soil	0[a]	●	●	●	●			●	●	●	●			●	●	●
	16[a]	●	●	●	●			●	●		●					
	48	●	●	●	●			●				●	●	●		
EnvirOceM soil	0[a]	●	●	●	●				●	●						
	16[a]	●	●	●	●			●	●		●					
	48	●	●	●	●		●	●				●	●	●		

[a] Blue Circle (2002)

[b] identified by clay separation (see full method in Chapter 2)

Kaolinite, montmorillonite, illite, feldspars and quartz are naturally occurring minerals and have been found in the untreated soil, while the other minerals are the result of the treatment of the soil with cement. The distribution of the minerals in the Astra soils is shown in Table 5.2. Secondary minerals such as ettringite, bassanite and calcium carbonate were present in the Portland cement and EnvirOceM soils, whilst a primary cement hydration compound such as portlandite, was observed mainly in the EnvirOceM soil.

3.2. Microstructure

Scanning electron and optical microscopy were employed to determine the microstructure of the S/S soils, in comparison to the untreated soil. A representative image of the untreated soil is shown in Figure 5.6. This consisted of masses of clay, mixed with slag and fragments of unidentified debris. Numerous cracks, thought to be caused by sample preparation, were readily observed throughout the sample.

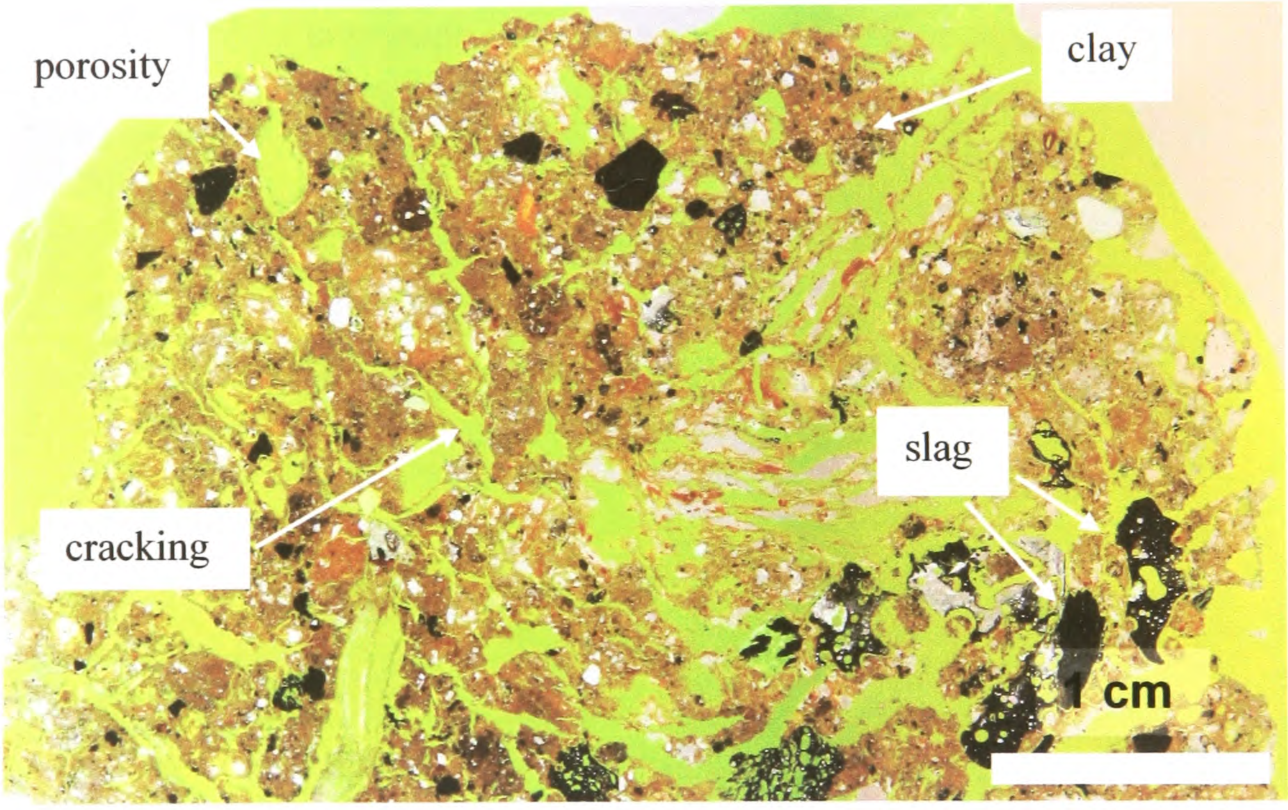


Figure 5.6 – Photograph of a thin section of the untreated soil

Figures 5.7 and 5.8 show an example of the macrostructure of the Portland cement and EnvirOcem soils. Clays, sand, construction debris, plant fragments and slag can be seen in a porous matrix of cement. The pores in the matrix can be distinguished, in the images below, by the yellow colour of the fluorescent resin used to cast the soil sample. It was apparent at this magnification that the EnvirOcem soil was less porous than the Portland cement soil, although they were subjected to identical treatment (see Chapter 4, section 2.1).

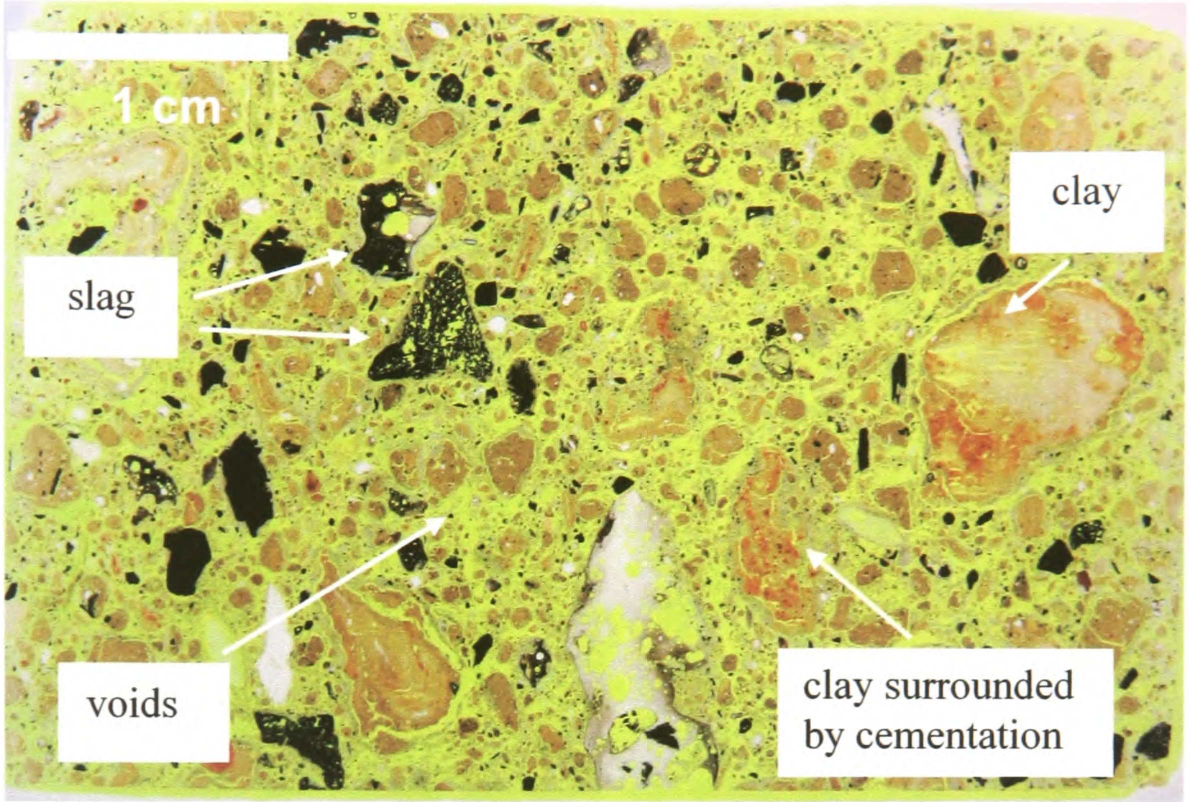


Figure 5.7 – Photograph of a thin section of Portland cement soil

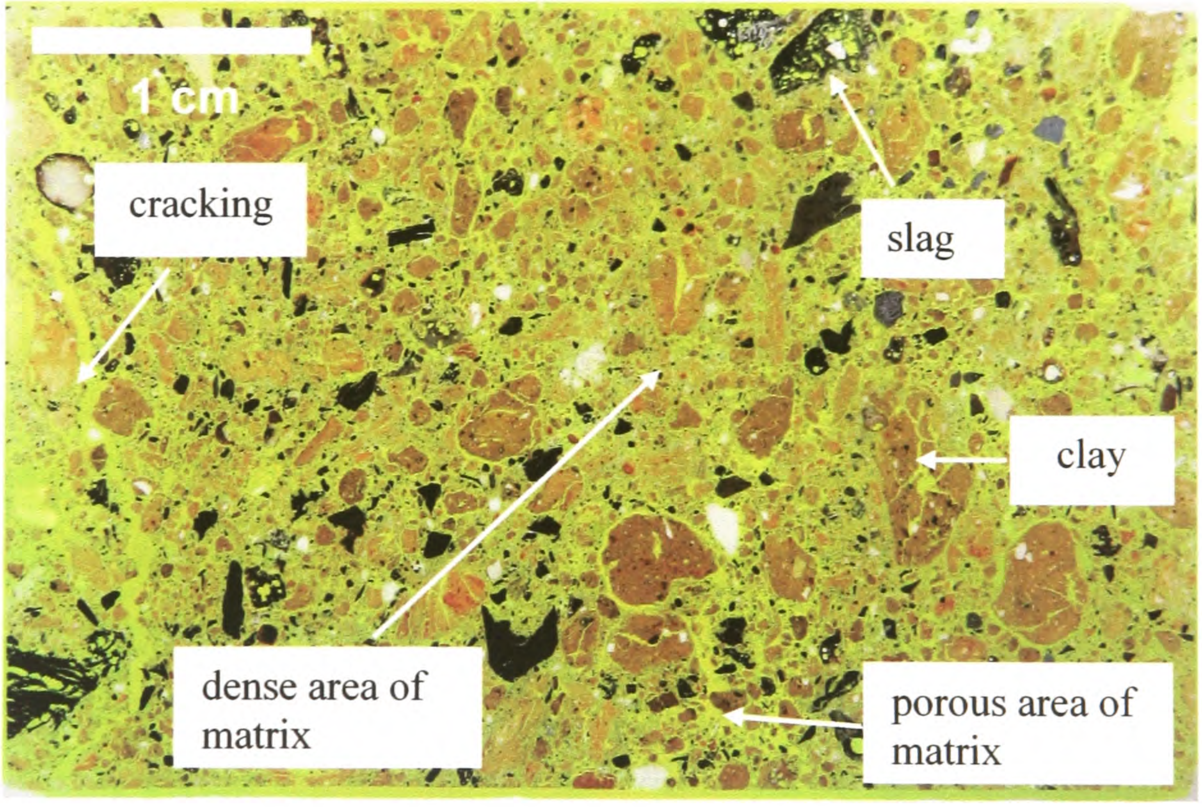


Figure 5.8 – Photograph of a thin section of EnvirOceM soil

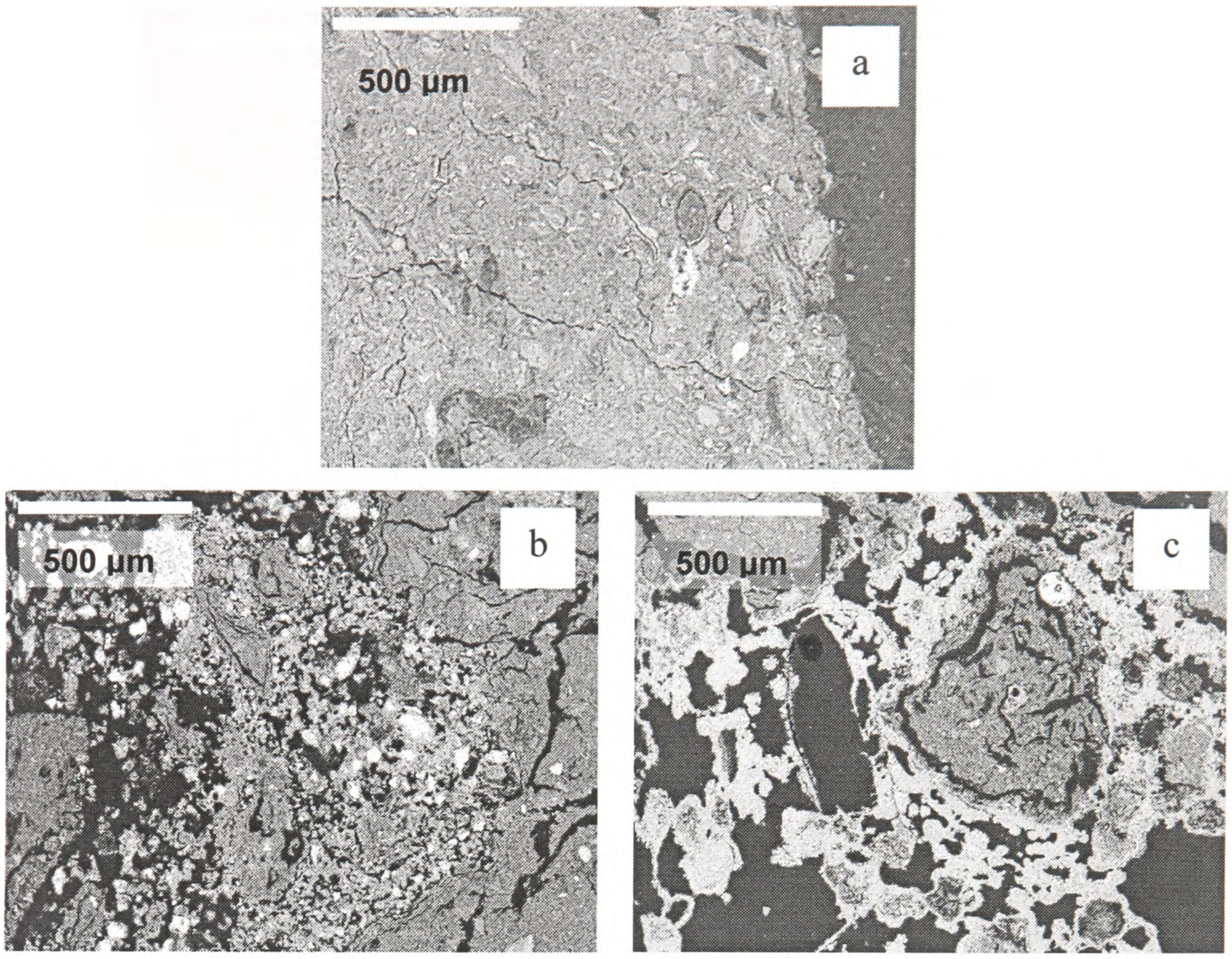


Figure 5.9 – Backscattered electron micrographs of a) untreated soil; b) Portland cement soil; c) EnvirOceM soil

Figure 5.9 shows typical backscattered electron micrographs of the untreated and treated soils. At low magnifications, the dense structure of the clays was noticed, mixed with quartz grains up to 500 µm and other minerals such as monazite, zircon, feldspars, hematite and pyrite, along with fragments of plant root and brick (not shown here).

Residual anhydrous cement grains were observed, mainly in the Portland cement soil. These grains were generally oversized between 40-100 µm across, but particles of less than 20 µm were also present.

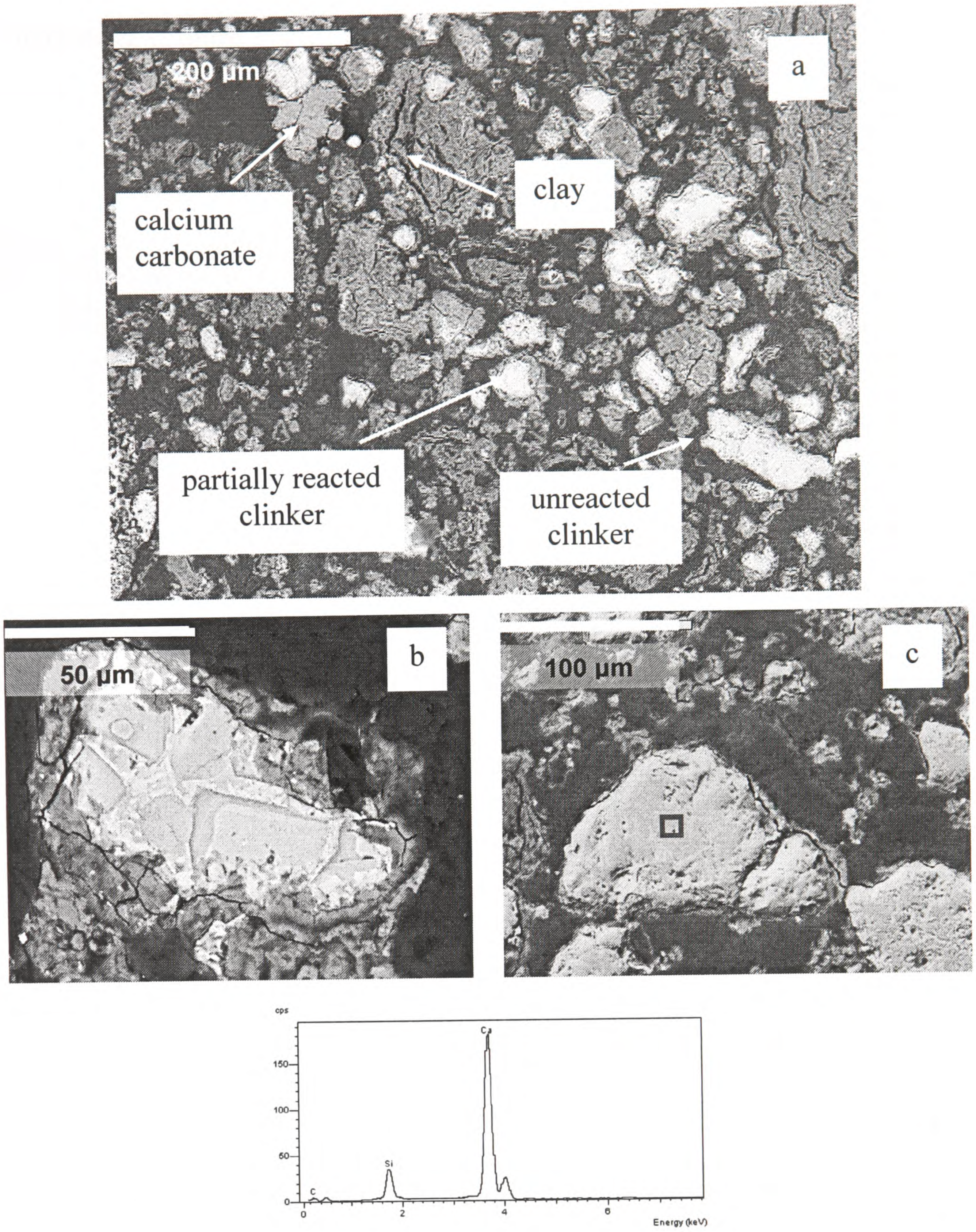


Figure 5.10 – Backscattered electron micrograph showing a) an area containing unreacted and partialy reacted cement grains; b) high magnification image of partially reacted cement grain; c) high magnification image of polymineralic unreacted cement grain and the spectrum, corresponding to C_3S phase (marked area)

Secondary electron imaging of the Portland cement soil revealed that some cement grains were partially hydrated and that the C-S-H gel morphology was characteristic of the earlier stages of hydration (Moser and Stark, 2002), rather than that of a mature cementitious system. At higher magnification (1500x), the cement matrix was characterised by individual clusters of C-S-H with needle-like morphology, typical of early stages of cement hydration (Figure 5.11a) and long interlocking and sharp needles of >10 µm, characteristic of mature cement pastes (Figure 5.11b).

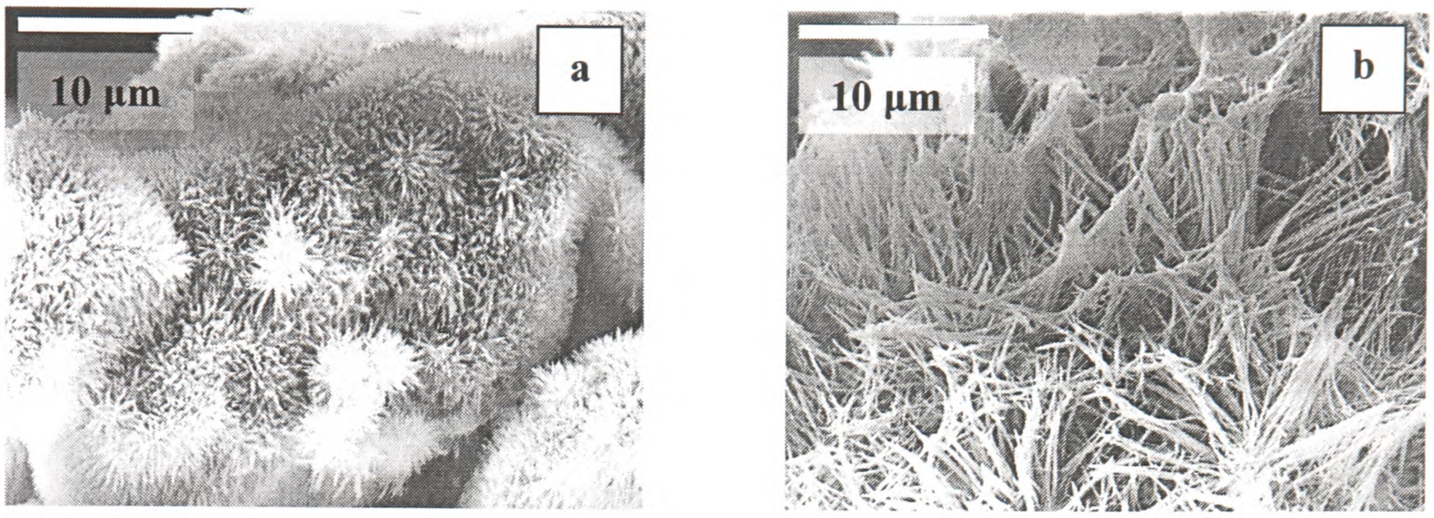


Figure 5.11 – Secondary electron image showing the morphology of early age (a) and mature C-S-H gel (b) from Portland cement treated soil.

The Portland cement and EnvirOceM treated soils also contained calcium carbonate, distributed throughout the matrix and infilling voids and pores. This mineral was present as a layered dense mass in large voids (Figure 5.12) and as fine crystals in the matrix.

Portlandite was readily observed in porous regions, particularly in the EnvirOceM soil (Figure 5.13), and in vicinity of ettringite. Two types of ettringite were found: large rods up to 200 µm in length easily identified with an optical microscope and fine needles of ettringite grouped in rosettes (Figures 5.14). Figure 5.15 shows a typical image of fine ettringite needles observed in pores and the corresponding EDS spectra.

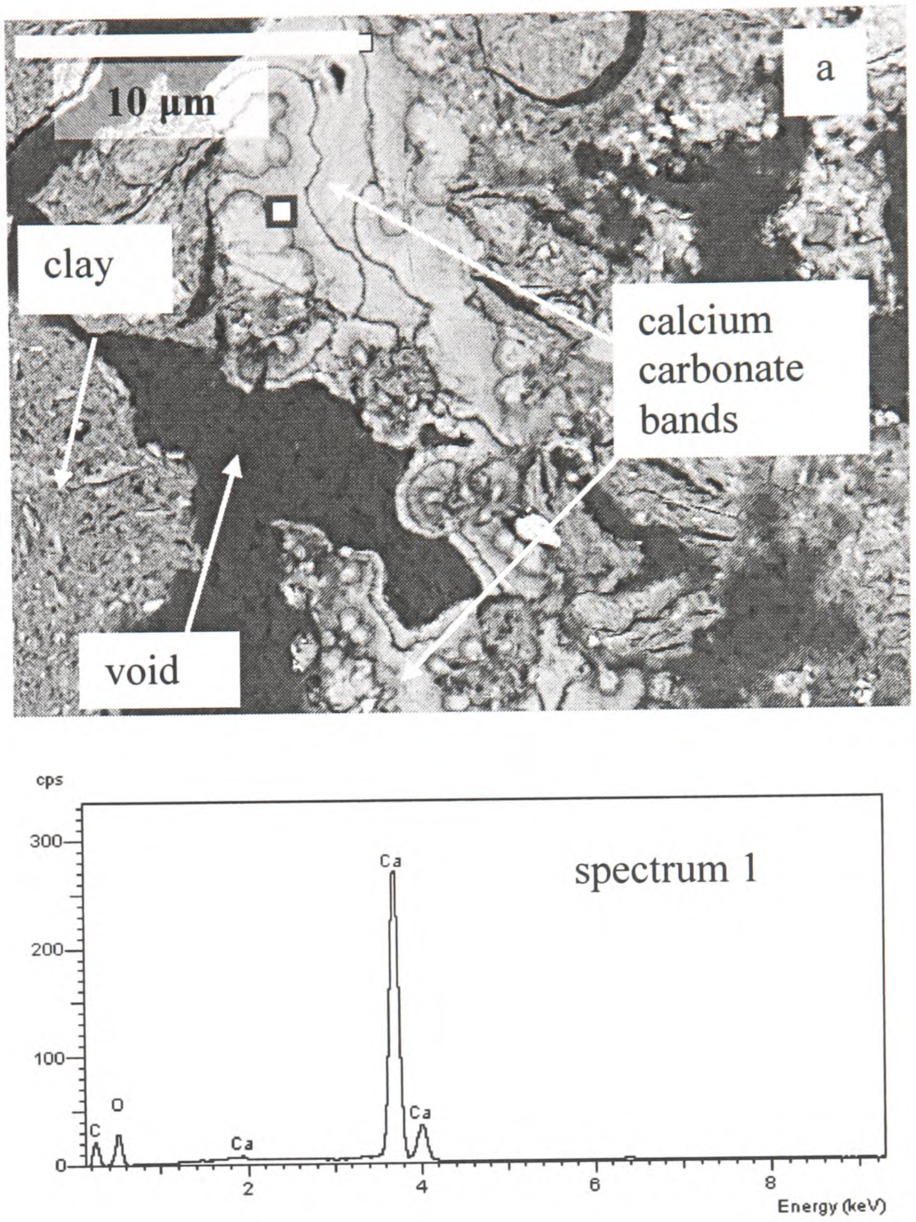


Figure 5.12 - Backscattered electron micrograph showing calcium carbonate layers in the EnvirOceM soil and the characteristic EDS spectrum (spectrum 1)

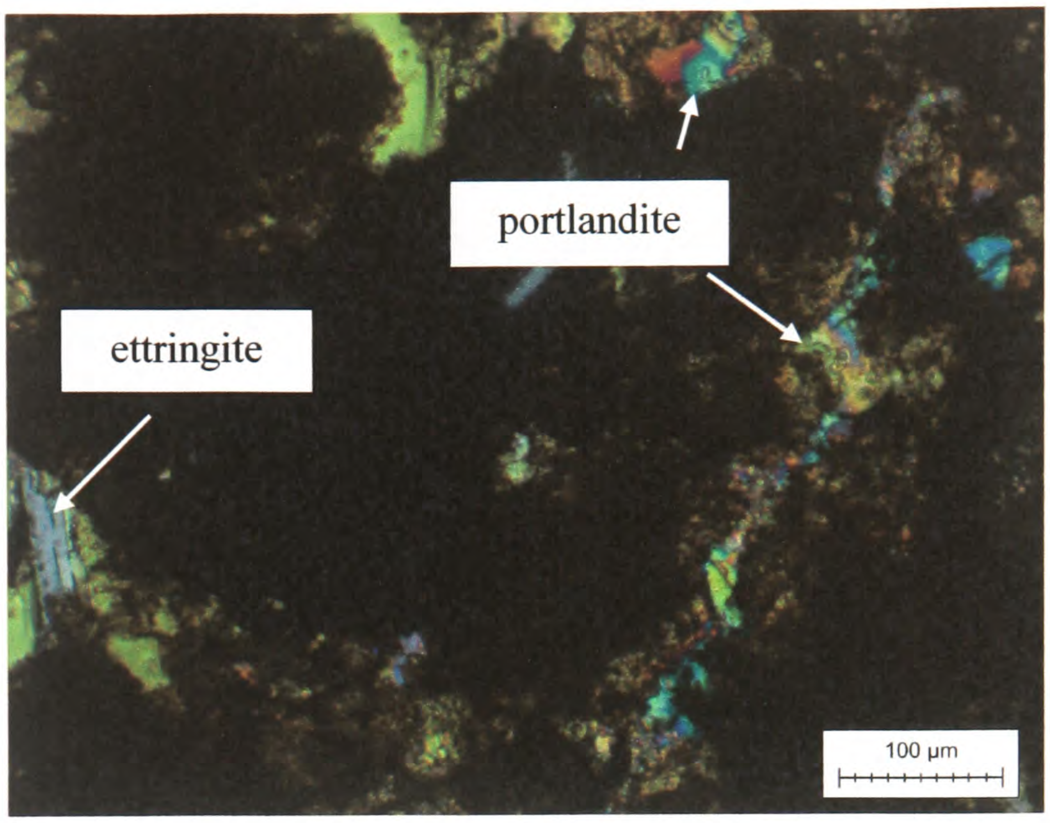


Figure 5.13 – Cross polarised light photomicrograph of portlandite and ettringite in the EnvirOceM soil

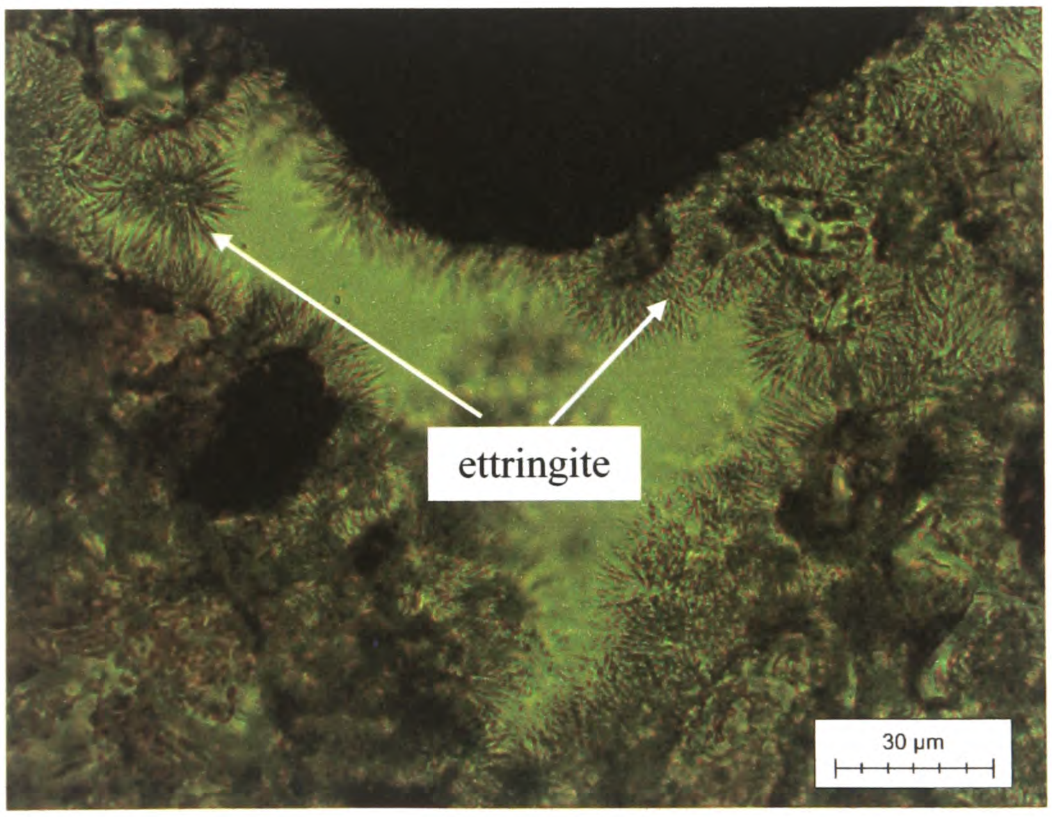


Figure 5.14 – Plane polarised light photomicrograph of rosette-like needles of ettringite developing in cracks, and around aggregates, in the Portland Cement soil

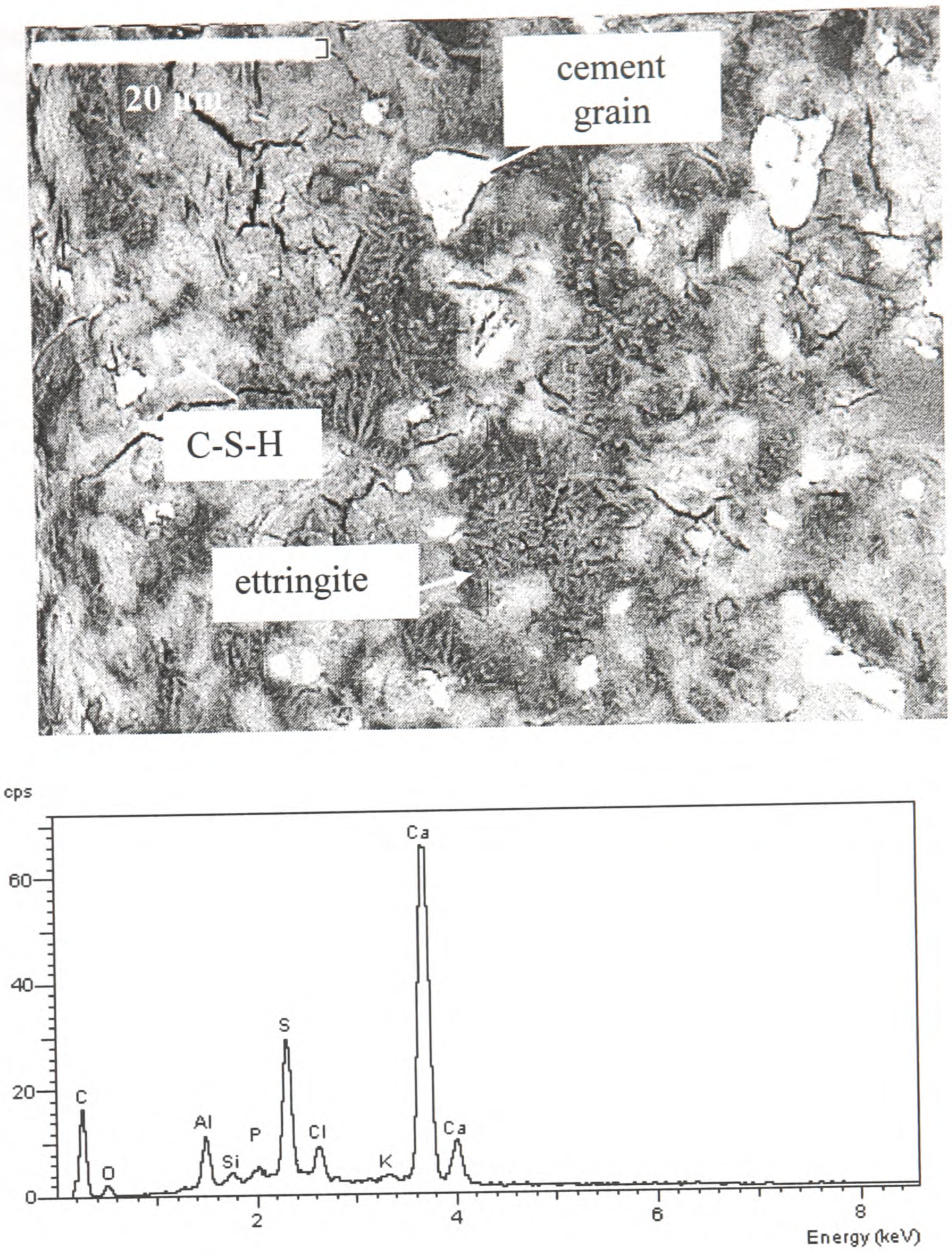


Figure 5.15 – Backscattered electron image of an area with cement grains undergoing hydration and ettringite needles infilling large capillary pores and the characteristic EDS spectrum of ettringite

The contaminants were only observed in the untreated soil. They were distributed as submicron metallic fragments in clay, waste agglomerations and distinct metal fragments (Figures 5.16 and 5.17). An interesting feature observed (shown in Figure 5.18) was the zinc sorbed on clays.

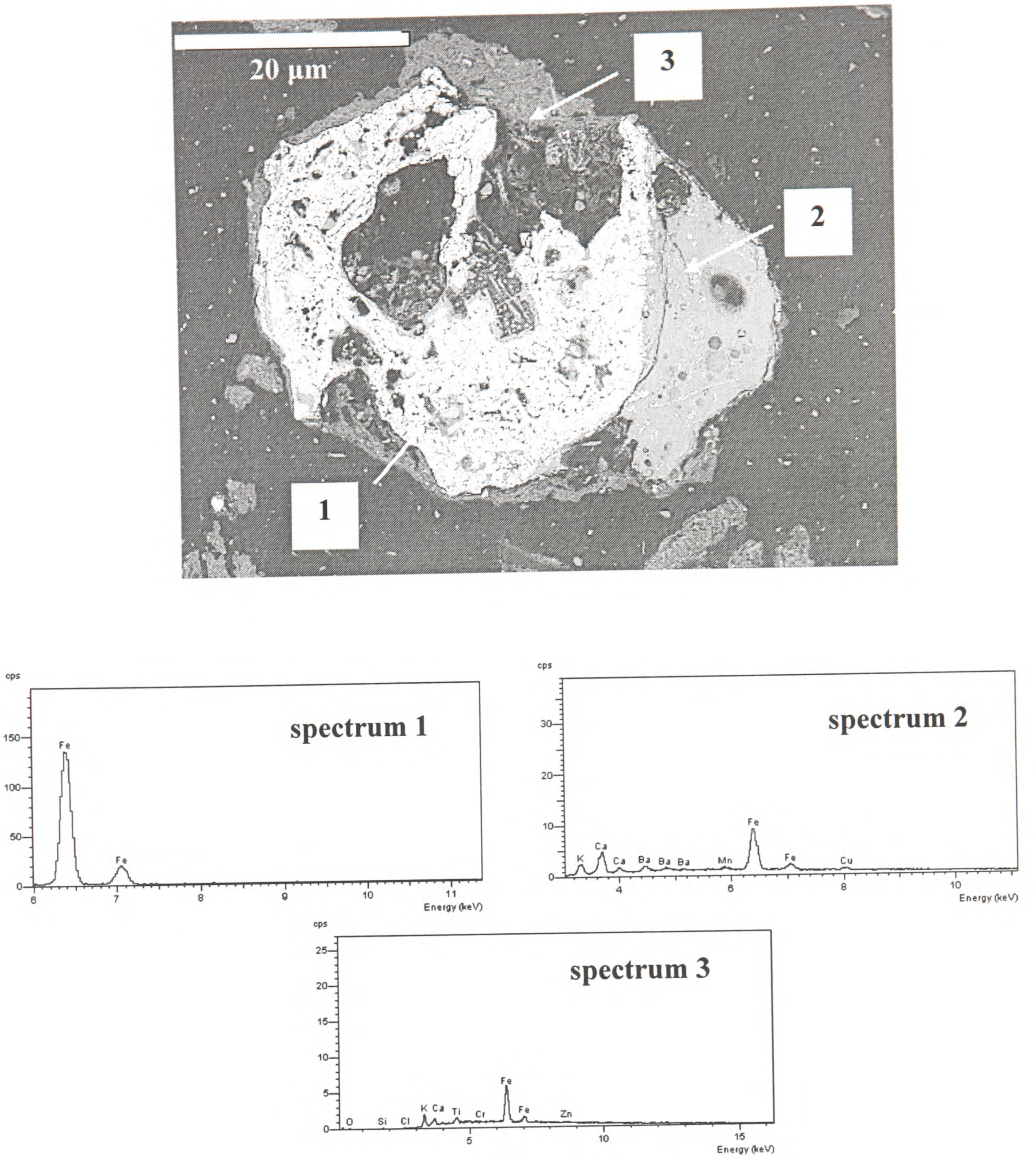


Figure 5.16 – Backscattered electron image of a waste agglomerate containing metallic iron (spectrum 1); mixture of metals (spectrum 2) and metals dispersed in a clay matrix (spectrum 3)

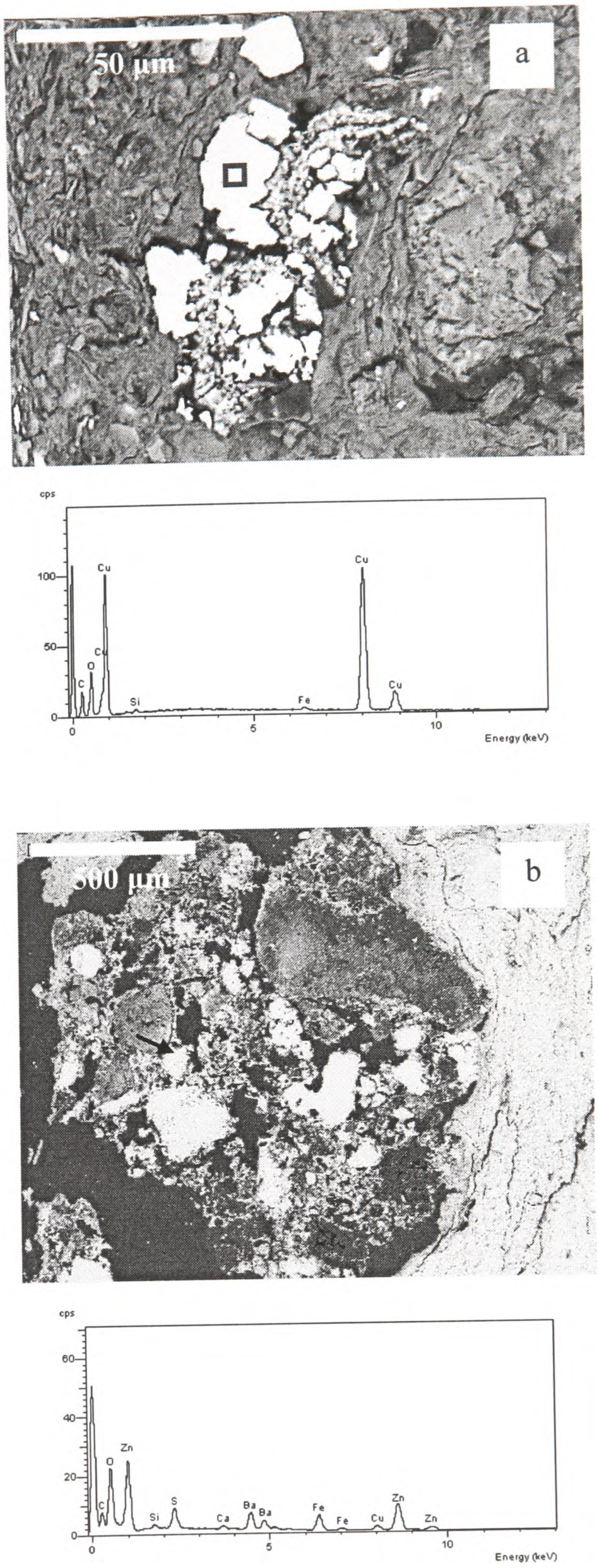


Figure 5.17 – Backcattered electron images of metal contaminants in the Astra Pyrotechnics soil. (a) copper carbonate and spectrum from spot analysis marked with red square; b - mixture of metals and EDS area analysis spectrum

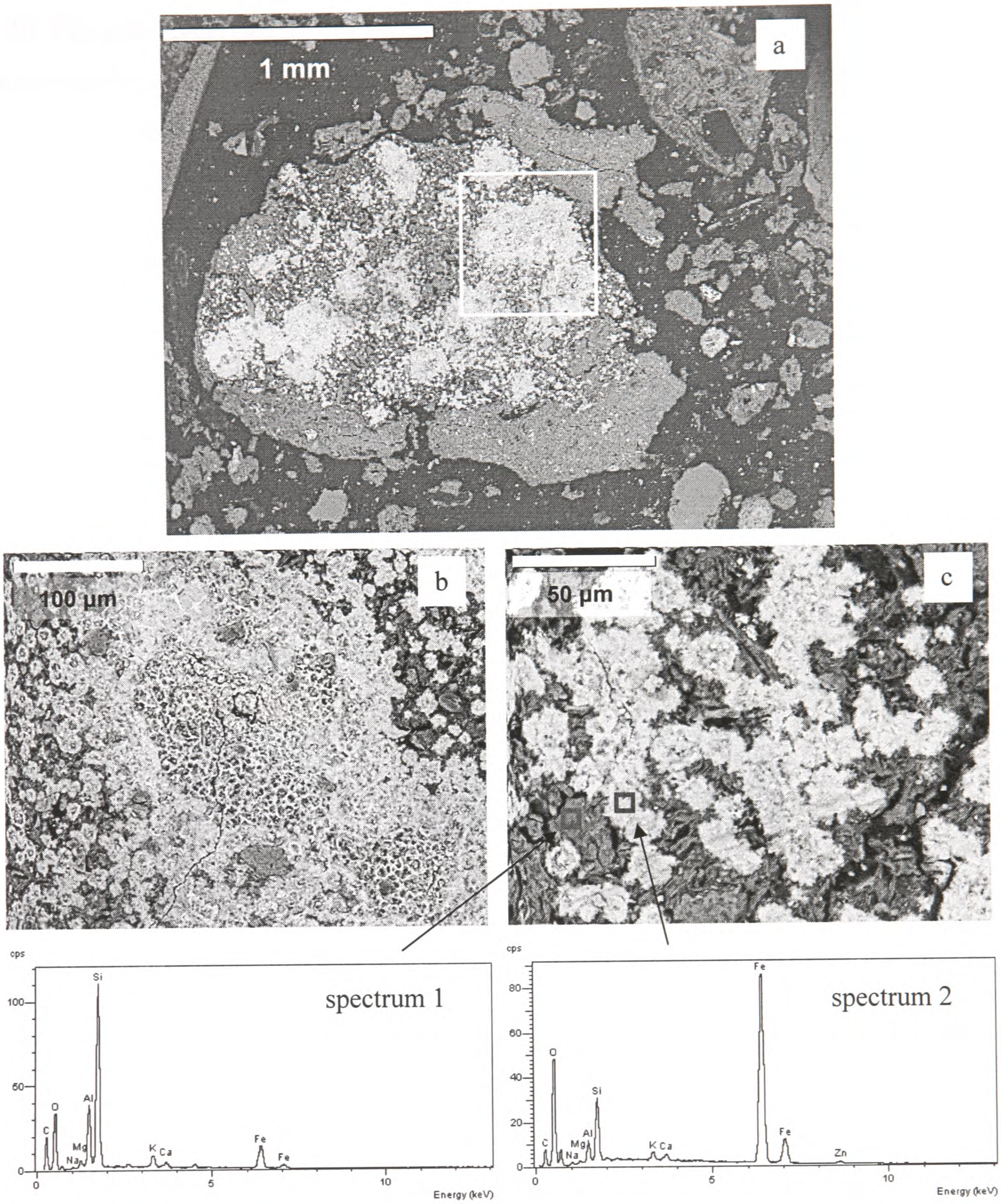


Figure 5.18 – Backscattered electron image of metallic deposit on clayey soils, in the untreated soil (a) (50x magnification); close up of the contaminated area (b), (c) and the corresponding EDS point analysis of the clay (spectrum 1), metal deposit (spectrum 2)

3.3. Chemical composition

The chemical composition of two replicate samples from each cell was determined by x-ray fluorescence for the major elements and loss on ignition for organic content (Figure

5.19). The soils comprised up to 49% silica, 15% alumina, 7% iron oxide and less than 3% alkalis and sulfur. Calcium accounted for up to 1.4% of the weight of the untreated soil and up to 20% of that of the treated soils. The organic matter content (loss on ignition) was an important contributor to the chemical composition of the soils, accounting for up to 25% of the sample weight, as measured according to the oven method described in Heiri *et al.* (2001).

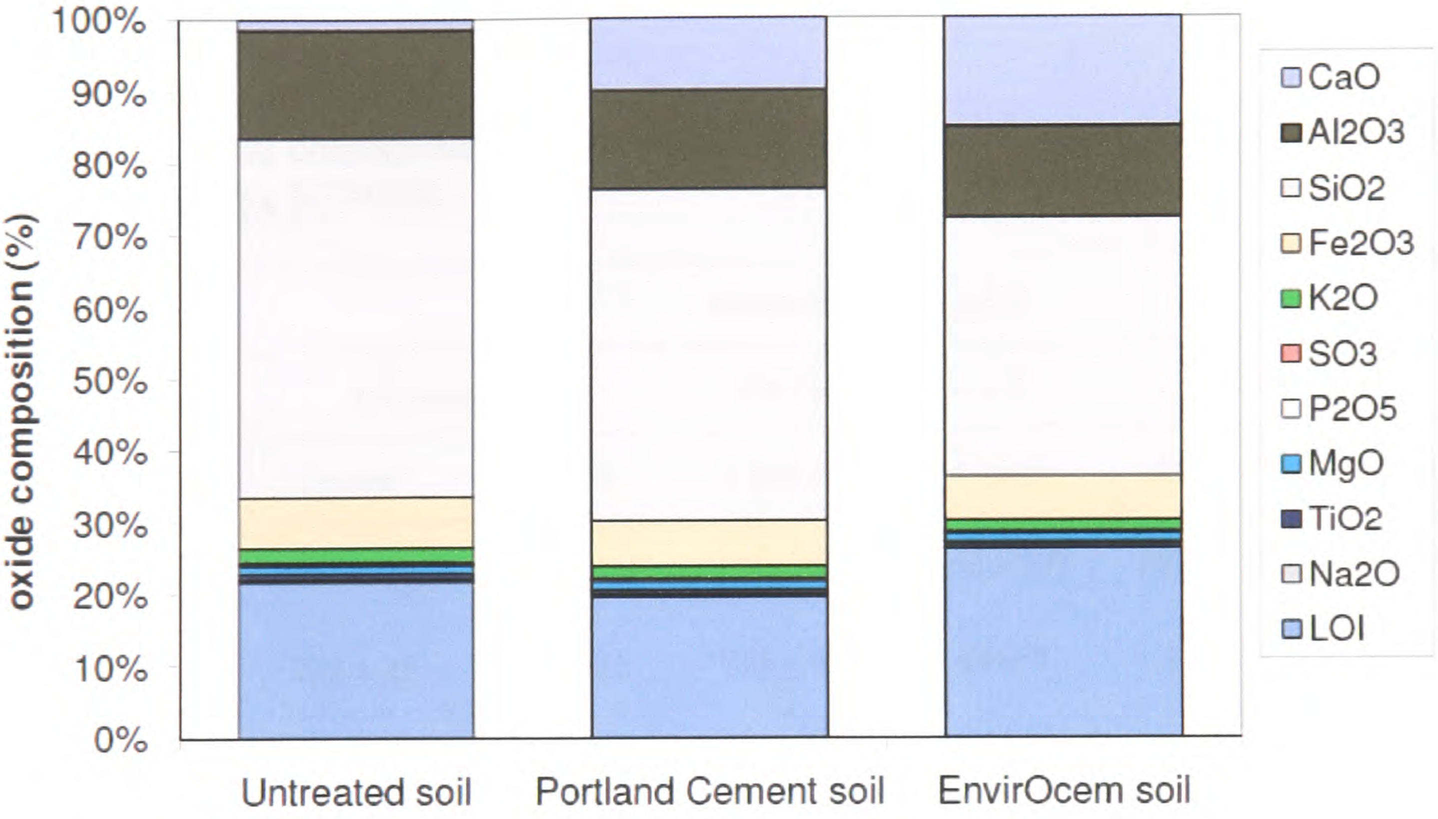


Figure 5.19 – Average oxide composition and loss on ignition (LOI) of untreated and S/S soils

4. Performance of soils with time

The performance of the S/S soils with time was assessed in two ways: i) by reproducing the tests carried out historically such as pass/fail leaching tests and total metal content and comparing the results obtained with the historical data; and ii) by performing specialist leaching tests (pH dependent leaching and acid neutralisation capacity).

4.1. Total metal content

The total concentration of the contaminants of concern (zinc, lead, chromium and copper) of the four year old soils was determined by acid digestion, as described in Chapter 2, section 3.2., and the results are presented in Table 5.3. The concentrations of heavy metals in the untreated soil were generally higher than in the treated soils, except for chromium. These values were compared with historical data (Cutter, 2002), performed according to the same method on the two year old soils (see Chapter 3, section 3.2). Given that this digestion method does not induce complete dissolution of the soil, the recovery rates for each element were considered and the results normalised (Table 5.3). The results showed that the total concentrations of lead and chromium were significantly different between the two and four years old S/S soils.

Table 5.3 – Total contaminant concentration in the untreated and treated soils at different ages measured by ICP-OES

	Concentration (mg/kg)					
Contaminant	Untreated soil		Portland cement soil		EnvirOceM soil	
	2 years*	4 years	2 years*	4 years	2 years*	4 years
Zinc	1245 ± 264	1376 ± 130	779 ± 193	592 ± 217	1073 ± 555	735 ± 79
Lead	224 ± 25	**155 ± 11**	146 ± 36	**89 ± 7**	124 ± 9	**85 ± 29**
Chromium	83 ± 11	**41 ± 9**	71 ± 6	**36 ± 2**	58 ± 2	**18 ± 2**
Copper	468 ± 144	630 ± 201	162 ± 63	147 ± 23	320 ± 97	228 ± 58

values are average of three samples
errors represent standard deviations
bold type represent significant different values
*Cutter (2002)

4.2. Compliance leaching tests

At the time when the Astra soil was remediated, in Autumn 2000, the leaching methods across Europe were not yet standardized and this is reflected in the methods chosen. A number of leaching tests were used to evaluate the metal immobilisation in the cement-treated soils by comparing the values obtained in the present work with the ones at the time of the treatment. This comparison enabled the monitoring of the changes that occurred as a result of environmental exposure.

The S/S samples were tested according to DIN 38414-S4 and TCLP 1311 protocols. Although the DIN 38414-S4 test is appropriate for assessing an immediate potential threat for contaminant release, their long-term release is not rigorously evaluated (Blue Circle, 2000). Not all contaminants are present in water soluble form; hence their immobilisation as a result of leaching with water is not sufficient. Therefore, TCLP 1311 was also carried out. More detailed explanation of these methods is given in Chapter 3.

4.2.1. DIN 38414-S4

The samples extracted from the untreated and treated soils were subjected to the DIN 38414-S4 leaching test and the leachates obtained analysed by ICP-OES (Table 5.4).

Table 5.4 – Metal leaching results obtained following DIN 38414 test, historically and four years after remediation

Contaminant	Leaching Limit[a]	Concentration (mg/l)					
		Untreated soil		Portland cement soil		EnvirOceM soil	
		Historical[b]	2004	Historical[b]	2004	Historical[b]	2004
Zn	5	0.18	1.17±0.26	0.02	0.01±0.01	0.03	0.01
Pb	0.05	0.02	**0.04±0.01**	n.d.	n.d.	n.d.	n.d.
Cr	0.1	0.01	n.d.	**0.11**	**0.13**	0.05	0.03
Cu	5	0.05	0.39±0.04	0.92	0.65±0.02	0.94	0.61±0.02
Final pH	-	nr	7.0	nr	10.5	nr	11.9

[a] 1991 EEC Landfill Directive Draft (EEC, 1991)
[b] from Blue Circle (2002)
bold type indicates values equal or higher than leaching limit
nd – not detected; nr – not reported
2004 values are average of three samples and the errors, standard deviation

The results showed that 0.39 mg/l and 0.65 mg/l of Cu leached from the untreated soil, and the treated soils respectively. Although the Cu leaching was increased by the cement treatment in comparison to the untreated soil, this remained within the prescribed regulatory limit of 5 mg/l. Similarly, Cr was released in higher concentrations from the treated than the untreated soil. The average concentration of Cr leached from the Portland cement and EnvirOceM soils was 0.13 mg/l and 0.03 mg/l respectively. While the EnvirOceM soil was safely within the regulatory threshold of 0.1 mg/l, the Portland cement soil exceeded it. No Cr leaching was measured in the untreated soil. The Pb and Zn leaching was significantly reduced by the S/S treatment by comparison with the untreated soil and remained within the leaching limit of 5 mg/l.

4.2.2. TCLP

Samples of untreated and treated soils were tested using the TCLP 1311 test and the leachates obtained analysed by ICP-OES (Table 5.5).

Table 5.5 – Metal leaching results obtained from TCLP 1311 test historically and four years after remediation

Contam.	Leaching Limit^{a}	Concentration (mg/l)					
		Untreated soil		Portland cement soil		EnvirOceM soil	
		Historical^{b}	2004	Historical^{b}	2004	Historical^{b}	2004
Zn	5	**391**	**9.02±1.64**	**25**	0.16±0.2	**82**	n.d.
Pb	5	0.18	0.14	n.d.	n.d.	0.02	n.d.
Cr	5	n.d	0.12	0.03	0.18±0.09	0.02	0.01
Cu	1	**152**	0.55±0.02	**3.64**	0.7±0.2	**11**	0.9
Final pH	-	nr	5.0	nr	9.6	nr	10.9

[a] USEPA (1998)
[b] from Blue Circle (2002)
bold type indicates values equal or higher than leaching limit
nr – not reported; nd – not detected

The concentrations of heavy metals in the treated soils were lower than in the untreated soil, with the exception of Cu and Cr, but within the prescribed leaching limits of 1 and 5 mg/l respectively. The Zn leaching from the untreated soil exceeded the regulatory limit of 5 mg/l, but was within limits for the Portland cement and EnvirOceM soils. The Pb leaching limits were exceeded by neither the untreated soil nor the S/S soils. The pH at the end of the test was slightly acidic for the untreated soil and mildly alkaline for the treated soils (Table 5.5).

4.3. Specialist leaching tests

4.3.1 pH dependent leaching test

The pH dependent leaching tests were performed to determine the mobilisation of the metals of concern from the S/S soils, at different pH values. Also, the acid neutralisation capacity was measured.

The cement treatment was observed to have improved the contaminant retention, compared to the untreated soil. Figure 5.20 shows the pH-dependent leaching results for the four metal contaminants of concern (Cr, Cu, Pb and Zn). The results showed that the untreated soil had low contaminant leaching at natural pH (Figure 5.20a).

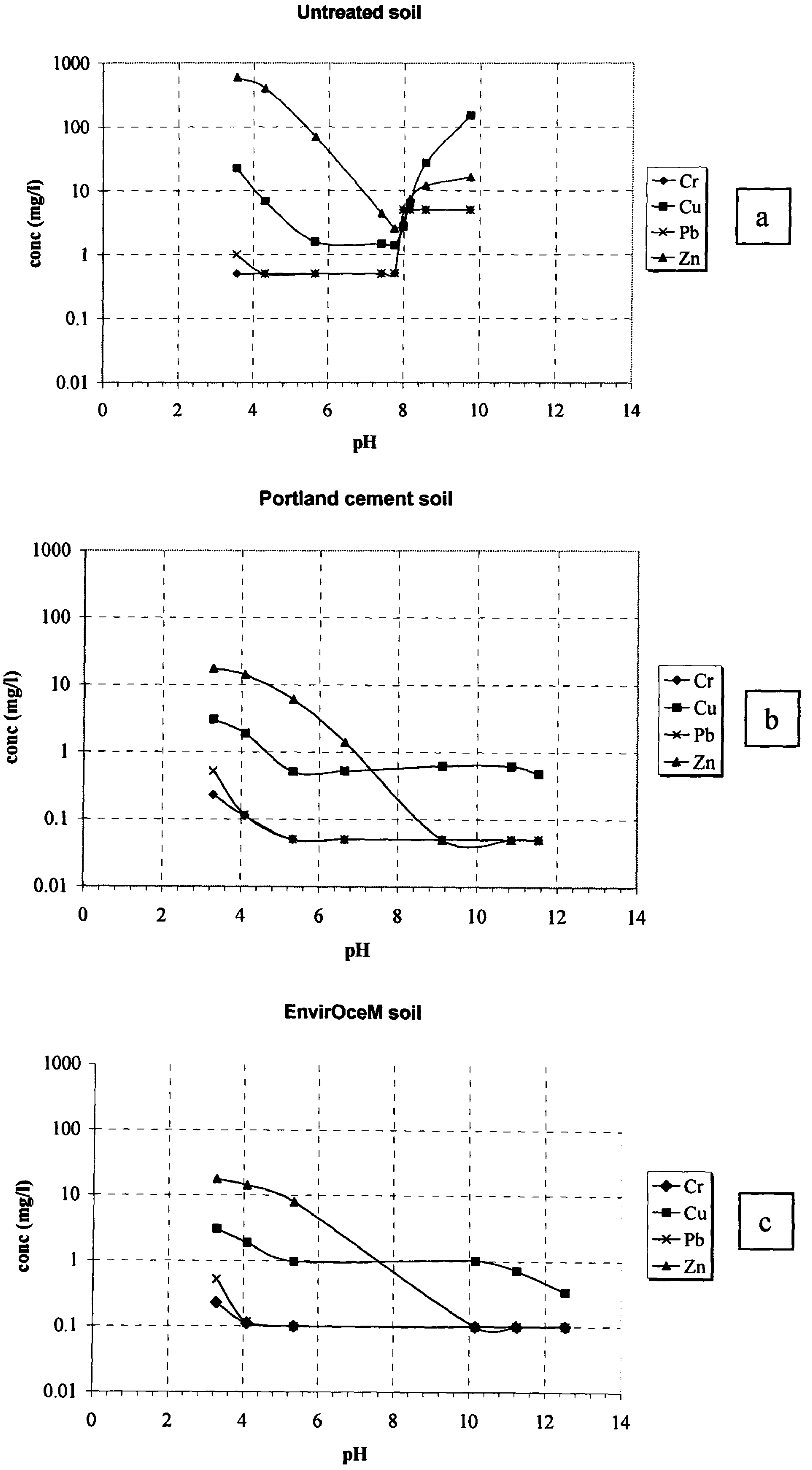


Figure 5.20 – Concentrations of metals released during the pH dependent leaching test on the untreated soil (a), Portland cement soil (b) and EnvirOceM soil (c)

All contaminants of concern displayed an amphoteric behaviour and a minimum solubility over an extended pH range (between 4 and 8), except for Zn. The leaching of Zn was at its lowest between pH 7.5 and 8, but increased sharply on both sides of this interval, particularly in near neutral and acidic pH. An elevated leaching was also noted for Cu, Cr and Pb, which increased by up to 2 orders of magnitude at a pH higher than 8.

Significant differences were observed in the contaminant leaching from the treated soils. The leaching of all contaminants decreased by up to 2 orders of magnitude compared to the untreated soil. Subsequent to the treatment with cement no amphoteric behaviour was observed for any of the contaminants analysed. Overall, the Zn leaching was decreased compared to the untreated soil, with the minimum leaching being achieved at pH 9 for the Portland cement soil and pH 10 for the EnvirOceM soil (Figure 5.20 b, c).

It was observed that the shape of the leaching curves changed dramatically upon treatment, providing a strong indication of different chemical phenomena governing the release of contaminants from the treated material. Modelling of the leaching behaviour was performed using Visual MINTEQ software and the findings were published in Antemir *et al.*, (2010a).

The modelling results suggested that the immobilisation of contaminants in the S/S soils is assured by either encapsulation or incorporation in the aluminosilicate hydration phases. Moreover, the leaching of contaminants from the untreated soil as a function of pH was not attributed to any mineral present in the thermodynamic database used for modelling, except for Cu under alkaline conditions, with tenorite (CuO) described the solubility of this metal at pH > 8. The absence of key phases for trace metals suggests that metal contaminants were present in the soil in complexes that are difficult to describe as pure solids. This is supported by the findings from microstructural observations, where, for example, Zn was associated with the clay particles.

4.3.2. Acid neutralisation capacity

The untreated soil had negligible acid neutralisation capacity (Figure 5.21). The pH showed a steep drop from near neutral pH to approximately pH = 4, after low acid addition (<0.1 meq/g).

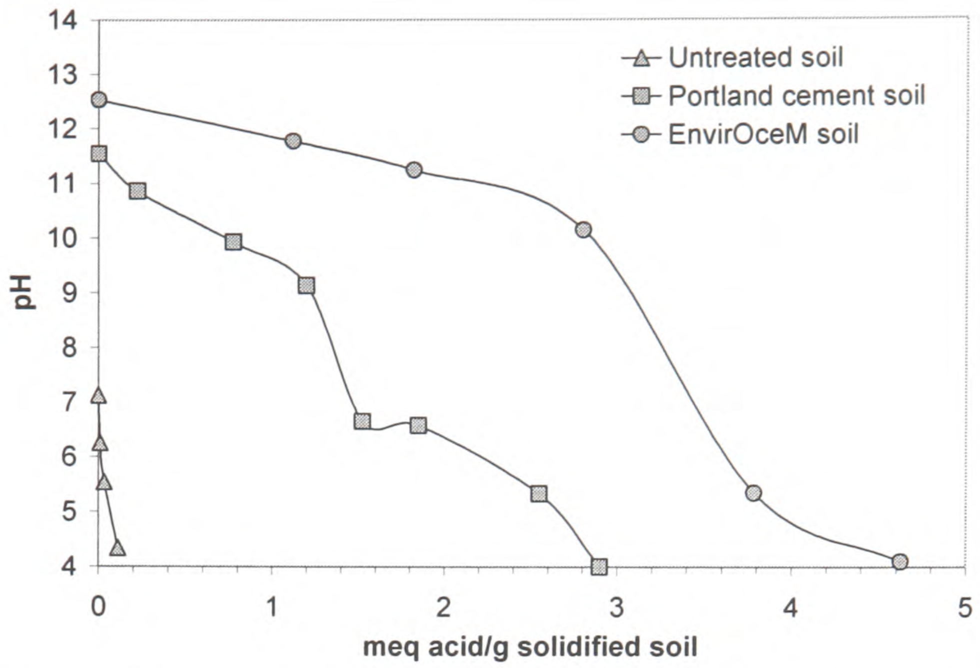


Figure 5.21 – Acid neutralization capacity curves of the untreated and S/S soils

The two treatments have resulted in different ANC curves, despite the use of identical binder content and exposure to similar environmental conditions. The Portland cement soil showed an initial gradient from the natural pH of 11.8 to a pH 9.1, followed by a sharp drop to pH 6.6 and a narrow plateau between pH 6.6 and 6.2. Below pH 6.2, there was a steady decrease to the final chosen pH=4. By contrast the EnvirOceM soil exhibited a plateau between natural pH=12.5 and pH=10.1, and a steady drop to pH=4. The total ANC to pH 4 ($ANC_{4.0}$) was highest for the EnvirOceM soil (4.6 meq/g), followed by the Portland cement (2.9 meq/g) and the untreated (0.1 meq/g) soils.

5. Discussion

5.1 Mineralogy and microstructure

The mineralogy of the Astra soil was examined at different ages following remediation. The examination revealed that the treated soils are metastable. According to Blue Circle (2002) the mineralogy of freshly treated soils and those 16 months old was composed of a number of crystalline phases and natural minerals, components of soil as shown in Table 5.2.

The mineralogy of the treated soils was identical, irrespective of the type of binder used. Most phases present are a result of cement hydration, but also of the environmental exposure.

Calcium carbonate was the most abundant phase formed. Since the treated soils were not capped, carbonation of the cement phases was expected as indicated in the conceptual model (see Chapter 4). It is obvious that, in the case of the Portland cement soil, carbonation started during processing of the material and continued after the soil placement. Contrary to this, no calcium carbonate was identified in the EnvirOceM soil until 16 months, suggesting in-situ carbonation. Initially, two calcium carbonate polymorphs had formed namely aragonite and calcite, which evolved with time towards the more stable calcite. This resulted mainly from the carbonation of portlandite by contact with rain water containing dissolved atmospheric CO_2 and was supported by the XRD results, which showed a decrease in portlandite peaks with increase of those of calcite (Figures 5.3 – 5.5).

Carbonation influenced the stabilised soils in several ways, through densification of the microstructure, and by a decrease of pH. It is well known that the volume change accompanied by this reaction contributes to an infilling of pores and voids (Lange *et al.*, 1996). For example, massive, stratified deposits of calcium carbonate were visible in the matrix porosity, indicating discontinuous episodes of precipitation during wetting and drying cycles (Figure 5.12). In the same way as in exposed concrete, carbonation of the S/S soils is aided during semi-dry weather and inhibited by wet weather, when the pores are saturated (Fernandez-Bertos *et al.,* 2004; St. John *et al.,* 1998). The examination of X-Ray diffactograms (Figures 5.3 – 5.4) indicated a deep carbonation in the S/S soil, which was more pronounced in the first 5 cm below the surface. Although not much data is available on the depth of penetration of carbonation in cement stabilized soils, most comparisons in the literature are made with the closest homologue, concrete. The literature showed that the surface of a good quality concrete generally carbonates at a rate of few mm/year (St. John *et al.,* 1998), therefore carbonation depths of up to 45 cm within 4 years may only be ascribed to the granular nature of the soil observed at sampling.

The S/S soils have also been affected by reactions involving sulfate ions. Ettringite and bassanite were identified by XRD and confirmed by SEM. Short, thin interlocking crystals were formed in pores within the matrix (Figure 5.15), whilst dense rosette-like clusters were formed in voids, where there were no spatial obstructions (Figure 5.14). The formation of ettringite is promoted by the water movement and pore fluid transport in the soil (St. John *et al.,* 1998), therefore the lack of compaction and capping have created the good conditions for ettringite to form in the treated Astra soils.

The literature considers ettringite formation as a degradation mechanism in concretes, however many authors have also recognised its benign effect. Ettringite, depositing in voids and cracks in the structure of cement-stabilised, soils is unlikely to cause any damage, as it is freely occupying available space (Taylor *et al.,* 2001; Diamond, 1996; Klich, 1997; St. John *et al.,* 1998). At the same time, interlocking ettringite crystals in the voids have been shown to contribute to strength development (Hills and Pollard, 1997) rather than disrupt the structure of the soils. This said, no deleterious effects were observed or are expected at the Astra site due to the presence of ettringite, because of the porous, granular nature of the soil, where expansive growth can be accommodated.

The presence of bassanite (dehydrated gypsum) in the treated soils may indicate that several mechanisms are active: gypsum may result from the decomposition of ettringite at pH below 10.5 (Klemm, 1998), or it can form instead of ettringite when the aluminium is depleted and soluble sulfates are present (Gollop and Taylor, 1995; Hime and Mather, 1999). Bassanite is not necessarily formed in the treated soils, but is rather an artefact of sample preparation. It is known that grinding a soil for X-Ray analysis can lead to high temperatures resulting in complete dehydration of gypsum into bassanite and anhydrite (Lawrence, 1998).

It is generally accepted that the mechanism of formation of gypsum determines the degree of expansion (Tian and Cohen, 2000). Through-solution formation is unlikely to cause any degradation, whilst formation by topochemical reaction is generally regarded as potentially damaging (Neville, 2004). As far as this study is concerned, the mechanism of formation of gypsum in the treated soils is unclear. However, in general, 'sulfate attack' describes damage caused by sulfate-bearing phases i.e. ettringite, gypsum and thaumasite, but in the Astra soils there were no apparent deleterious effects associated with their presence.

Unhydrated cement was abundant in the Portland cement-treated soil. St. John *et al.* (1998) recognised that large grains of cement are highly resistant to hydration, even in concretes exposed to the air over longer periods of time. Although this is true in highly impermeable systems like concrete, the presence of large amounts of unreacted cement grains in four-year old cement treated soils is unusual, given that they were exposed to frequent wetting and drying episodes in the environment. The retardation of cement hydration was not anticipated, but may have been caused by the presence of soil organic matter (SOM), clays or heavy metals (Conner, 1990). The SEM observations revealed the presence of the early age C-S-H gel 4 years after treatment, which suggests that the retardation of hydration is time-dependent rather than permanent.

The lack of hydration of the Portland cement soil was reflected in its buffering capacity. Although by comparison to the untreated soil, the buffering capacity of both treated soils was significantly improved (Figure 5.21), the Portland cement soil had a lower buffering capacity than the EnvirOceM soil. The main difference between the two soils was noted in the high pH range (10-12.5), which can be ascribed to the reduced presence of $Ca(OH)_2$ and C-S-H in the Portland cement soil (Giampaolo *et al.,* 2002; Sweeney, 2001). Moreover, the XRD results showed the presence of trace amounts of portlandite, in the Portland cement soil, which is refected by the shape of the ANC curve produced.

Whilst the EnvirOceM soil ANC is mainly assured by the minerals at high pH, that of the Portland cement soil is a combination between minerals at high pH and carbonates at pH between 6-7 (Sweeney, 2001).

5.2. Leaching behaviour

One of the aims of this chapter was to reproduce the tests performed historically and compare the results with those from the current work (leaching and total content).

The total metal concentration at two and four years showed that the metal contaminants are not permanently immobilised in the S/S soils, as described in the literature (Conner, 1990; Perera *et al.,* 2005a). However, the accelerated laboratory tests and the pH dependent leaching test indicated that the Cu, Cr, Pb and Zn leaching from the S/S soils was gradual and within the prescribed thresholds. The contaminants from the untreated soil were released in concentrations exceeding the prescribed thresholds, therefore representing a potential environmental risk.

The results from geochemical modelling suggested that, in the untreated soil, Zn may be involved in surface precipitation or complexation, as no Zn-bearing minerals in the database fitted the experimental curves for this element (Antemir *et al.*, 2010a). This is in keeping with the SEM observations, which reveal Zn/Fe precipitates on the surface of clayey soil (Figure 5.18) and is supported by the literature (Conner, 1990).

There was a clear indication of the improved immobilisation of the contaminants in both treated soils, compared to the untreated soil. Non-amphoteric behaviour was observed after the cement treatment, suggesting that the contaminants were incorporated in the cement hydrates rather than as precipitated metal hydroxides. Stegemann (2005) reported that in S/S soils, Cu and Pb are immobilised via sorption to the silicate layers of the C-S-H hydrates rather than substituted in the C-S-H structure.

5.3 Acid neutralisation capacity

The response of hydrated cement to acid addition is dependent on the hydration products formed (Stegemann *et al.*, 1997). The EnvirOceM soil displayed the strongest buffering capacity at high pH ($ANC_{9.0}$). The contributing phases within the pH interval 12 – 10 are portlandite and variable Ca/Si ratio C-S-H, but also ettringite (Gianpaolo *et al.,* 2002). Despite the identification of calcium carbonate by SEM and XRD, there was no distinct plateau due to the buffering of this mineral. As shown by the SEM examination the Portland cement soil ANC was characterised by carbonates and to a lesser extent cement hydrates due to the delay in cement hydration. The resultant overall $ANC_{4.0}$ was lower for the Portland cement soil than the EnvirOceM soil; however this is expected to improve as the cement continues to hydrate.

The investigation highlighted that microstructure, mineralogy, and leaching were key performance indicators. Therefore, the following chapter will examine microstructural and mineralogical indicators in the full scale remedial operations. Chapter 7 will explore the leaching behaviour of the full scale sites.

6. Conclusions

In this chapter, the performance with time of the Astra Pyrotechnics soil was studied. This site was considered as a worst-case scenario for exposure of an S/S soil, since it was in direct contact with the atmosphere and was granular rather than monolithic in nature. A number of tests were employed to characterise the S/S soils such as SEM and XRD.

Regulatory and specialist leaching tests were used to evaluate the contaminants release from the S/S soils.

The conclusions of this chapter are:

- The mineralogy and microstructure of the S/S soils consisted of naturally occurring minerals, cement hydrates and compounds as a result of weathering that were characteristic of those found in cementitious systems such as ettringite, calcium carbonate and bassanite.

- Carbonation was the main phenomenon taking place in the Portland cement and EnvirOcem soils. Carbonation resulted in physical improvement of the soils by blocking the voids in the matrix, therefore reducing the porosity. Carbonation led to a decrease in pH at air exposed surfaces, but was more pronounced in the Portland cement treated soil.

- The presence of ettringite and bassanite was noted in both treated soils, but no damaging effects were apparent. The granular, opened matrix was able to accommodate the volume increase, generally associated with the formation of ettringite.

- Unhydrated cement was frequently observed in the four year old Portland cement soil, which indicated a delay of the binder hydration. The C-S-H gel morphology showed mixed characteristics of both early stage of cement hydration, as well as mature stage. This suggested that the inhibition of the cement hydration is time dependent rather than permanent. The cause of this phenomenon remains unknown.

- The acid neutralisation capacity of the S/S soils was superior to that of the untreated soil and increased in the following order: untreated soil < Portland cement soil < EnvirOcem soil. The ANC of the EnvirOcem soil at high pH was controlled by minerals such as portlandite and the C-S-H. For Portland cement, ANC was due to carbonates and cement hydrates.

- The contaminant leaching was within the prescribed limits for TCLP, but exceeded the drinking water quality limit, following DIN leaching test, for chromium.

However, the metal retention indicated an improvement with time, as shown by comparison with historical tests.

- By performing SEM analyses of the S/S soil important information on the location of contaminants, integrity of the microstructure, composition of the hydration phases as well as location of secondary products were obtained. The presence of certain minerals determined by XRD was not sufficient to imply damage to the S/S soil matrix; therefore the use of SEM combined with XRD offers a better understanding of the processes and their effects on the S/S soil.

- The factors which represent potential risk indicators for the performance of S/S soils are carbonation, ettringite and bassanite formation. Although these minerals did not represent a risk for the Astra soil, they may affect the monolithic soils.

The next chapter examines the physical, chemical and microstructural properties of S/S soils obtained from full scale remedial operations. The risk indicators identified in this chapter form the basis of the study.

Chapter 6 Characterisation of full-scale S/S soils

1. Introduction

In the previous chapter the behaviour of a pilot scale S/S soil with time was assessed through a series of chemical, mineralogical and microstructural analyses. The study yielded information for the design of the experimental investigation of samples obtained from full scale sites. The results showed that the four year old S/S soil, underwent mineralogical and microstructural changes and the most common processes taking place were carbonation and sulfate mineral formation (e.g. ettringite and bassanite).

This chapter examines the samples obtained from seven full-scale remedial operations. Microscopy, diffractometry and mechanical tests are used to evaluate the materials after several years in the service environment.

2. Sites summary

In order to assess the performance of S/S, sites with a variety of contaminants, environmental scenarios, soil types, remediation formulations, S/S implementation methods and ages were selected. The sites examined were contaminated with heavy metals, metalloids and organic compounds including PAH, BTEX, TPH and dioxins. As usually found in real situations, the contamination at any one site was a mixture of inorganic and/or organic compounds. However, the highest concentration and highest risk contaminant(s), termed contaminants of concern, were considered for the purpose of remediation and subsequently for this study. A full description of the level of contaminantion at each site is given in Table 6.1.

The environmental setting varied from savannah to humid subtropical climate, in the US, to humid temperate climate, in the UK (Earth System Research Laboratory, 2010). The location of each site in the US and the UK is shown in Figure 6.1 and a summary of their site specific characteristics is presented in Table 6.1. To date, the oldest S/S soils from real applications that have been studied were 6 years old (Klich, 1996), whereas the sites examined here extend to up to 16 years.

Figure 6.1 – Location of the S/S sites studied

Table 6.1 - Characteristics, contaminants and remediation formulation of the cement-stabilised sites studied and the date of sampling for each site

Site and location (abbreviation)	Contaminants of concern	Contaminant concentrations	T Date	S Date	Type of remediation and cover system	Depth of remediation	Remediation formulation
Pepper Steel, USA (PS)	Lead; PCBs	2,000 mg/kg; 116 mg/kg	1989	2003	Ex situ S/S (compacted) Capped with crushed limestone	0.6 – 2.4 m	8% PFA + 12% PC mix
Columbus MGP, USA (MGP)	PAHs; TPH	2,400 mg/kg; 5,500 mg/kg	1992	2004	Ex situ and in situ S/S HDPE cap and topsoil	10 m	10% PC (site) 25% PC (retaining wall)
Quarry Dump, USA (QD)	TPH	1,200 mg/kg	1994	2004	In situ S/S	1.2 -1.5 m	25% PC
South 8th Street, USA (S8)	Lead in waste oil residuals, sulphuric acid	22,000 mg/kg pH often less than 1.0	2000	2004	In situ S/S GCL cap and topsoil	5.1 m	25% crushed limestone (pre-treatment of acidic soil) 20% PC + 10% PFA mix
American Creosote, USA (AC)	Arsenic, PAHs, PCPs, Dioxins, in creosote/soil	225 mg/kg; 335 mg/kg; 3000 mg/kg; 0.00225 mg/kg	2000	2003	Ex situ S/S (compacted) GCL cap and topsoil	0.6 – 1.5 m	5% PC + 4.5% PFA + 1.3% activated carbon
Halton, UK (HA)	Lead, Arsenic, Zinc, Copper	1,550 mg/kg 825 mg/kg; 980 mg/kg; 639 mg/kg	2000	2005	In situ S/S Railway ballast, permeable membrane and topsoil	0.3 m	6% PC + 0.5 % proprietary additive
Caerphilly, UK (CA)	PAHs, TPHs	32,960 mg/kg and TPHs up to 27,845 mg/kg	2006	2006	In situ S/S Topsoil	1 -1.5 m	4% PC + 8% pozzolana

T Date – treatment date; S date – sampling date; HDPE – high density polyethylene, GCL – geosynthetic clay liner, PAH – polyaromatic hydrocarbons, PCP – pentachlorophenol, PCB – polychlorinated biphenyls. Mix percentages reported as ratios to soil

3. Results

3.1. Physical characterisation

3.1.1 Visual observations

Although cement-treated soils are compared to concretes (Klich, 1996), this is inappropriate, as observed from sampling. The majority of the S/S soils were poorly-indurated materials as shown in Table 6.2. At a microscopic level the microstructures are heterogeneous and complex, and these will be described in the following sections.

Table 6.2 – Characteristics of S/S soils sampled

Site	Colour[1]	Appearance
PS	Grey (10YR6/1)	Monolithic
MGP	Light grey (5Y7/2)	Monolithic
QD	Very pale brown (10YR7/3)	Poorly indurated
S8	Grey (10YR6/1)	Poorly indurated
AC	Grey (10YR5/1)	Monolithic
HA	Grayish brown (10YR5/2)	Monolithic
CA	Dark grey (10YR4/1)	Poorly indurated

[1] Munsell soil colour charts, 1994

With an unaided eye, the S/S soils contained large voids and fine cracks, as seen in Figure 6.2. The colour of the soil/cement matrices under transmitted light was usually greenish brown to dark brown. The darker brown colouration appeared to be due to the presence of fly ash. The typical grain size of the matrices varied from clay-sized to fine and coarse sand-sized particles. All the S/S soils were heterogeneous and contained numerous inclusions of 'foreign' material which were mostly white or black in colour, but also red, tan and grey, representing fragments of rock, coal, limestone, slag and contaminated materials (Table 6.3).

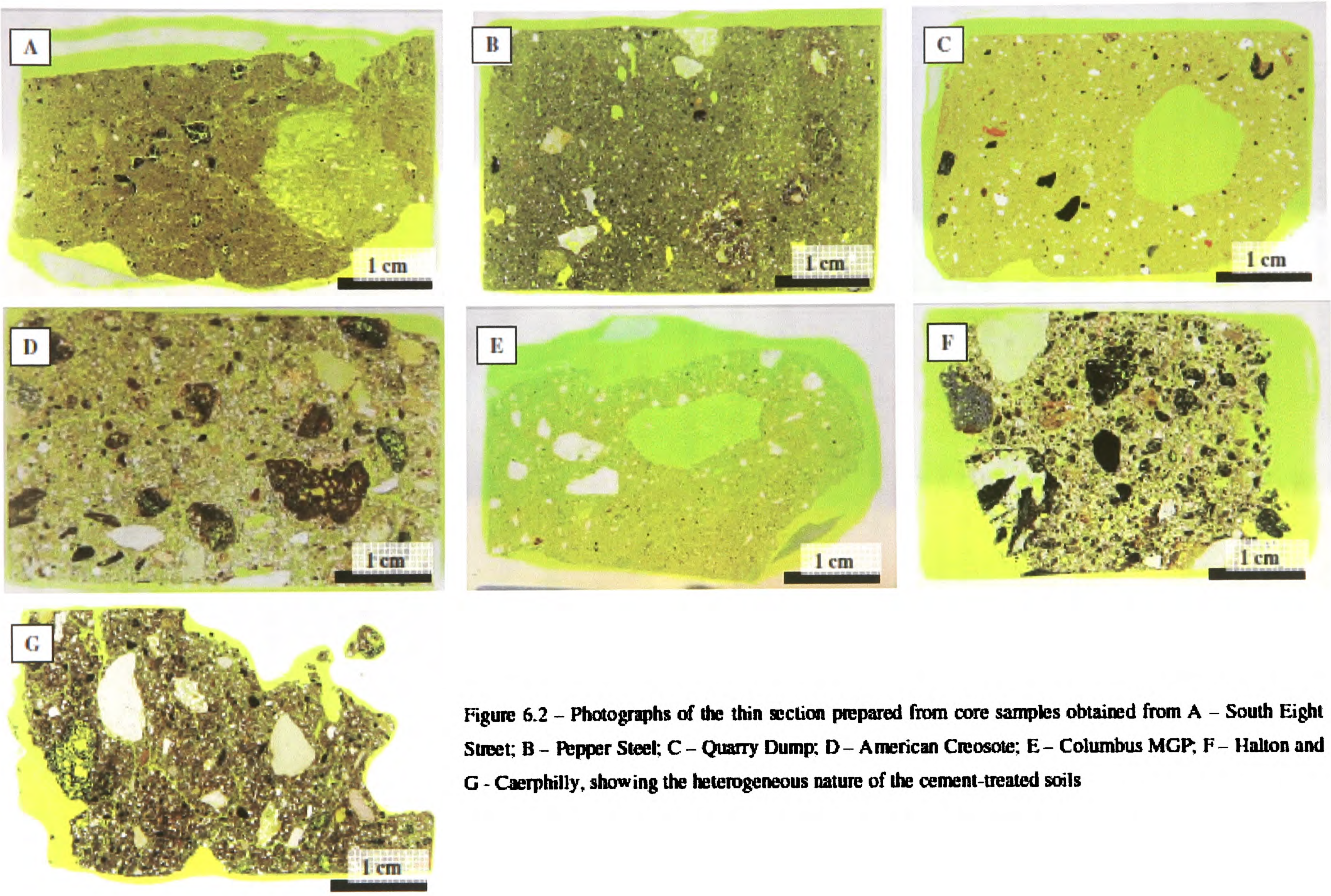


Figure 6.2 – Photographs of the thin section prepared from core samples obtained from A – South Eight Street; B – Pepper Steel; C – Quarry Dump; D – American Creosote; E – Columbus MGP; F – Halton and G - Caerphilly, showing the heterogeneous nature of the cement-treated soils

Table 6.3 – Visual observations of S/S soils prepared in thin section

Site	Inclusions[1]	Voids[2]	Cracks[3]
PS	1% angular, very angular stone fragments (up to 5 mm)	3% elongated and rounded voids	Rare, fine cracks
MGP	3% white white rounded, sub-rounded and sub-angular inclusions (up to 0.5 cm across)	1 cm clean void; 1% 2mm elongated voids	Not observed
QD	1% very angular black inclusions of opaque fragments; 10% white sub-rounded and rounded inclusions of various sizes	1 cm rounded void	Not observed
S8	5% dark organic inclusions	Rare	Frequent, parallel
AC	7% dark sub-rounded, organic inclusions (up to 1cm across) 10 % white rounded inclusions	<1% elongated voids	Rare, zig zag
HA	1% white sub-rounded fragments; 10% black rounded inclusions	Compound packing voids, <1% sub-rounded voids	Not observed
CA	2% sub rounded and angular white fragments of rock	Compound packing voids	Frequent, zig zag and intersecting

[1-3] St John *et al.*, 1998

3.1.2 Unconfined compressive strength (UCS)

The determination of UCS was carried out as part of the wider study (Gardner, 2005). This was aimed at assessing the performance of the S/S soils versus their site specific remediation target values. The strength measurements were performed on a variable numbers of samples from each site. The number of samples retrieved depended on the sampling locations, ease of material recovery and the integrity of the samples recovered, as some S/S soils were more granular than monolithic in nature, therefore UCS was difficult to perform.

Figure 6.3 shows the UCS values recorded for the samples recovered from the US and UK sites. Since the UK sites did not have any defined remedial targets for UCS and permeability, the values for the HA and CA sites are given for reference only.

The results showed that in all cases but one, the UCS exceeded the site specific remedial target values by up to one order of magnitude, and averaged between 0.1 MPa and approximately 4 MPa (Figure 6.3). Intact cores proved difficult to obtain from in the AC, HA, and CA sites, meaning only one sample per site could be tested.

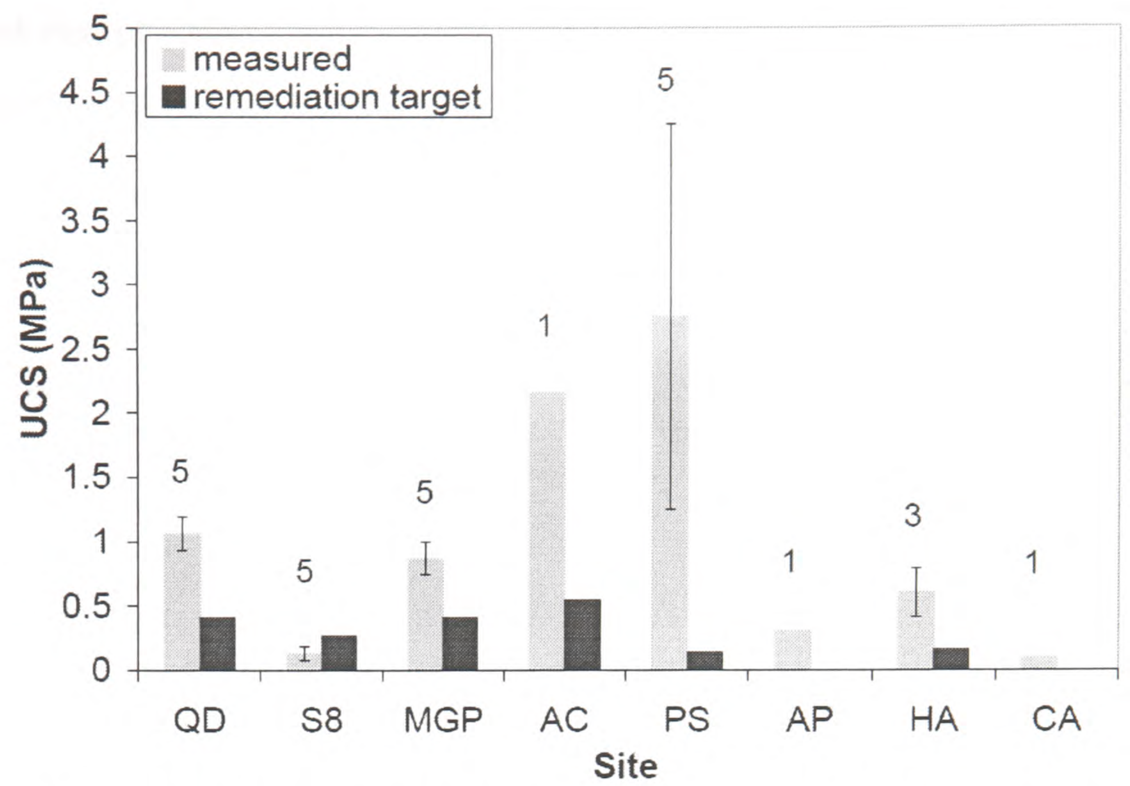


Figure 6.3 - Unconfined compressive strength of the S/S soils measured on variable number of samples at each site, as indicated by the numbers on graph (error bars interquartile range)

3.1.3 Permeability

The permeability of the retrieved S/S soils ranged from 10^{-6} to 10^{-8} m/s (Figure 6.4), and was within the same order of magnitude as the remediation targets.

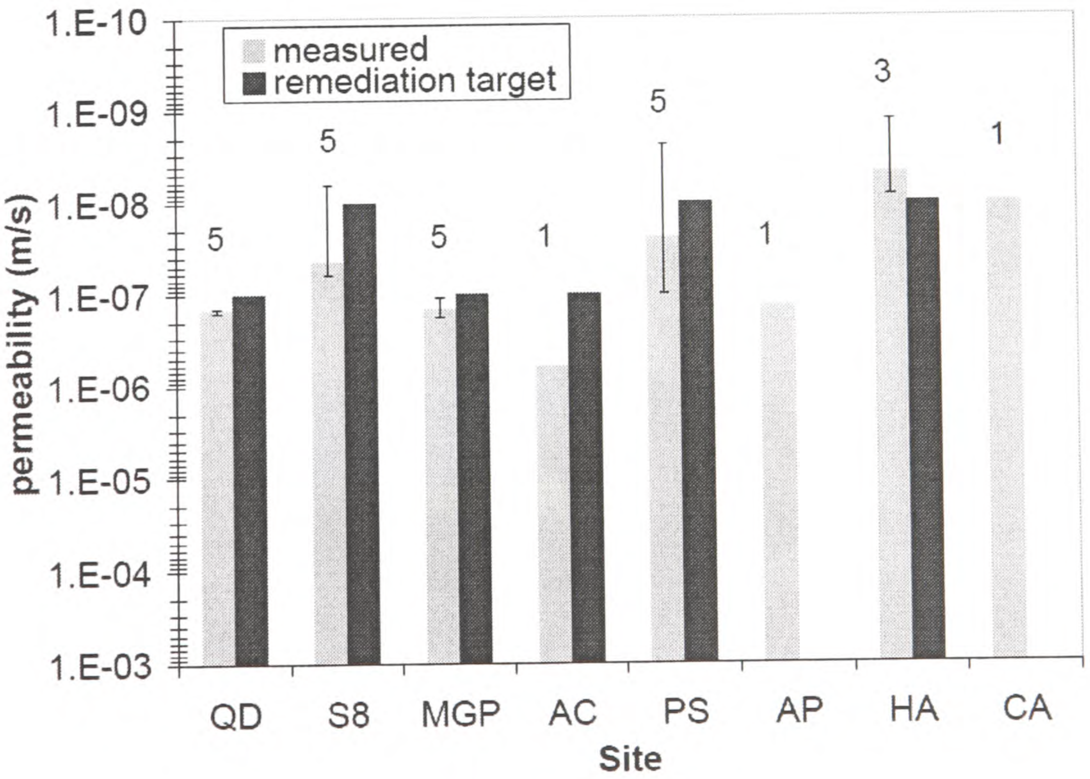


Figure 6.4 - Permeability of the S/S soils measured on variable number of samples at each site, as indicated by the numbers on graph (error bars interquartile range)

3.2. Chemical composition

The oxide composition of the aged cement-stabilised soils is shown in Figure 6.5.

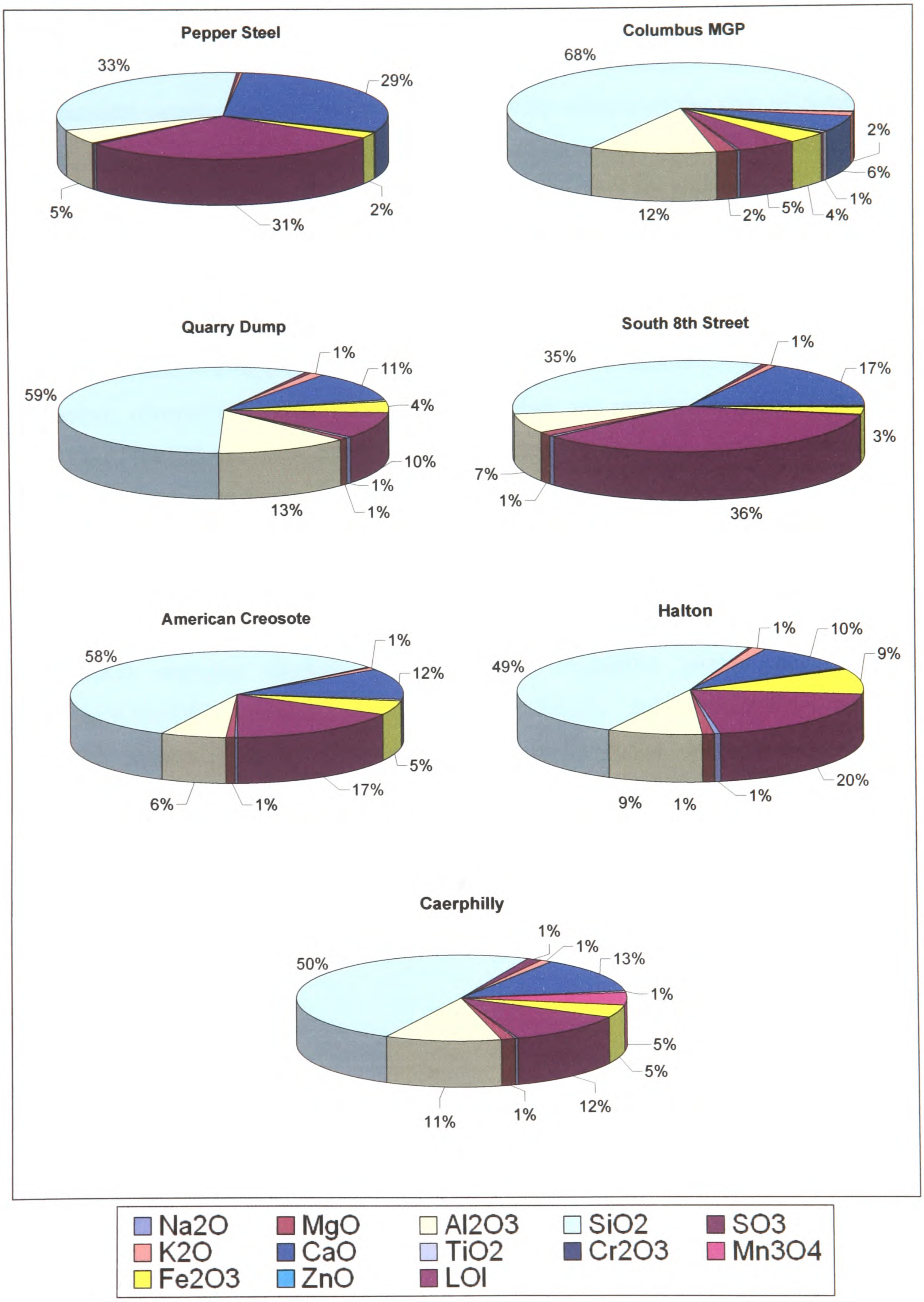


Figure 6.5 - Elemental oxide composition and loss on ignition (LOI) for S/S soils, up to 16 years old

This contains elements naturally present in soils and those added as part of the stabilising mix. Differentiating between the original oxide composition of the soil and binder was not possible because of the lack of information regarding their composition at the time of remediation. The reports from the remedial operations obtained did not normally contain the chemical composition of untreated soil, and very often even the type of cementitious binder used was vaguely mentioned, or poorly characterised with no references to the manufacturer. Similarly, the source of secondary binders was not recorded.

The major and trace element composition of the S/S soils was determined by XRF and the results are presented in Figure 6.5. The S/S soils contained up to 68% SiO_2, 29% CaO, 14% Al_2O_3, and 9% Fe_2O_3. The minor elements identified included magnesium, sodium, potassium, chromium, titanium, zinc, lead, chromium and manganese, accounting for less than 1% of the S/S soil mass. The loss on ignition had a significant contribution to the total oxide content of up to 31%.

3.3. Mineralogical characterisation

3.3.1. XRD

The XRD analyses showed that the main crystalline phases were ettringite ($Ca_6Al_2(SO_4)_3(OH)_{16}{\cdot}26H_2O$), gypsum ($CaSO_4{\cdot}2H_2O$), calcite ($CaCO_3$), aragonite ($CaCO_3$), mullite ($3Al_2O_32SiO_2$), quartz ($SiO_2$), pyrite ($FeS_2$), dolomite ($CaMg(CO_3)_2$), clay minerals, mica, and feldspar. These minerals are soil-derived and cement hydrates. The mineralogy was dependent upon the soil and binder type and the extent of environmental exposure (see Table 6.4). The original X-ray diffractograms are presented in Appendix 1.

Table 6.4 - Mineral phases identified by x-ray techniques within the S/S soils

Site	Quartz	Clays	Pyrite	Micas	Mullite	Calcite	Gypsum	Feldspars	Dolomite	Ettringite
AC	✓					✓		✓	✓	✓
PS	✓				✓	✓	✓			✓
S8	✓					✓	✓	✓		✓
MGP	✓	✓		✓				✓		
QD	✓	✓		✓		✓		✓		
HA	✓	✓	✓			✓	✓	✓		✓
CA	✓	✓			✓	✓			✓	✓

3.3.2. Thermal analysis

TGA was used to identify mineral phases such as sulfate compounds (ettringite, gypsum), carbonate, soil organic matter, volatile organic compounds and clay. The distribution of these compounds is shown in Table 6.5.

Table 6.5 – Phases identified by TGA in S/S soils

Site	SOM	C-S-H	Calcite	Ettringite	Portlandite	Kaolinite	Gypsum	Dolomite
QD	✓	✓	✓	✓		✓		
S8	✓	✓	✓	✓		✓	✓	
MGP	✓	✓	✓	✓		✓		
AC		✓	✓	✓	✓			
PS		✓	✓	✓	✓		✓	
HA		✓	✓	✓	✓	✓	✓	
CA	✓	✓	✓	✓	✓	✓		✓

SOM – soil organic matter

3.4. Microstructural characterisation

Replicate thin sections from each S/S soil were prepared, as detailed in Chapter 3 and examined by SEM and optical microscopy. Scanning electron microscopy was used to examine the microstructure of the S/S soils and identify the metal contaminants, whereas optical microscopy was employed to observed the microtextures and identify any degradation signs, the minerals present, voids and cracking. It must be noted that, although optical microscopy is a valuable tool for microstructural examination, the effective resolution is limited to 1 μm (St. John *et al.*, 1998). Since the reaction products of cement hydration are submicroscopic, a combination of SEM and optical microscopy is generally used.

The results showed that the S/S soils had similar microstructures, but the distribution of the key microstructural features was variable. A summary of the variation of these features with each site is shown in Table 6.6. Different polymorphs of calcium carbonate, sulfate minerals (ettringite and gypsum), unhydrated cement grains, remnant secondary binders (PFA) and weathered minerals were identified. Cracks and voids were noted in all the S/S soils.

Table 6.6 – Key microstructural features observed in the S/S soils

Site	Unhydrated binder	Secondary binders	Cracking	Voids	Ettringite	Gypsum	Calcite	Aragonite	Altered mica
QD			✓	✓	✓		✓		✓
S8		✓	✓	✓	✓	✓	✓		
MGP	✓		✓	✓	✓		✓		✓
AC	✓	✓	✓	✓	✓		✓		
PS		✓	✓	✓	✓		✓	✓	
HA	✓		✓	✓	✓	✓	✓	✓	
CA	✓	✓	✓	✓	✓		✓		

3.4.1. Unhydrated binder

The treated soils had isolated remnant cement grains, despite often many years of service since placement. The remnant grains were observable with an optical microscope and were mainly oversized, 60 – 100 μm. These were recognised by the angular grains and the interstitial ferrite phase, which also has a high relief (Figure 6.6).

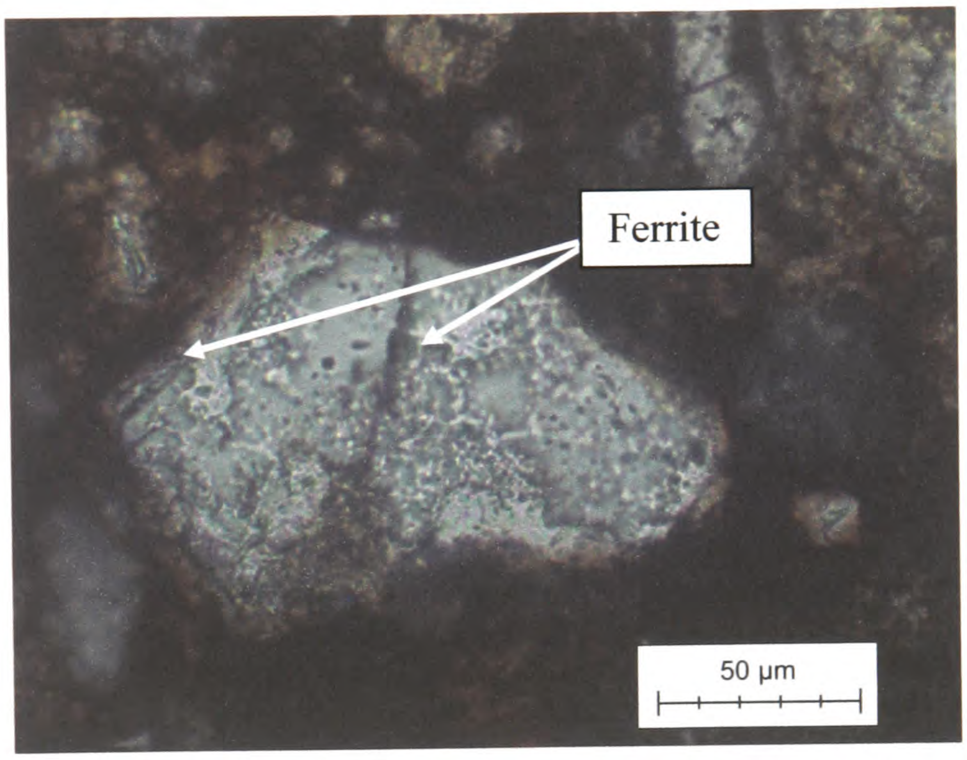


Figure 6.6 – Remnant cement clinker in aged cement-solidified soils (S8 site)

The Ca/Si atomic ratios of the inner C-S-H gel were determined using quantitative EDS point analysis on polished blocks prepared from each S/S soil. The average Ca/Si ratio varied from 0.5 to 1.0. Figure 6.7 shows typical (Ca/Si) elemental ratios taken from previous research (Taylor, 1997; Bye, 1999; Lawrence, 1998, Glasser, 1998). The (Ca/Si) elemental ratios of the inner C-S-H gel were highly variable. However, on average, all sites had significantly lower ratios than expected for Portland cement. The average recorded for CA and PS are similar to the low-end range for blended Portland cements, but MGP, QD, HA and S8 have Ca/Si ratios significantly lower than that reported for both blended and non-blended Portland cement (Taylor, 1997, Lawrence, 1998, Glasser, 1998; Bye, 1999).

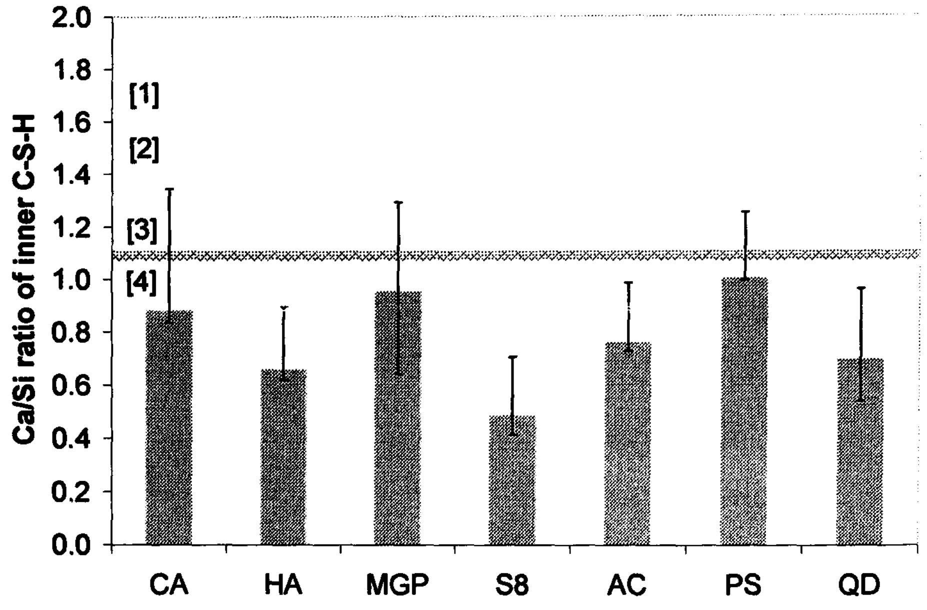


Figure 6.7 - Average Ca/Si ratios for the inner C-S-H gel from the S/S sites (error bars interquartile range). [1] Portland cement (Taylor, 1997; Bye, 1999); [2], [3], [4] fly ash blended cements (Taylor, 1997, Lawrence, 1998, Glasser, 1998 respectively)

3.4.2. Secondary binders

Secondary binders, including PFA, were used in combination with Portland cement for the treatment of the contaminated soils, as indicated in Table 6.1. The effects of PFA addition can decrease permeability and pH, improving the retention of cationic species (Shi, 2005; Hoeffner *at al.*, 2005).

The sites treated with formulations containing PFA were easily identified from relict or partially reacted material (Figure 6.8 (a), (b)). Even in the older S/S soils, large quantities of residual fly ash still persisted (St. John *et al.*, 1998). In the first stages of the alkali activation, PFA particles will undergo alkali dissolution and the resultant gel products will form in the area of higher matrix porosity, recognisable by darker halos in the BSE image (Figure 6.8a). A higher magnification image of a PFA sphere and its interfacial zone is given in Figure 6.8b. The interfacial zone between fly ash spheres and the matrix can assist in the propagation of fractures/cracks (Zhang, 1995), as observed in this work (Figure 6.8a).

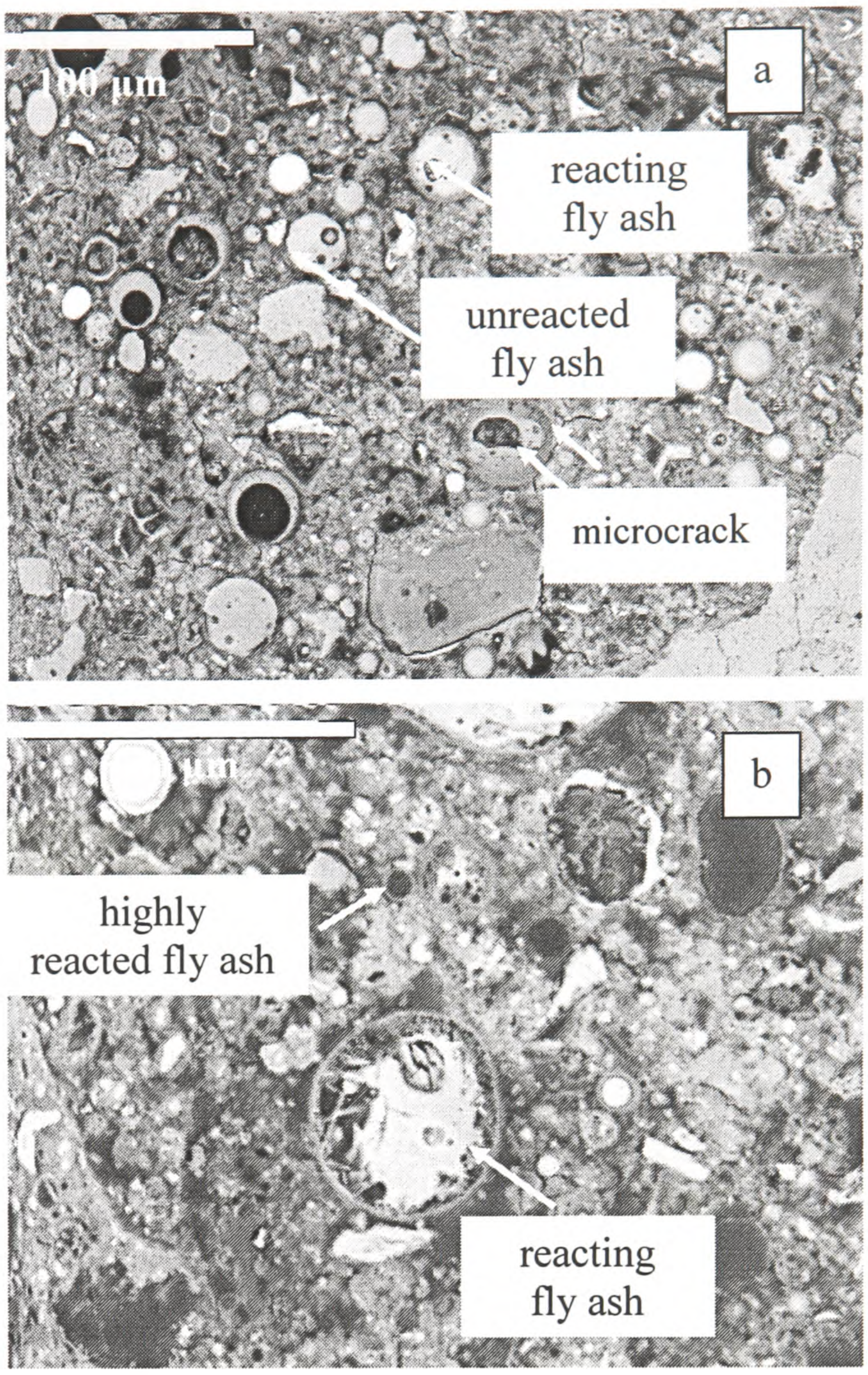


Figure 6.8 – Backscattered electron micrograph of PS S/S soil showing a) fly ash particles in different stages of reactivity and microcracking ash particle-matrix interface (white arrows); b) high magnification image of a fly ash undergoing reaction, showing the darker porous region at the fly ash-matrix interface

3.4.3. Cracks and voids

Cracking can result from drying shrinkage, plastic settlement, freeze-thaw, as well as deleterious chemical reactions such as alkali aggregate reaction, sulfate attack or carbonation (Klich *et al.*, 1999). Cracking was observed in all the cores recovered. Cracks varying from 1 micron to a few tens of microns were noted, but in many cases the cracks appeared to be empty (Figure 6.9a), suggesting they may have occurred as a result of the sampling process. However, some cracks were partially or completely filled with secondary products, such as ettringite (Figure 6.9b) or calcium carbonate, indicating that they must have formed in-situ, after treatment. It should be noted that some samples were significantly cracked, but this was not caused by the formation of secondary products such as ettringite (Taylor *et al.*, 2001).

The S/S soils contained abundant voids with sizes varying from 10-20 µm to over 2 mm in diameter. The large voids (entrapped air voids and water voids) were typically irregular and planar interconnected, and were often infilled by ettringite, calcium carbonate or portlandite. Irregular shaped voids occurred in the product matrix, but also at the boundaries of coarse aggregate particles, or were simply trapped between aggregate grains. Entrapped air voids such as these may be due to incomplete compaction of the soil during placement (St. John *et al.*, 1998).

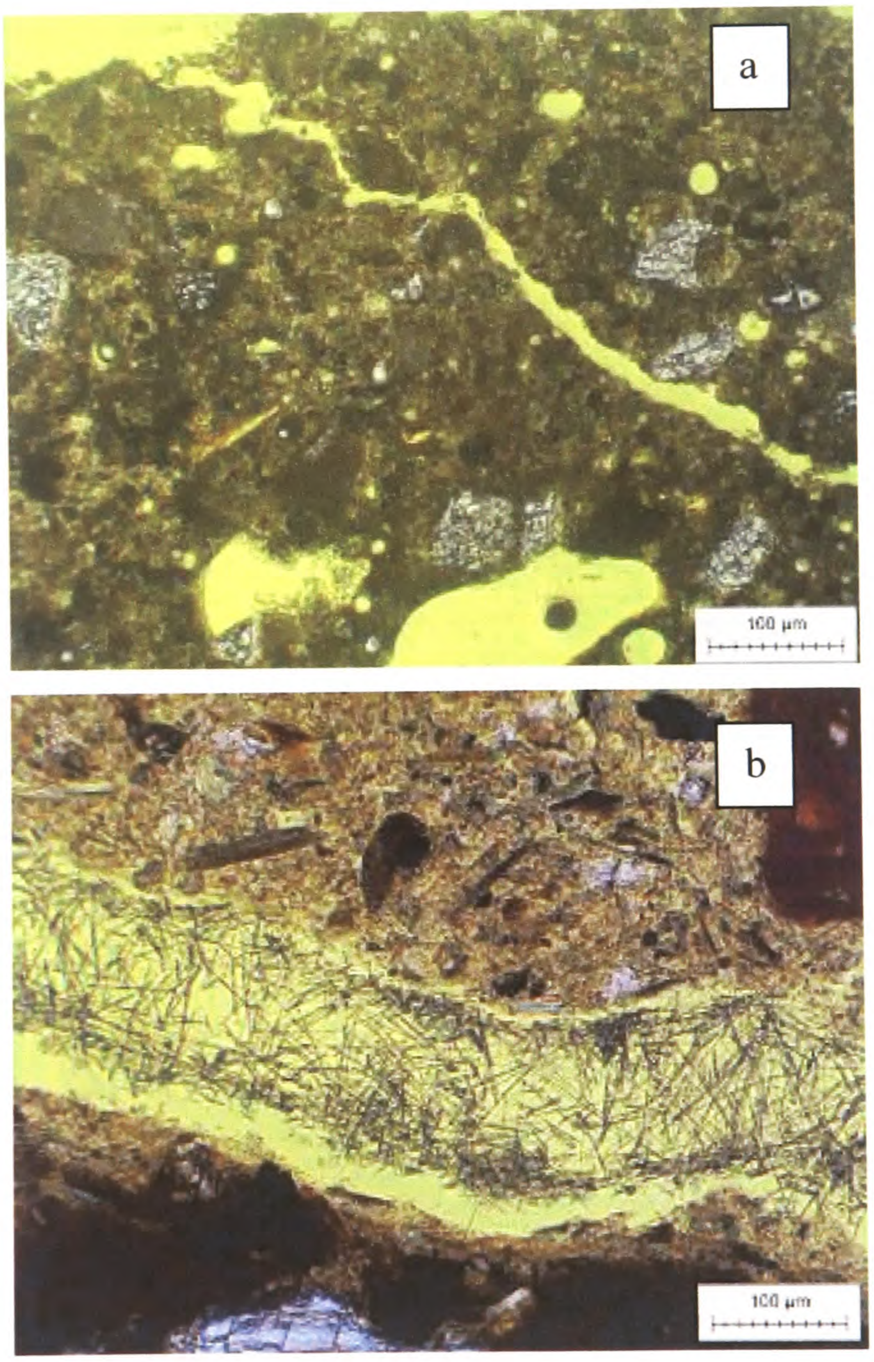


Figure 6.9 – Backscattered electron image of (a) a fine crack (15 µm) formed within the monolith, possibly as a result of sampling and voids (PS site); (b) secondary ettringite formation in a macrocrack (120 µm) in the matrix, binder matrix (QD site)

3.4.4. Carbonation

As can be seen from Table 6.2, all S/S soils were affected by carbonation and this was irrespective of their age. Calcium carbonate was found occurring predominantly in voids (Figure 6.10a-b), but also within and around microcracks and in the matrix (Figure 6.11a-b), primarily leading to a densification of the S/S soil matrix.

As indicated by the XRD results, the most common calcium carbonate polymorph identified was calcite. Rosettes of well-formed blade like-crystals, between 20-30 µm in size were noted in some soils (Figure 6.11), indicative of sufficient space available for their growth (St. John *et al.*, 1998). In confined spaces, calcium carbonate was observed as crustiform banding (Figure 6.10b). These bands of calcium carbonate were indicative of successive episodes of wetting and drying.

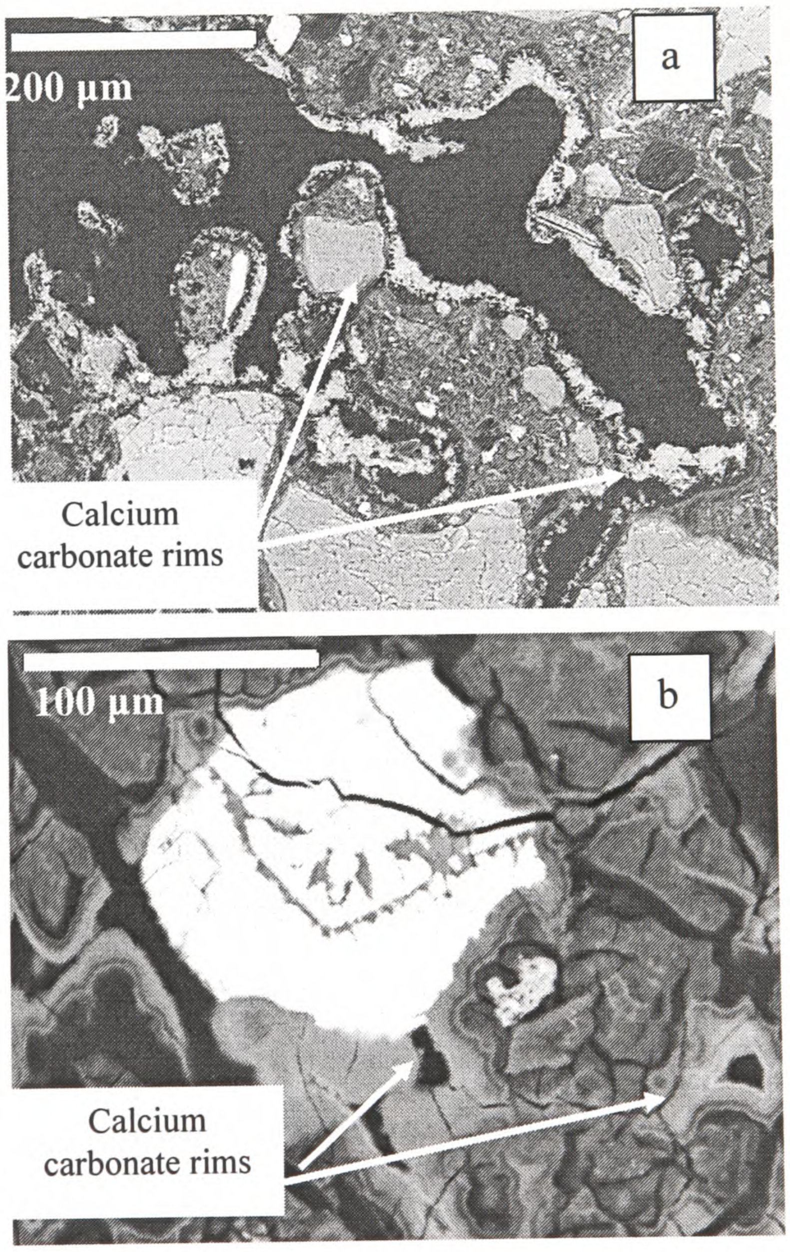


Figure 6.10 – Backscattered electron micrograph of (a) Calcium carbonate crystals infilling large voids in the microstructure and (b) layers of calcium carbonate precipitate infilling voids (HA site)

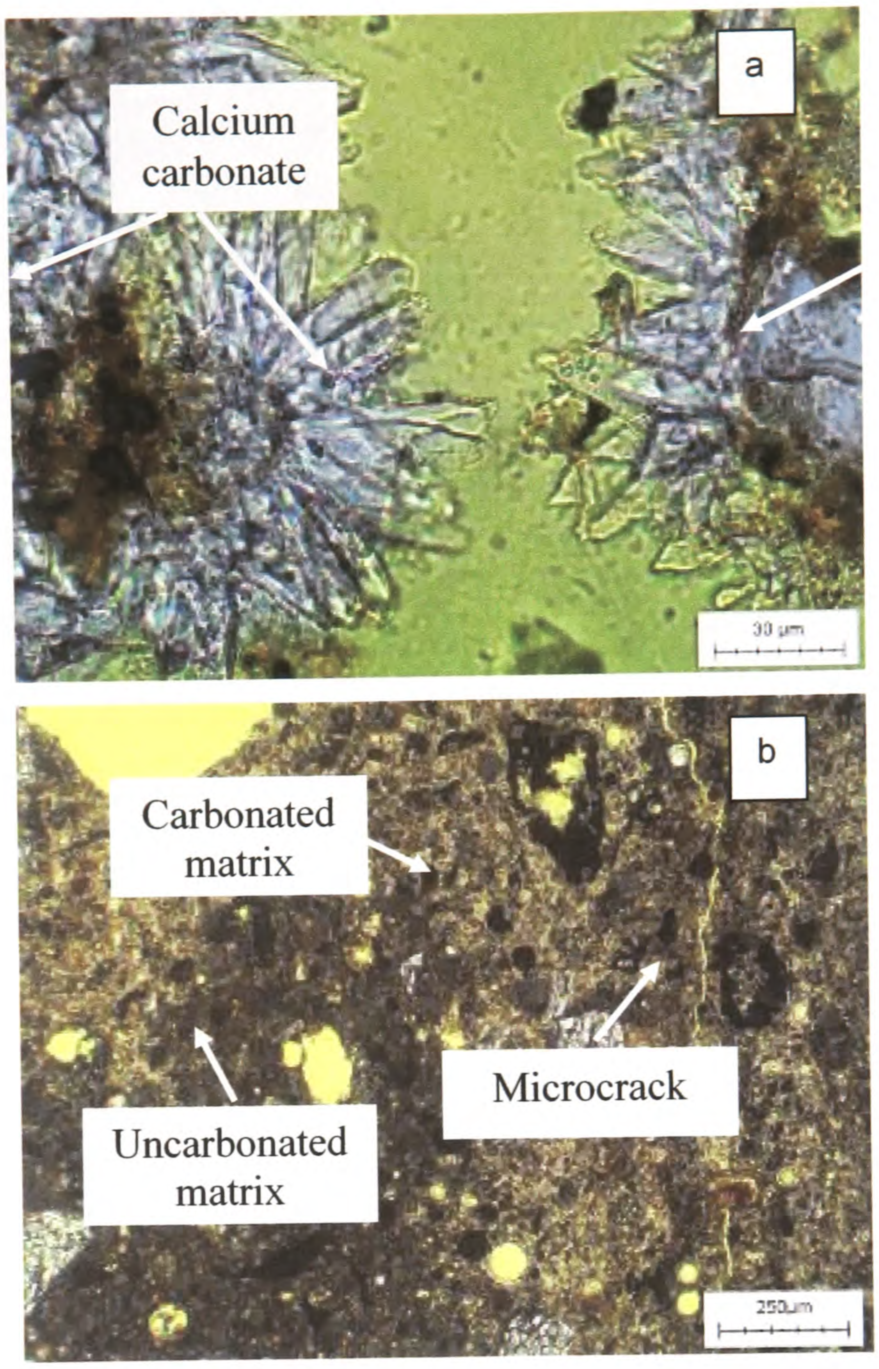


Figure 6.11 - Transmitted light photomicrographs of well crystallised calcium carbonate infilling large pore spaces in the S/S soil; (a) plane polarised light 'dog's tooth' crystals of calcite (HA site); (b) carbonated matrix around microcrack (PS site)

Needle-like crystalline calcium carbonate was also identified by SEM, and may indicate the presence of aragonite (Figure 6.12). Aragonite is a less stable polymorph of calcium carbonate and converts over time to calcite. Hidalgo *et al.* (2008) reported that calcite and aragonite could occur simultaneously in naturally carbonated cementitious materials and that calcite was generally formed from the carbonation of portlandite and C-S-H gel. Aragonite, on the other hand, formed preferentially by carbonation of the C-S-H gel with low Ca/Si ratio. This said, the presence of aragonite was only identified by SEM, which may indicate a localised distribution of this polymorph or insufficient quantity.

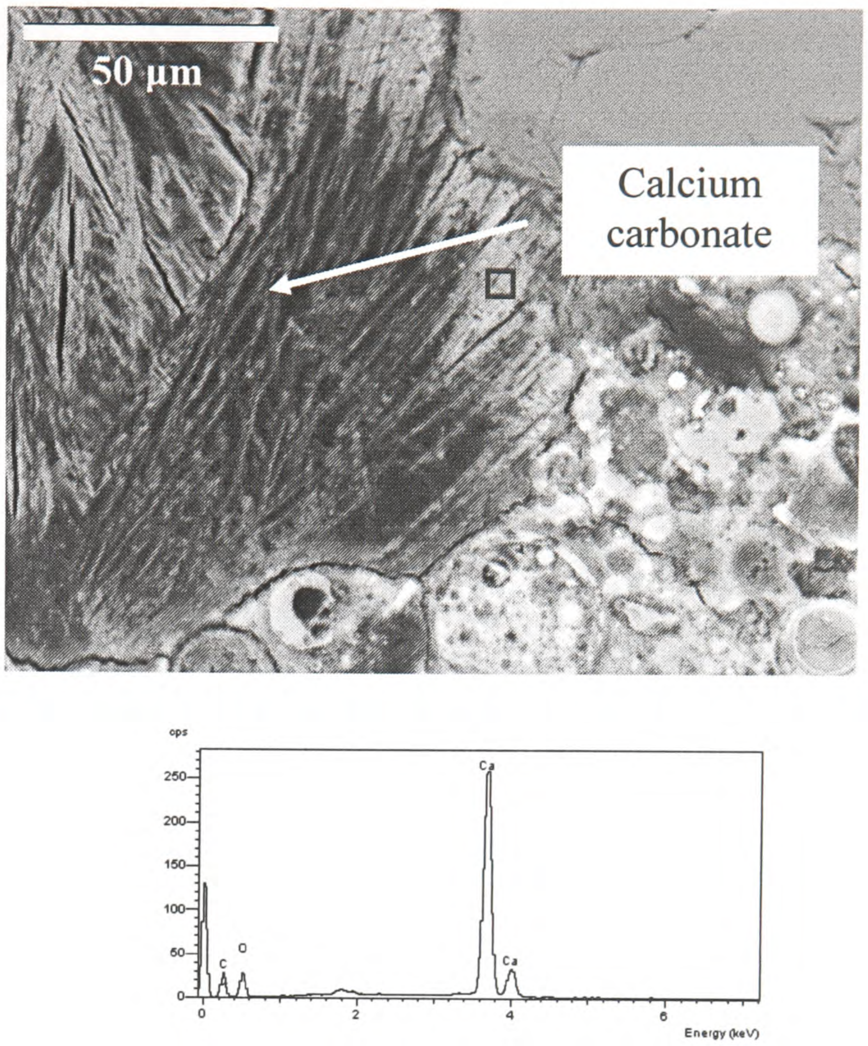


Figure 6.12 – Backscattered electron image of needle-like calcium carbonate infilling a void, and the EDS point analysis spectrum corresponding to the red marker (PS site)

3.4.5. Ettringite

Ettringite was observed in all the S/S soils retrieved. This mineral formed predominantly in large voids or within entrapped air voids, at the aggregate-paste interface, in spaces within porous carbon-rich/coal particles, between mica lamellae, and less frequently in the S/S soil matrices (Figs 6.14, 6.15). Different ettringite morphologies were observed in the S/S soils. Tightly packed masses of crystals with various orientations were identified in large voids of up to 2 mm across and in macrocracks (as shown in Figure 6.9b). Fine cracks became infilled with ettringite growing perpendicular to the crack walls, whereas radiating clusters of ettringite crystals developed in unobstructed areas. A site by site summary of the ettringite distribution is presented in Table 6.7.

Table 6.7 – Site by site distribution of ettringite in the S/S soils

	Voids, cracks	Matrix	Surrounding aggregate	Compound voids	Feldspars, mica
QD	●		●	●	●
S8	●	●	●		
MGP	●				●
AC	●				
PS	●				
HA	●	●			
CA	●				

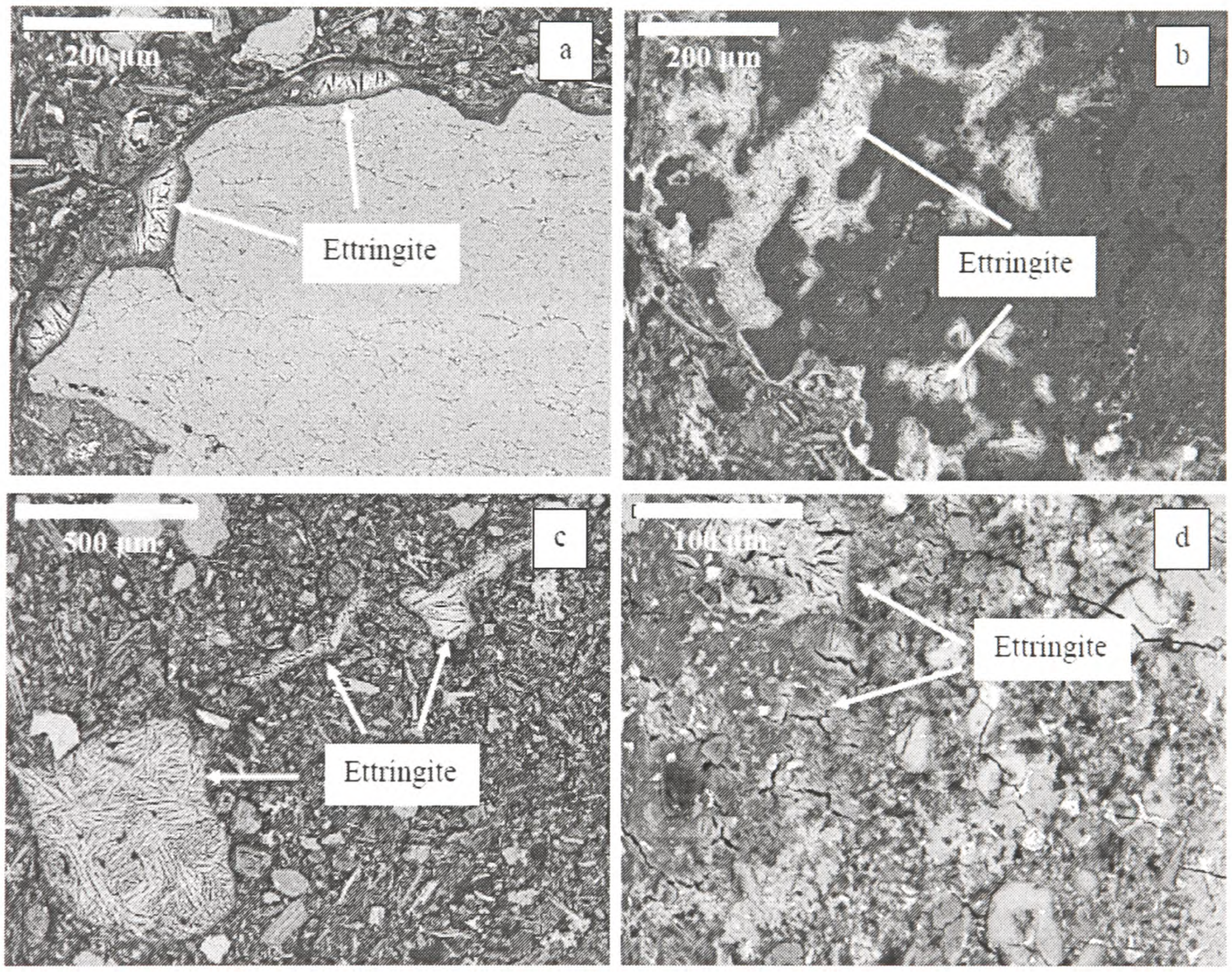


Figure 6.14 – Backscattered electron images of ettringite formed at: (a) the interfacial regions of an aggregate particle (QD site); (b) in interconnected voids within an carbon rich/unburnt coal particle (QD site); (c) in voids and microcracks (QD site); (d) in matrix (HA site)

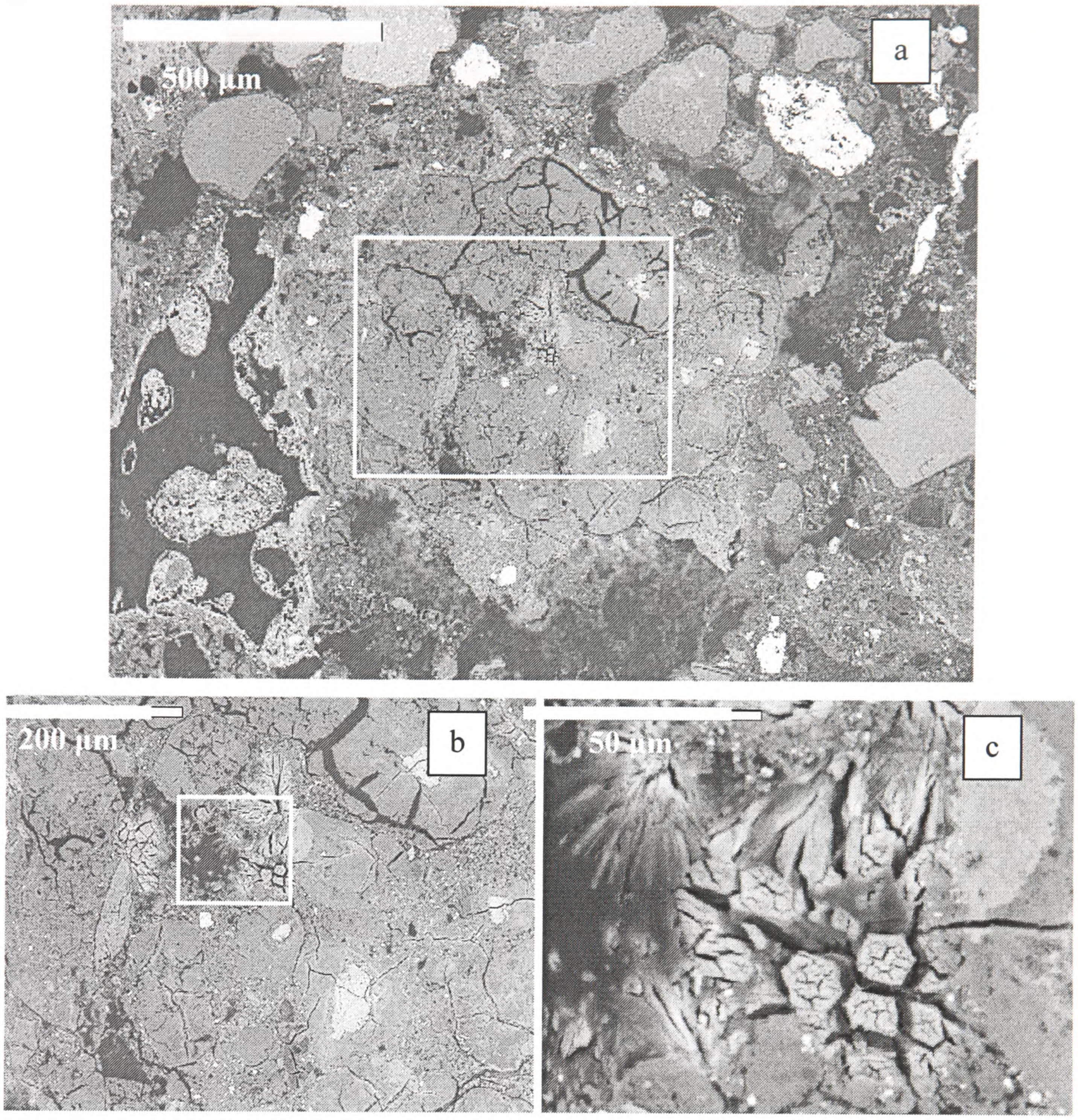


Figure 6.15 - Backscattered electron images of ettringite formed within the matrix (HA); (a) low magnification of the area presenting ettringite; (b), (c) high magnification image of the ettringite rods

3.4.6. Gypsum

Gypsum, another sulfate bearing mineral, was identified in the S/S soils. Unlike ettringite, gypsum was not commonly formed and was only found at S8 and HA. Figure 6.16 shows anhedral crystals of gypsum in an entrapped air void, with no apparent signs of distress to the matrix (Figure 6.13 a, b).

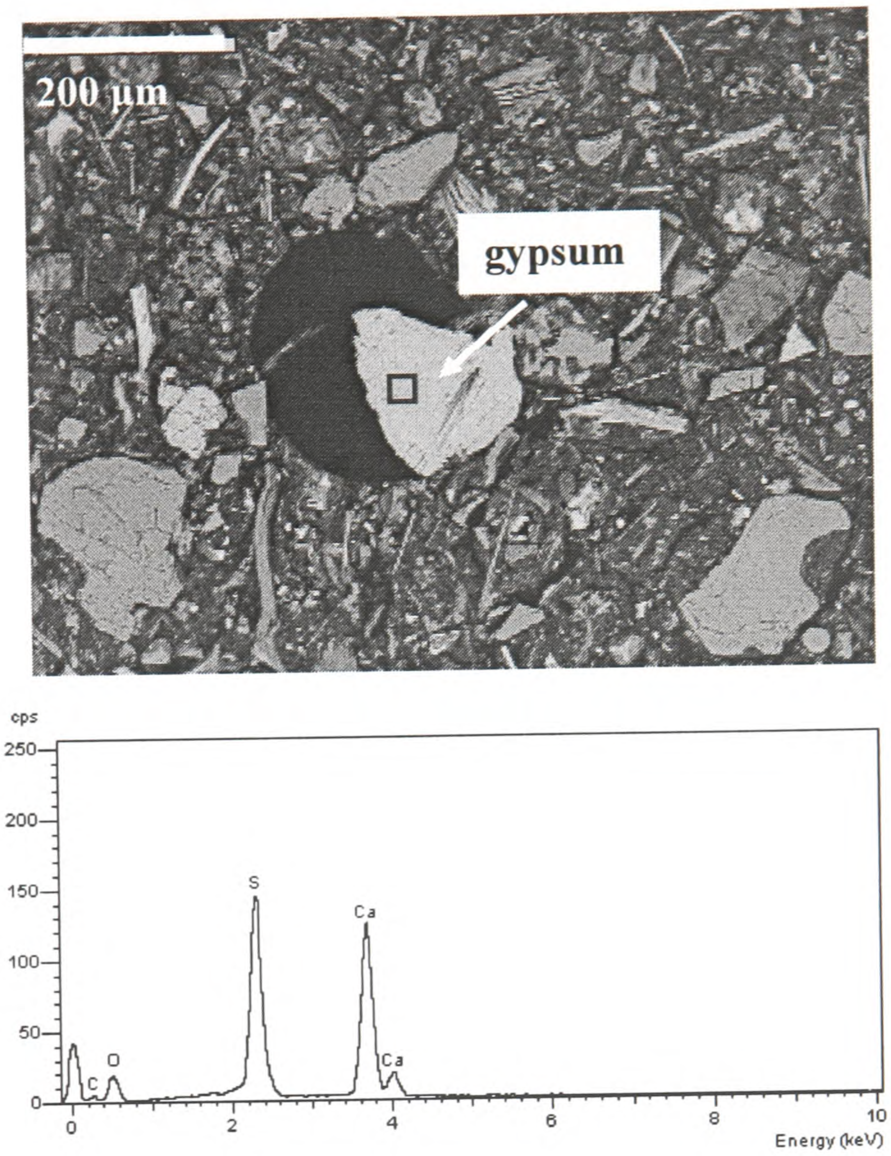


Figure 6.16 – Backscattered electron images of gypsum crystals growing in voids at QD and the EDS spectrum corresponding to the marked area

3.4.7. Weathered minerals

Altered mica was identified in the S/S soils in the two southern sites, QD and MGP (Figure 6.17). The alteration of mica may be ascribed to natural weathering of the soil prior to the remediation, rather than degradation in the high pH conditions of a cement-bound system (Jollicoeur *et al.*, 2000).

Highly altered alkali-bearing mica and feldspar are known to be potentially deleterious by an increased risk of alkali release into the pore solution, promoting alkali aggregate reaction (Leemann and Holtzer, 2005; Lu *et al.*, 2006). However, no evidence of alkali aggregate reactivity in the soil samples examined was obtained. Instead, a rather interesting reaction within the weathered mica was observed. Ettringite was found forming between the mica lamellae, forcing the layers apart, and causing the crystal to bulge. Figure 6.18 shows an example of a grain of mica containing ettringite identified by elemental mapping (Figure 6.19) and the typical shrinkage and cracking morphology (Diamond, 1996).

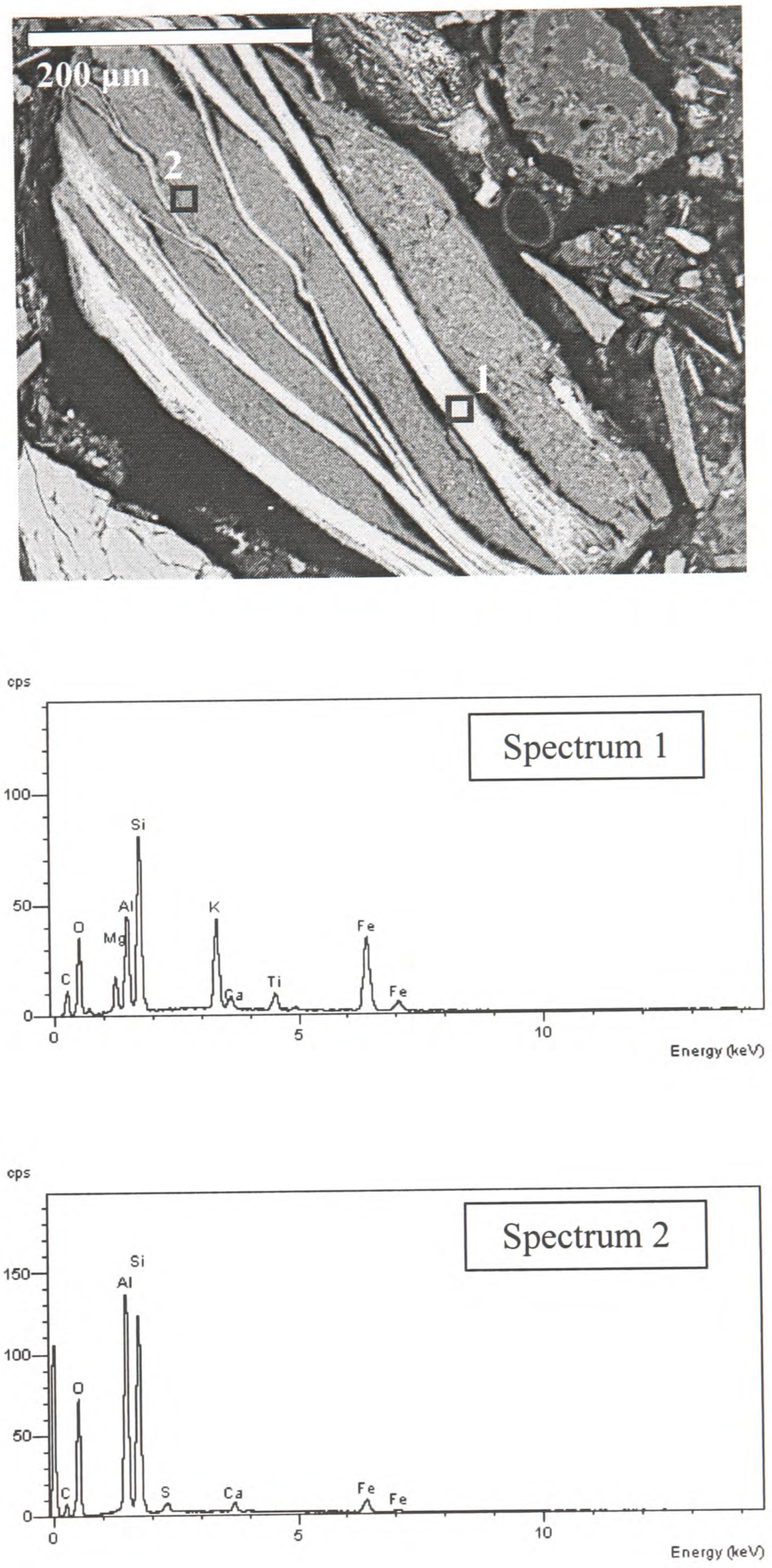


Figure 6.17 - Backscattered electron image of fine exfoliations and deposits in thin section from a sample from QD site; a) unweathered laths of biotite; b) Fe-enriched kaolinite

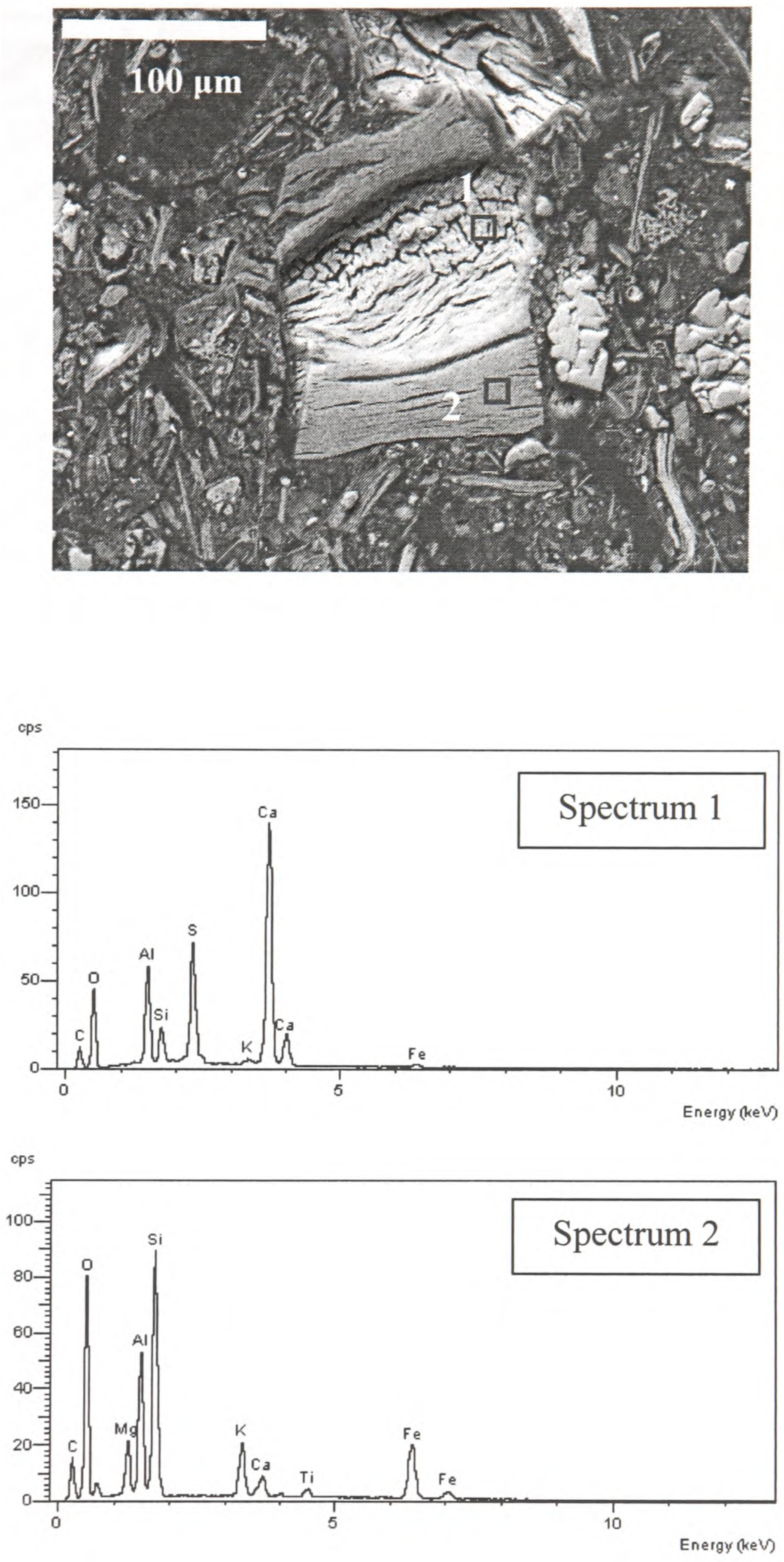


Figure 6.18 – Backscattered electron image of ettringite formed between mica (biotite) lamellae, and the corresponding EDS spectra of a) ettringite; b) unaltered biotite

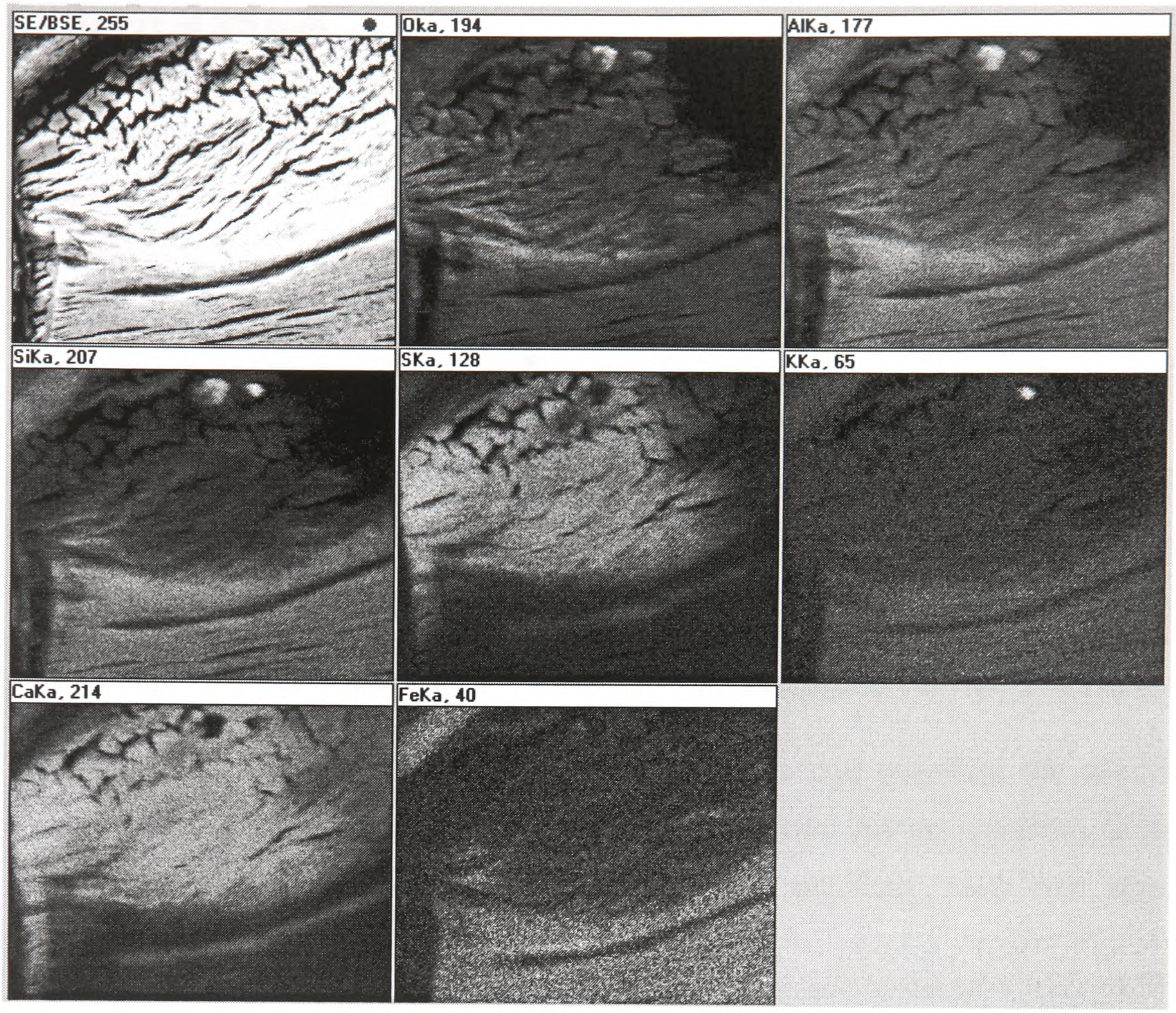


Figure 6.19 – X-ray map group showing the element distribution in the mica - ettringite intergrowth

4. Discussion

In the literature review, a number of extrinsic and intrinsic factors, reported to influence the durability of cementitious materials, have been identified. In Chapter 3, the conceptual models for the S/S soils indicated that the extrinsic factors were the potential major contributors to the degradation of these systems. However, intrinsic factors resulting from the metastable nature of cement phases and their interactions with the soil components may have played an important role in the durability of S/S soils.

The main phenomena occurred over time in the soils from full scale remedial operations, were identified using SEM and XRD, and are summarized in the next sections.

4.1. Nature of S/S soils

The seven S/S soils examined, exhibited different physical properties (Figs. 6.3 and 6.4). Although the S/S soils are often compared with concrete, this is not appropriate as shown in Figs. 6.20 and 6.21. The S/S soils were comparatively weaker and this was not a result of degradation, but it is a consequence of the remedial design.

Depending on the intended end use of a treated site and the type of S/S treatment applied, the solid can be either monolithic or granular in nature. This was reflected in the unconfined compressive strength of the samples recovered (Figure 6.20). The unconfined compressive strength of S/S soils was comparable to stiff and hard soils or to very weak and weak rock. Concretes are typically stronger, and have strengths comparable to moderately weak and strong rock (Mehta and Monteiro, 2006).

The consistency between UCS measurements indicates that generally the sites were homogeneous, except for the PS site. Gardner (2005) reported that the variability of the PS sample was likely to be caused by fracturing during sampling rather than monolith degradation.

Permeability is a key property for long-term durability, which affects the penetration of external agents in the S/S soils. The results showed that the permeability of the S/S soils was several orders of magnitude higher than that of concrete (Figure 6.21), but still within the low to very low permeability range.

The chemical composition of the S/S soils was dominated by silica, aluminium, calcium and iron, as indicated in Figure 6.22. Despite the addition of cement up to 25% by weight of soil, the composition was similar to a mean composition of concrete, blastfurnace slag and clayey soil.

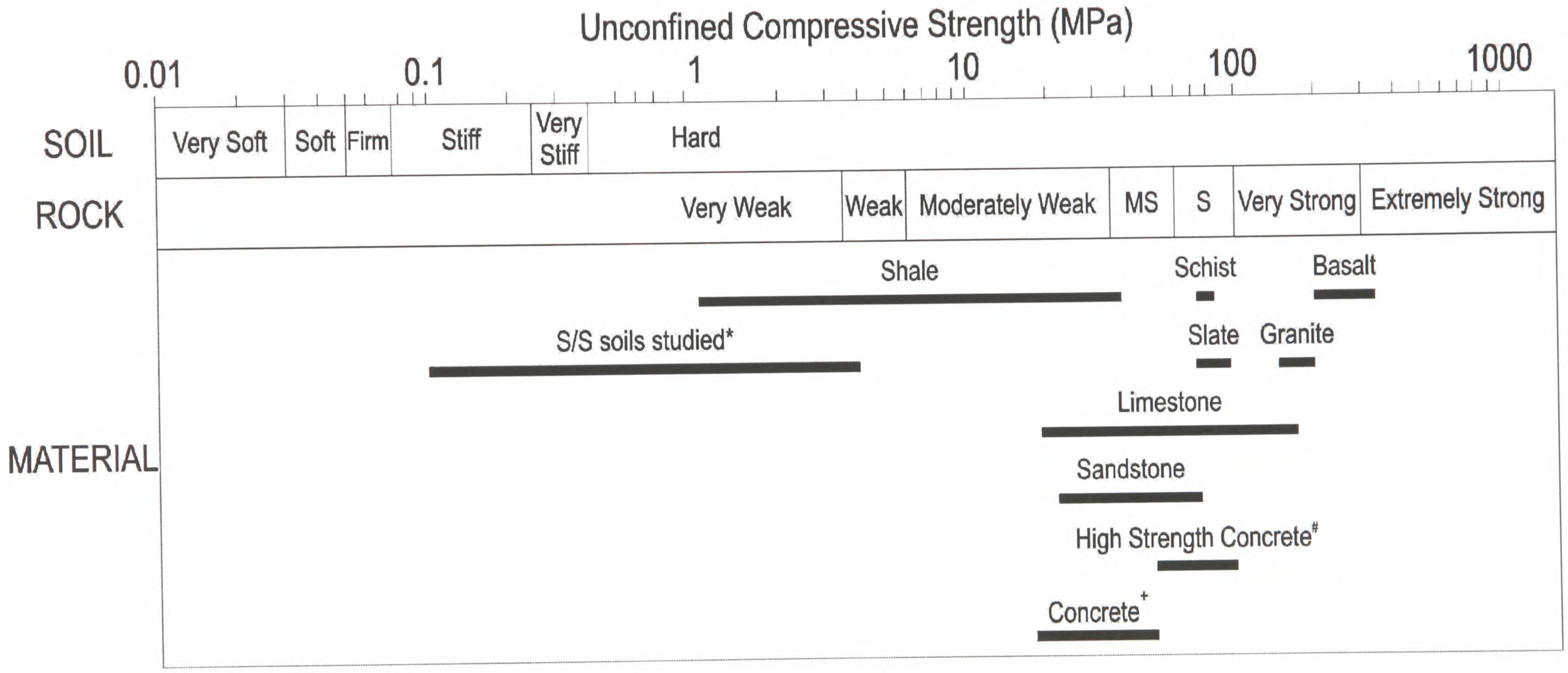


Figure 20 - UCS of S/S soils in comparison with that of cohesive soils and intact rocks (modified from Bell, 2007) MS = moderately strong; S = strong

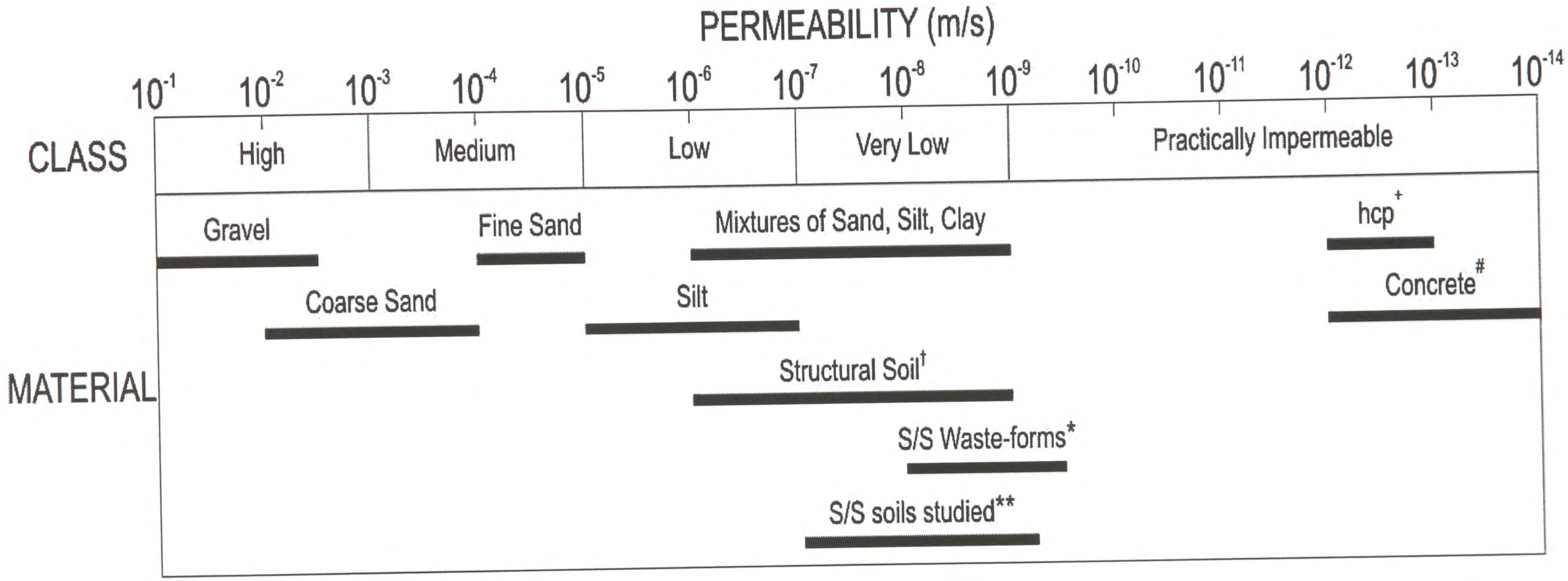


Figure 6.21- Permeability of S/S soils in comparison with various materials (modified from Klute and Dirksen, 1986); + hcp – hydrated cement paste from Lawrence (1988); * Shi and Spence (2005), * * Gardner (2005), # Hilsdorf (1995), † Wong *et al.* (2008)

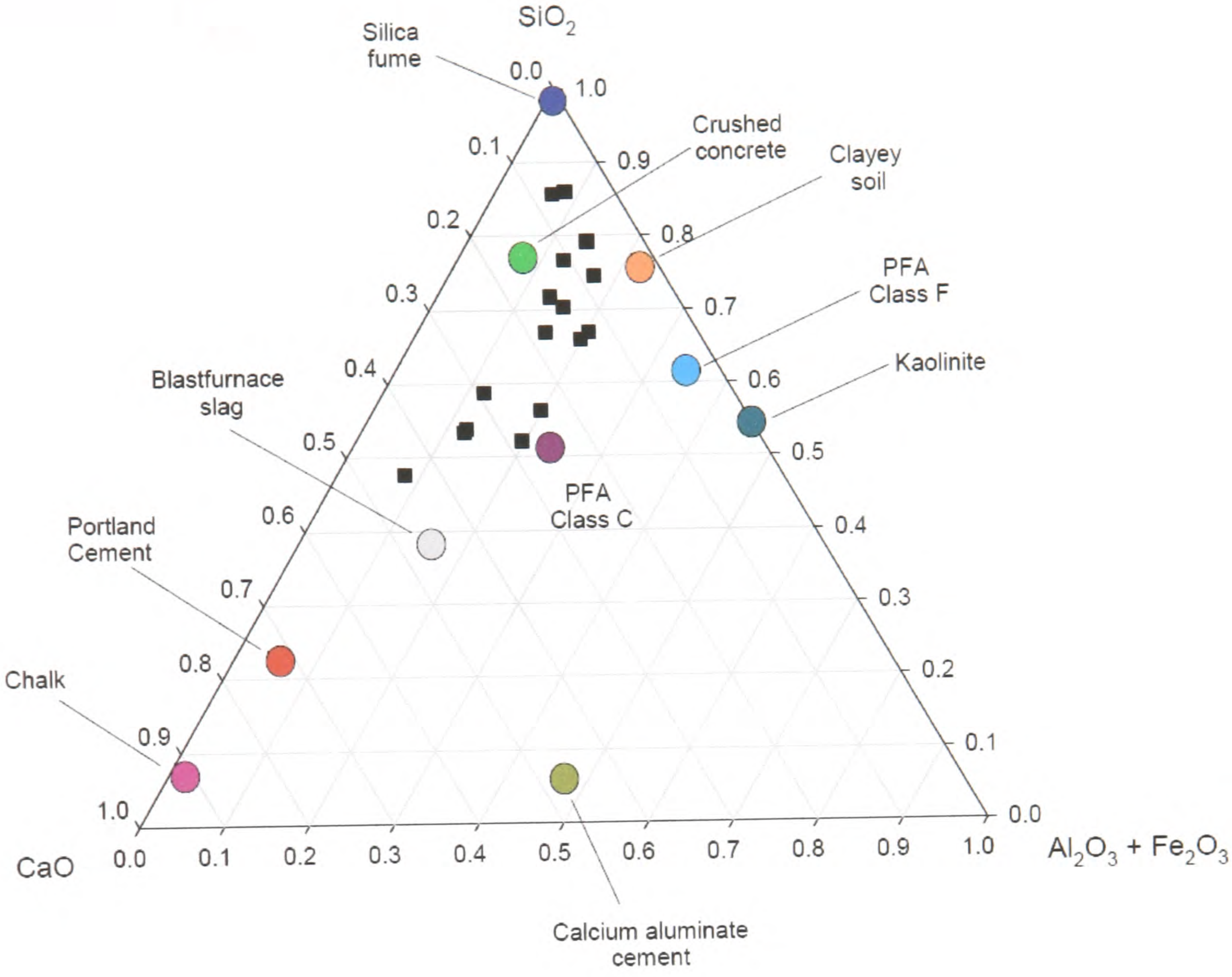


Figure 6.22 - Ternary diagram of CaO-SiO_2-Al_2O_3+Fe_2O_3 showing the chemical composition of the S/S soils (black squares) with respect to common hydraulic binders and supplementary materials represented by coloured dots. PFA – Pulverised Fly Ash

4.2 Performance over time

The microstructural study identified a number of potential key risk indicators for the performance of S/S soils, which are described diagrammatically in Figure 6.25. Carbonation, formation of sulfate bearing minerals (ettringite, gypsum), presence of weathered minerals (mica), unreacted fly ash and microcraking may pose a concern for the long term stability of the S/S soil, but this depends entirely on the site specific conditions prevailing at any one site.

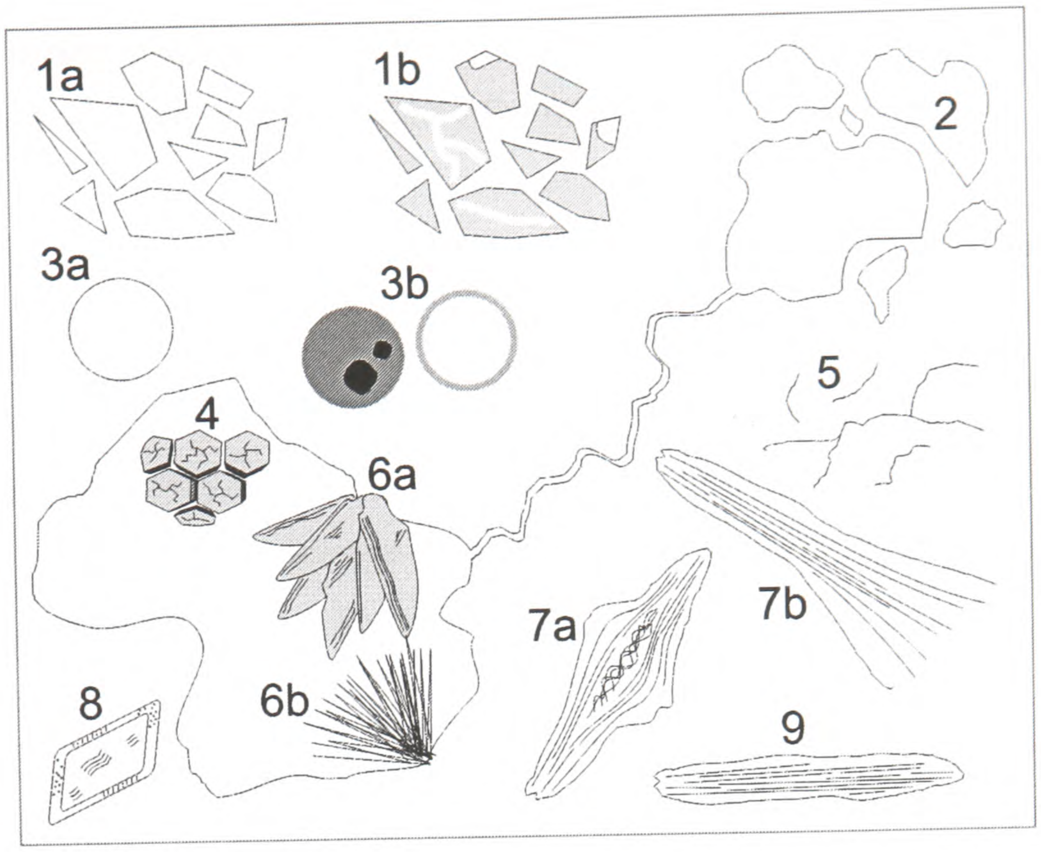


Figure 6.25 - Schematic representation of the main features identified in the S/S soils based on microscopical studies: 1a- unhydrated cement grains; 1b – hydrated cement grain "relics"; 2 - microcracks 3a – unreacted fly ash; 3b – partially reacted fly ash cenospheres; 4 – ettringite; 5 – microcracks; 6a – calcite; 6b – aragonite; 7a – mica and ettringite intergrowth; 7b – kaolinised mica; 7b – kaolinised mica; 8 – gypsum; 9 - feldspar

4.2.1. Carbonation

Carbonation affected all the sites to different extents, irrespective of their exposure environment. This process is likely to be extrinsic, as a result of the reaction between atmospheric CO_2 and the cement hydrates.

The main consequence of carbonation was the densification of the matrix, by precipitation of calcium carbonate in porosity. Calcite was predominantly formed in carbonated soils, but aragonite was occasionally observed by SEM, but not detectable by XRD, due to its localised nature or scarcity.

The calcium carbonate crystals had generally a crustiform appearance; however, well formed rhombohedral crystals were also distinguished. As reported by St. John *et al.* (1998) this type of crystallisation is characteristic for materials where sufficient space is available for the calcium carbonate to precipitate freely from solution. Carbonation was observed along cracks suggesting that this was the pathway for carbon dioxide to penetrate in the S/S soil, representing a potential risk for the long-tem durability.

The carbonation was more extensive in sites with a permeable cap such as crushed limestone, railway ballast or top-soil than for those where GCL or HDPE was applied. Successive layers of calcium carbonate were noted in the S/S soils suggesting exposure to periodic wetting and drying cycles (Figure 6.12). However, the depth of carbonation could not be fully assessed since the precise location of samples was not clearly identified. This was unavoidable and an omission from this work.

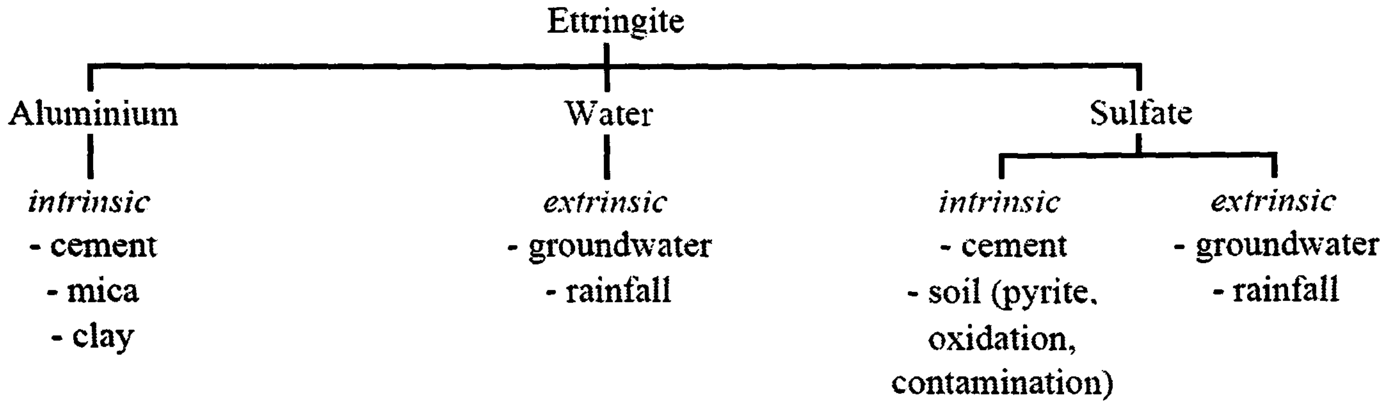
An analysis of the composition of the outer C-S-H gel across the S/S soils revealed that the Ca/Si ratio was lower than the reported values in the literature for pure and PFA blended cements (Taylor, 1997; Bye, 1999; Taylor, 1997, Lawrence, 1998, Glasser, 1998); the average being between 0.5 and 1. It is unclear whether carbonation is responsible for this decrease, since the use of supplementary siliceous materials such as PFA can result in a lowering of the Ca/Si ratio of the C-S-H. Nevertheless, the Ca/Si ratio of the C-S-H gel is very important since this phase plays a key role in metal immobilisation and the resistance of cementitious materials to acid attack (Conner, 1990; Shi, 2005). Depending on the Ca/Si molar ratio of the C-S-H gel the incorporation of anions or cations is favoured. Glasser (1997) showed that at low Ca/Si ratios, the surface charge of C-S-H gel is negative and cation absorption favoured. Since the main contaminants in the S/S soils studied are heavy metals, a Ca/Si ratio of lower than 1 is ideal for their retention (Shi, 2005).

4.2.2. Sulfate reactions

4.2.2.1. Ettringite

The SEM and XRD results indicated that ettringite was present in all the S/S soils. This mineral was most commonly observed in voids and cracks, but also occasionally within weathered grains of mica. Ettringite was occasionally observed in compounds packing voids, in the S/S soil groundmass or at aggregate edges. A site by site description of the location where ettringite was observed is provided in Table 6.5.

Ettringite formation can be either an intrinsic or an extrinsic process, as previously discussed in Chapter 2 (see section 3.4.1). In this work, it was not always possible to distinguish between the two types, since the groundwater composition, groundwater contact with the S/S soil or rainfall composition, were not available. However, there are a number of conditions, which must be satisfied for ettringite to form and they are summarized below.



Ettringite requires a supply of aluminium and sulfate ions, in the presence of water and medium to high alkalinity to form. The source of aluminium is always internal to the S/S soil, but it is not only the cement binder (see section 4.2.2.1, literature review). Sulfate ions can be available from either internal sources such as cement or contamination, but also external ones i.e. groundwater or acid rain (see section 4.2.2.2, literature review). The water plays an important role in the ettringite formation, since this reaction takes place in solution (see section 4.2.2.3, literature review).

4.2.2.1.1. Aluminium sources

The SEM examination revealed that in two soils (QD and MGP) alkali bearing micas were associated with ettringite formation, as shown in Figure 6.18. Previous research investigating sulfate attack on concrete focused on the ettringite formation as a result of reaction between sulfates ions and the aluminate phase from Portland cements (Neville, 2004). However, da Sousa Coutihno (1979) showed that ettringite can form without the presence of aluminate phase from cements, if a reactive source of alumina is available. In particular, kaolinized feldspars or mica have been involved in forming ettringite following their reaction with sulfate ions, in alkaline environments (St. John *et al.*, 1998). The kaolinite dissolves in highly alkaline conditions created by Portland cement (pH 12.5) releasing aluminium, which in turn combines with the calcium and sulfate ions to form. In conditions of supersaturation with respect to $Ca(OH)_2$, however the aluminate ions cannot migrate far from the original source and form preferentially on the surface of the precursor phase in a topochemical reaction (Skalny *et al.*, 2002). This phenomenon is illustrated in Figure 6.18.

Mica undergoing weathering to clay is another source of aluminium. Most often, mica weathers through potassium release and charge reduction to form interstratified mica-vermiculite, vermiculite or smectite. However, in the more extreme climate conditions of tropical or subtropical regions, such as found at QD and MGP, trioctahedral micas can ultimately form kaolinite (Jollicoeur *et al.*, 2000).

Since mica or feldspar cannot be separated from soil prior to the treatment by S/S, the prevention of ettringite formation must be considered at the treatment design stage. de Sousa Coutinho (1979) has shown that ettringite forms from kaolinised minerals only in conditions of saturation with respect to calcium hydroxide. Therefore this reaction could be prevented by limiting the amount of calcium hydroxide available in the S/S soils by the addition of pozzolana, or by forced aging the S/S soil by carbonation.

4.2.2.1.2. Sulfate sources

Ettringite formation is especially enhanced by the availability of sulfate ions, which can be derived either from internal or external sources. Pyrite (FeS_2), found in soils is an internal source of sulfates. This mineral can oxidize in contact with the air and produce sulfate ions. Pyrite was noted in one of the S/S soils studied (HA), in particular, in the vicinity of clusters of ettringite, suggesting a relationship with this mineral. Other internal sources of sulfate include pozzolana, admixtures or soil contamination e.g. sulfuric acid (Lee *et al.*, 2005b).

Sulfate from polluted groundwater or sulfur-rich acid rain can penetrate into the S/S soil and combine with aluminium to produce ettringite. External sources of sulfates were not evaluated in this work due to the lack of information on hydrogeology and rainfall at the sites.

4.2.2.1.3. Water

The maintenance of the S/S soil away from moisture, limits further interaction between the ions and subsequently ettringite formation. Since all the reactions involving sulfates take place in solution or in the presence of moisture, the isolation of S/S soils from water is essential.

4.2.2.1.4. Effect of ettringite formation

There was no apparent damage to the S/S soils caused by ettringite formation; however the potential longer-term effect of its presence cannot be dismissed. In the literature, the consequence of ettringite formation in cementitious materials varies and this is the subject of continuous debate. A summary of the effects of ettringite at different locations within cement matrix is presented in Table 6.8.

Table 6.8 – Effects of ettringite on the microstructure of concretes reported in the literature

Ettringite at the paste-aggregate interface	Non deleterious, the presence of ettringite in voids at aggregate edge is a consequence of the cracking and not a cause. Its presence is a sign uniform and isotropic swelling/shrinkage of the matrix, but the establishment of the cause requires more in depth study. Potential reactions include alkali aggregate reaction or clay swelling (Taylor *et al.*, 2001)
Ettringite in voids, cracks	Common in concretes (St. John *et al.*, 1998), forms through solution mechanism and is deemed to be mechanically passive; does not affect the structural integrity of the matrix (Diamond, 1996). Infilling air voids might change the frost resistance of the matrix, but this is rare as this implies that all voids will be infilled. The formation of ettringite in small areas is unlikely to cause damage as the volume affected is too small (Taylor *et al.*, 2001).
Ettringite infilling compound voids	Occupies space readily available in voids found in rocks, therefore no effect on the microstructure is expected (Klich, 1997).
Ettringite between mica lamellae	Precipitates in between the parallel lamellae of mica, the weak points in their structure. Ettringite exerts pressure on the structure, forcing the lamellae apart and inducing expansion in the direction normal to the layers (Diamond, 1996).
Ettringite in matrix	Potentially deleterious, if the volume expansion is not accommodated. However, the occurrence of damage depends upon the strength of the cement-treated soil, the void system and therefore of the capacity of the soil to adapt to volume changes (Collepardi, 2003).

The presence of ettringite in voids and cracks is an indication of water movement through the stabilised soil; ettringite is hardly detectable in concretes/cement pastes exposed to dry climate conditions. The mechanisms of expansion and ettringite formation in cementitious systems have been discussed in detail in Taylor *et al.* (2001) and Collepardi (2003). Stark and Ballmann (n.d.) and Klich (1997) argue that large ettringite crystals often appear in the available space offered by pre-existing cracks and voids, and are generally not the result of expansive reactions involving this mineral. The formation of ettringite in pore space may indeed be benign, and may not impact adversely upon the physical integrity of S/S soils (Taylor *et al.*, 2001; Klich, 1997; St. John *et al.*, 1998). However, other material properties such as elasticity or resistance to freezing and thawing may be affected (Diamond, 1996). Since the sites studied are located in subtropical regions or were placed below the depth of frost action, the freeze/thaw resistance of the S/S soil is unlikely to be of concern.

The ettringite growing between mica lamellae was reported by Diamond (1996) and previously by da Sousa Coutihno (1966) to be an expansive reaction in concrete. In the S/S soils studied, no apparent degradation occurred due to ettringite formation. However, the separation of quartz particles from the matrix, and presence of ettringite in the gaps around the perimeter of the aggregates may indicate dimensional changes i.e. matrix swelling or shrinking.

4.2.2. Gypsum

Gypsum was present in less than half of the S/S soils and although it was readily identified by XRD, it was scarcely observed by SEM. This may be caused by the similarity between its backscattered coefficient and that of calcium carbonate or the localised distribution of this mineral. Gypsum was found deposited in voids, with the aid of EDS point analysis (Figure 6.16).

Depending on the disposal scenario and the treatment applied, three potential mechanisms of gypsum formation were likely to have taken place in the S/S soils (eq. 6.1-6.3).

- limestone + sulfuric acid – pre-treatment (as known at S8)

$$\underset{\text{limestone}}{CaCO_3} + H_2SO_4 \rightarrow \underset{\text{gypsum}}{CaSO_4} + H_2O + CO_2 \qquad (6.1)$$

- sulfate attack, through-solution mechanism

$$xCa(OH)_2 + M_2^x(SO_4)_x + 2xH_2O \rightarrow xCaSO_4 \cdot 2H_2O + 2M^x(OH)_x \quad (6.2)$$

portlandite — gypsum

- decomposition of ettringite by carbonation

$$Ca_6Al_2O_3(SO_4)_3(OH)_{12} \cdot 26H_2O + 3CO_2 \rightarrow 3CaCO_3 + 3(CaSO_4 \cdot 2H_2O) +$$

ettringite — calcite — gypsum

$$+ Al_2O_3 \cdot xH_2O + (26\text{-}x)H_2O \quad (6.3)$$

aluminium gel

The pre-conditioning of acidic soils with crushed limestone prior to the S/S treatment resulted in gypsum formation (see eq. 6.1). Although gypsum is not expansive in these conditions, it can react with aluminium, from cement or soils, to form ettringite which is potentially deleterious (Taylor *et al.*, 2003, Diamond, 1998). The mechanism of ettringite formation from gypsum was discussed in detail in Collepardi (2003).

The effect of gypsum formed by through-solution (eq. 6.2) on the microstructure of the S/S soils is not clear cut. Authors have reported conflicting results on the consequence of gypsum precipitation (Tian and Cohen, 2000), but there is a general consensus that over time it causes matrix softening and loss of strength (Shanahan and Zayed, 2007). Another mechanism of gypsum formation was noted in partially carbonated soils, where ettringite can decompose according to eq. 6.3. No consequences to the microstructure were reported for this type of gypsum formation.

Under the circumstances mentioned above, gypsum can be potentially damaging, but any prediction or interpretation should consider the prevailing site-specific conditions. The strength results indicated that the S8 soil did not meet the design criteria. The SEM examination did not reveal any expansive reactions involving gypsum and ettringite, but a rather granular, loose matrix crossed by numerous parallel cracks. Since the S8 soil was poorly indurated, sampling and handling may well have contributed to matrix cracking and the low strength.

5. Conclusions

This chapter described the findings from the laboratory examination of seven samples extracted from full-scale S/S remedial operations, with ages between 6 months to 16 years. The major conclusions were:

- The unconfined compressive strength and permeability of the waste forms examined generally indicated that all S/S soils met their design criteria, except for one. Reactions involving sulfate or damage due to sampling may be responsible for the lower strength measured at this site.

- The S/S soils resembled structural stabilised soils rather than concretes, as previously postulated. In four out of seven cases, the S/S soils were monolithic and the remainder was granular in nature.

- The S/S soils were susceptible to the same degradation processes as concrete, but other processes involving soil-cement interactions took place. Clay minerals and mica present in soils favoured ettringite formation. This was possible through the supply of aluminium ions as a result of either dissolution of clays in high alkaline conditions or through solid state reactions. The use of pozzolanic material or forced carbonation is recommended to prevent this reaction from taking place.

- the source of aluminium for ettringite formation was internal, however the origin of the sulfate ions could not be identified. At one site (HA) pyrite was identified in the vicinity of ettringite clusters, which may have been the source of sulfates.

- When assessing the effect of potentially degradative or expansive reactions in S/S soils, the mechanical and geotechnical properties of the waste form must be considered. The presence of a known expansive mineral does not mean damage has occurred. The presence of sulfate – bearing minerals occupying vacant space such as voids and cracks was benign, whilst ettringite growing in weathered minerals or within the S/S soil matrix could be potentially damaging.

- Carbonation occurred at all sites investigated independent of their exposure scenario or their age. However, the soils protected by secondary containment e.g. impermeable capping layers appeared less carbonated than those bound by permeable materials such as compacted topsoil, gravel, crushed limestone or permeable membranes, despite their low permeability.

- A number of risk indicators have been identified that may impact upon the long-term stability of the S/S soils i.e. sulfate reactions, carbonation, reactive mica, cracking, unreacted binders.

Previous chapters have indicated that the S/S soils are metastable. Changes in the microstructure have taken place over the years, and these may affect the contaminant immobilisation. Therefore, the next chapter aims to evaluate the S/S soil performance with respect to contaminant immobilization and the resistance to dissolution due to acid attack.

Chapter 7 Metal immobilisation in S/S soils

1. Introduction

In the previous chapter, the mechanical properties, microstructure and mineralogy of seven full-scale S/S soils with ages between 6 months and 16 years were studied. The S/S soils were susceptible to the same degradation processes as cementitious systems, but other processes involving soil-cement interactions have taken place. Minerals such as ettringite, gypsum and calcium carbonate formed as a result of environmental exposure, but did not result in damage to the microstructure up to 16 years in the service environment. The strength and permeability measurements indicated that all the S/S soils except one were still meeting their design criteria. Carbonation was the most prevalent process occurring in the S/S soils, and resulted in a decrease in porosity.

In this chapter, the effects of carbonation on the chemical immobilisation of contaminants and the acid neutralisation capacity of the S/S soils will be reporting on the results from a number of leaching tests.

2. Results

The contaminant immobilisation in the S/S soils was assessed by two types of leaching tests: compliance and specialist tests and the results presented in the next sections. The findings from leaching tests were correlated with the SEM observations.

2.2 Metal immobilisation

2.2.1 Compliance leaching

To obtain an insight on the current performance of the S/S soils, a number of compliance leaching tests were carried out to evaluate the metal leaching from the S/S soil and the results are compared against target values set at the time of remediation.

Table 7.1 shows the leaching of contaminants from the S/S soils, following a number of pass/fail leaching tests such as Synthetic Precipitation Leaching Test (SPLP 1312), National Rivers Authority (NRA) and the Dutch tank test (NEN 7573). The results obtained were compared, where available, with the site specific performance criteria (SSPC) for the S/S soils. In the absence of an SSPC, guideline values, represented by the State maximum contaminant limit or MCL in the groundwater, were considered for the US soils, and the drinking water quality limits for the UK soils. These values are indicated in brackets and *italics*, in Table 7.1.

Table 7.1 – Contaminant leaching from the S/S soils up to 16 years following remediation

Contaminant	Leaching concentration (in mg/l)						
	SPLP					NRA	NEN
	AC (4 yr)	PS (16 yr)	S8 (4 yr)	QD (10 yr)	MGP (12 yr)	HA (5 yr)	CA (6 mo)
Lead		**0.029** *(0.015)*	**0.04** (0.015)			**0.06** *(0.025)*	
Arsenic	**0.020** (0.050)	**0.006** *(0.010)*	**bdl** (0.010)			**0.06** *(0.010)*	
Copper						**0.07** *(2)*	
Zinc						**0.1** *(0.8)*	
TPH				**bdl** (0.001)			**0.5**[c] *(0.8)*
PAH	**0** (0.01)[a]				**0.37** (10)		**0.2**[c] *(0.1)*
Dioxin	**0.003×10^{-3}** (0.03×10^{-3})[b]						
PCP	**0.16** (0.2)						
Cyanide					**0.001** (0.2)		

Values represent the average of 5 samples for AC, PS, S8, QD and MGP (Gardner, 2005) and average of 3 sample for HA and CA (Celtic, 2006).
In brackets, the site specific remedial target values or *guideline values*, as appropriate
[a] Benzo α pyrene (BaP) equivalent
[b] TEQ equivalent
[c] cumulative leaching from 8 stages
bdl signifies values below detection limit

2.2.1.1 American Creosote

The main contaminants at AC were arsenic, PCP, PAH and dioxins. The prescribed performance criteria for all contaminants at AC were derived using risk-based model to achieve cancer risk protection for the workers, in an industrial use of the site scenario (USEPA, 2004a). The criteria were expressed as benzo-α-pyrene equivalency (BaP) for PAH and toxicity equivalencies (TEQ) for dioxin and were set for the leachability of contaminants from the S/S soils following an SPLP test.

Five samples from random locations on site were leach tested and the average of the results shown in Table 7.1. It can be seen that all contaminants at AC were within the SSPC.

2.2.1.2 Pepper Steel

The PS soil was mainly contaminated with arsenic and lead, but no SSPC were set for the SPLP leaching. Instead the State MCL was used for comparing the leaching results and for determining the performance of the S/S soil. It should be noted that the MCL is not an enforceable limit for metal release from the S/S soil, but is a guideline value. In the State of Florida, the MCL for arsenic and lead was 0.05 mg/l at the time when the remediation of the PS site took place; however since 2007, the MCL was reduced to 0.01 mg/l for arsenic and 0.015 mg/l for lead (USEPA, 2007). Although the SPLP leaching results, of 0.029 mg/l and 0.006 mg/l were below the initial MCL for arsenic and lead, after 2007 only the arsenic was within the prescribed limit (see Table 7.1).

2.2.1.3 South 8th Street

The contaminant of concern at S8 was lead. For this contaminant SSPC was established for the leaching from the S/S soil, following SPLP. These were equal to the State MCL for lead of 0.015 mg/l. The SPLP results for S8 showed that three out of five samples leached lead above the MCL; Table 7.1 shows the average value for lead leaching from five samples analysed. Due to the high soil heterogeneity, the USEPA set an allowance for contaminant leaching exceedance. Hence 20% of samples were allowed to be twice the MCL limit, and for 10% of samples to exceed by a factor of five, provided that the average of all samples tested met the MCL (USEPA, 2004b). As seen from Table 7.1, the lead leaching was not within this allowance. However it should be mentioned that, despite the lead leaching following the SPLP test, the groundwater concentrations have not reached the prescribed MCL (USEPA, 2009). Therefore, the treatment of the four year old soil is still protective of the groundwater, which was identified as the main risk for contamination.

2.2.1.4 Columbus MGP

The MGP soil was contaminated with cyanide and PAH. The SSPC were risk-based and considered the future land use, the depth of material, groundwater impacts, and potential human exposure (Fleri and Whetstone, 2005). The SSPC were 10 mg/l for PAH and 0.2 mg/l for cyanide. The leaching results are presented in Table 7.1. These show that average of five samples leached was 0.001 mg/l for cyanide and 0.37 mg/l for PAH, below the SSPC.

2.2.1.5 Quarry Dump

The QD soil was leach tested the SPLP leaching test. At this site, the contamination was represented by petroleoum hydrocarbons (TPH) and the SSPC set at the time of the remediation, was equal to 0.001 mg/l. The SPLP results were below detection limit for all samples analysed.

2.2.1.6 Halton

At Halton, the contamination was mainly with metals and metalloids i.e. lead, copper, zinc and arsenic. The leaching test performed for assessing the efficacy of the metal retention five years after remediation was the NRA and the results are indicated in Table 7.1. Since the goal of the contaminated soil treatment was to decrease leachable metals concentration, no specific SSPC were set. The initial concentrations measured in the leachates were 1.29 mg/l lead, 1.5 mg/l zinc and 0.59 mg/l arsenic (Curtis and Holt, 2003). These were considered excessively high due to the potential risk of future contamination of the river situated in the vicinity of the site (Curtis and Holt, 2004). Thus, the UK drinking water quality limits (DWL) were chosen for comparison of the NRA leaching results. The average of the three samples analysed was 0.06 mg/l for lead and arsenic, higher than the corresponding DWL of 0.025 mg/l and 0.010 mg/l, respectively. The concentrations of copper and zinc of 0.07 mg/l and 0.1 mg/l were below the DWL, as shown in Table 7.1. Compared with the initial concentrations in the leachates, the metal leaching was still up to two orders of magnitude lower. However, the results suggested that the S/S treatment was more efficient for copper and zinc, than for arsenic and lead. Since this behaviour was also observed by other authors, at the time of the remediation, it cannot be attributed to a degradation of the S/S soil over time (Curtis and Holt, 2005).

2.2.1.7 Caerphilly

The soil at CA contained a mixed contamination of organics and metals, but the contaminants of concern were PAHs and TPHs. There were no SSPC established for this remediation; however guideline values were reported by the site contractor (Celtic, 2006). These were 0.1 mg/l for PAH and 0.8 mg/l for TPH.

Six months after remediation NEN 7375 was performed by the site contractor and the average results presented in Table 7.1. These indicated that the TPH concentrations were below the guideline value, whist the PAHs concentration was twice the corresponding guideline value. The treatment was sufficient for redevelopment as a residential complex, three years after the remediation was carried out.

2.3 pH dependent leaching

Acid resistance, represented by the acid neutralisation capacity of an S/S system, is an important aspect of durability (Stegemann *et al.*, 1997). However, the pH at which the metal precipitates become soluble may not necessarily coincide with that at which the S/S matrix starts to dissolve. Therefore consideration of pH dependency and acid neutralisation capacity is key for understanding the long-term behaviour of the S/S soils.

2.3.1 Metal leaching

The leaching results following pH dependent leaching test of each S/S soils will presented in the next sections.

2.3.1.1 Halton

The main contaminants of concern at HA were lead, zinc, copper and arsenic. In order to assess the influence of pH on the release of these metals from the S/S soil, it was necessary to plot the leaching concentrations of each metal against pH. The results obtained are illustrated in Figure 7.1.

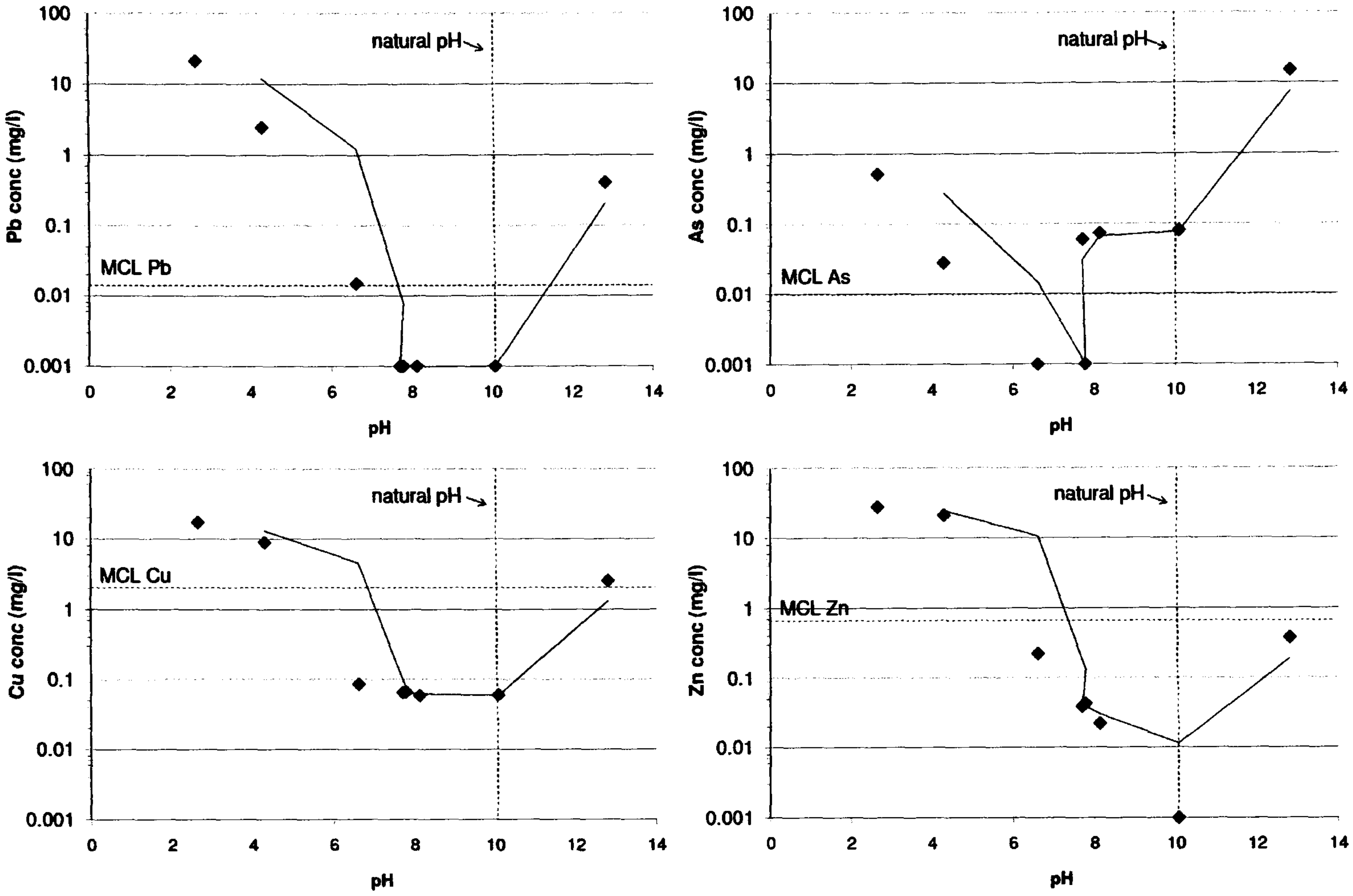


Figure 7.1 – pH dependent leaching of lead, arsenic, copper and zinc from HA soils

The results indicated an amphoteric behaviour for all metals analysed. The metal contaminants had minimum solubility between pH 6-8 and exhibited an increase in leachate concentrations on both sides of this interval, by up to six orders of magnitude.

2.3.1.2 Pepper Steel

Figure 7.2 shows the pH dependent behaviour of lead and arsenic, the main contaminants at PS. Similarly to the HA soils, these elements displayed amphoteric characteristics; however the minimum solubility was distinct for the two metals. The arsenic was least soluble in the pH interval 6-7, whilst the lead was at pH between 9-10. The metal concentration in leachate was significantly increased below and above the minimum solubility intervals. This increase was most pronounced for lead, in the near neutral to low pH interval, reaching up to six orders of magnitude.

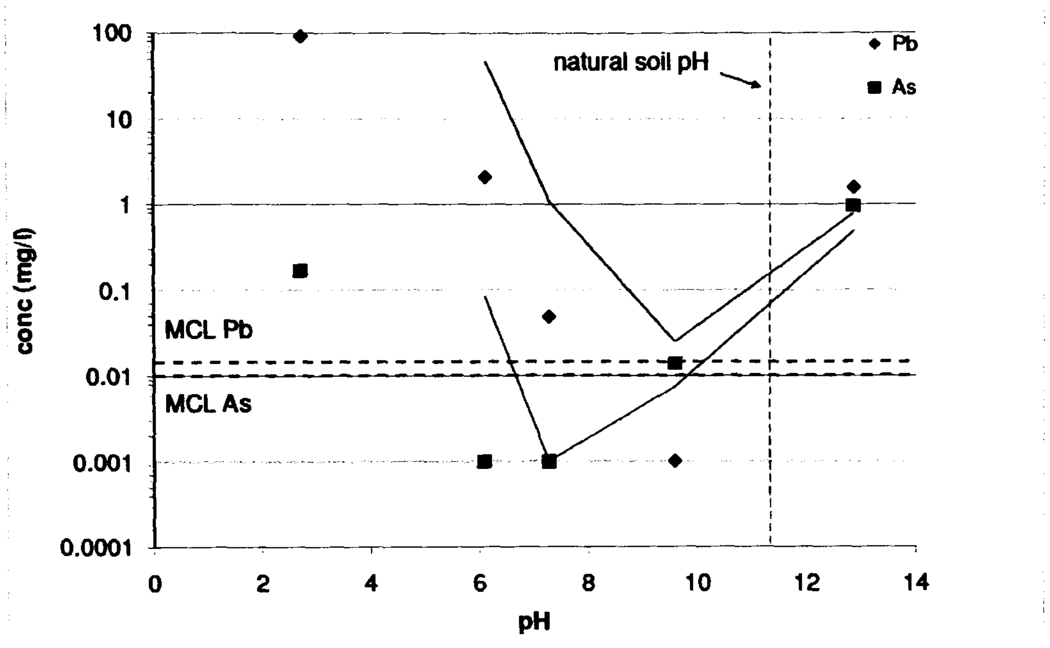


Figure 7.2 – pH dependent leaching of lead and arsenic from PS soils

2.3.1.3 South 8th Street

Lead and arsenic were the metals of concern at S8, along with PAH. These elements showed a typical amphoteric behaviour and a large pH interval of minimum solubility between pH 8-12 (Figure 7.3).

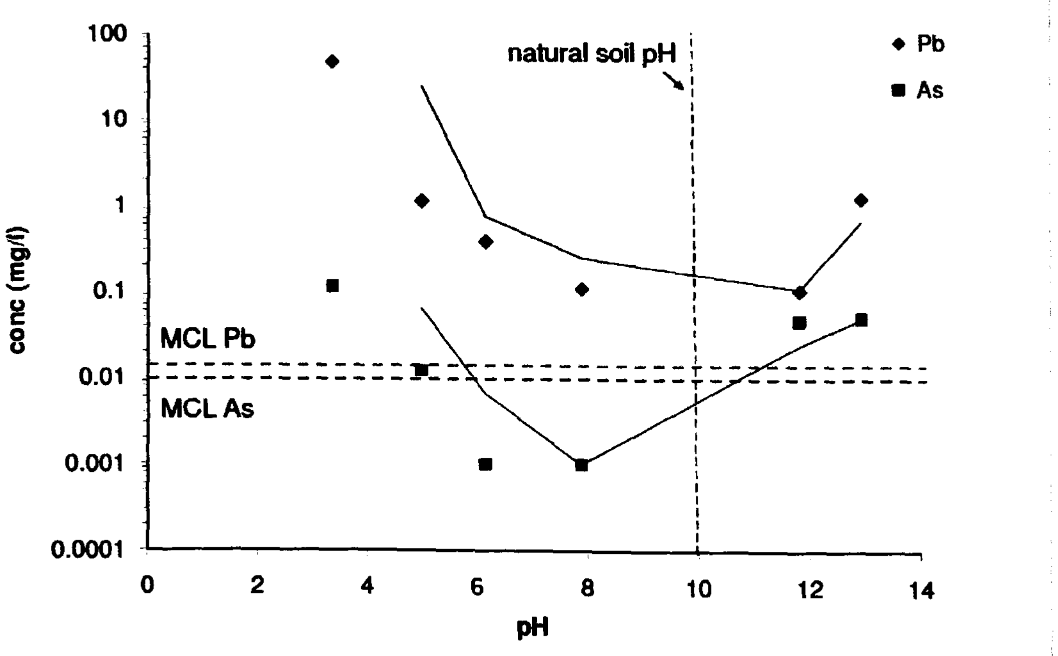


Figure 7.3 – pH dependent leaching of metal contaminants from S8 soils

The concentrations of lead in leachates increased up to two orders of magnitude on each side of this interval. Similarly to the other soils, the arsenic had a minimum solubility in the interval 6-7 and an amphoteric behaviour.

2.3.1.4 Other sites

The pH dependent leaching was not carried out for QD, CA and MGP since the contaminants of concern were organic compounds. It is well established in the literature that the organic contaminants and in particular PAH and TPH are immobilised in cement systems by physical entrapment (Mulder *et al.*, 2001; Karamalidis and Voudrias, 2007; Leonard and Stegemann, 2010), therefore equilibrium tests were not performed.

The AC soil contained arsenic and organic compounds, as contaminants of concern. However, during the pH dependent leaching test, the concentration of arsenic in the leachate was below detection limit of the instrument throughout the pH interval 4-12. Therefore the results have not been included here.

2.3.2 Acid neutralisation capacity (ANC)

For each S/S soil, the pH evolution against increasing amounts of acid was plotted. Selected data representing the characteristic features of the plots are shown in Figs 7.4 -7.10. The ANC behaviour depends on the type of buffering minerals present (Gianpaolo *et al.*, 2004; Stegemann *et al.*, 1997). These developed as a result of binder addition and/or the exposure to the environment, or were present in the soil prior to remediation.

Two groups of binders were added to the S/S soils and they were Portland cement and a mixture of Portland cement and PFA. Since the chemistry of the two groups is different they will be presented separately in the next sections.

2.3.2.1 Portland cement formulations

Figs 7.4-7.6 show the coresponding ANC curves for HA, MGP and QD soils. These were treated with Portland cement in proportion of 6, 10 and 25% (by weight of untreated soil), respectively. The natural pH was lowest (pH 8) for the soils containing the highest percentage of Portland cement binder, whilst the highest pH of 10 was measured for that containing the lowest percentage of binder.

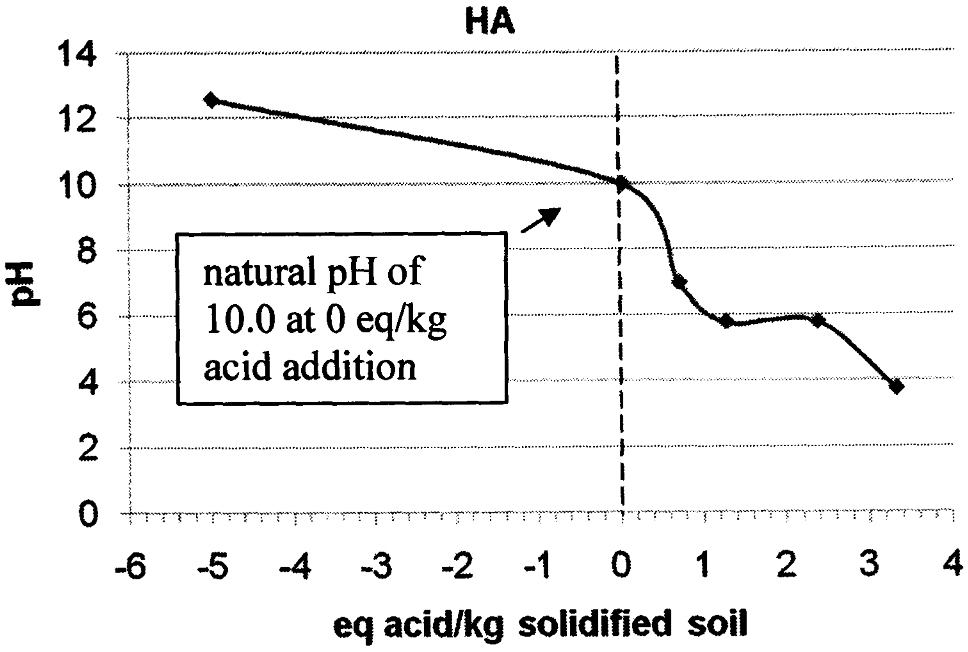


Figure 7.4 – Acid/alkali neutralisation capacity (eq·kg^{-1}) against pH obtained for Halton

The results in Figs 7.4-7.6 indicate that all three soils lacked buffering at high pH (>10). The shape of the ANC curves was similar for the three S/S soils and was characterised by a steep drop from the natural pH to pH 5-6, followed by a plateau at pH 6, for the HA and QD soils, and at pH 5 for MGP soil. A second plateau was noted for the QD soils between pH 4.6 - 5.

The ANC to pH 4 ($ANC_{4.0}$) achieved by the HA soil, was 3.3 eq/kg, which was higher than that of MGP and QD soils equal to 1.4 and 2.7 eq/kg respectively.

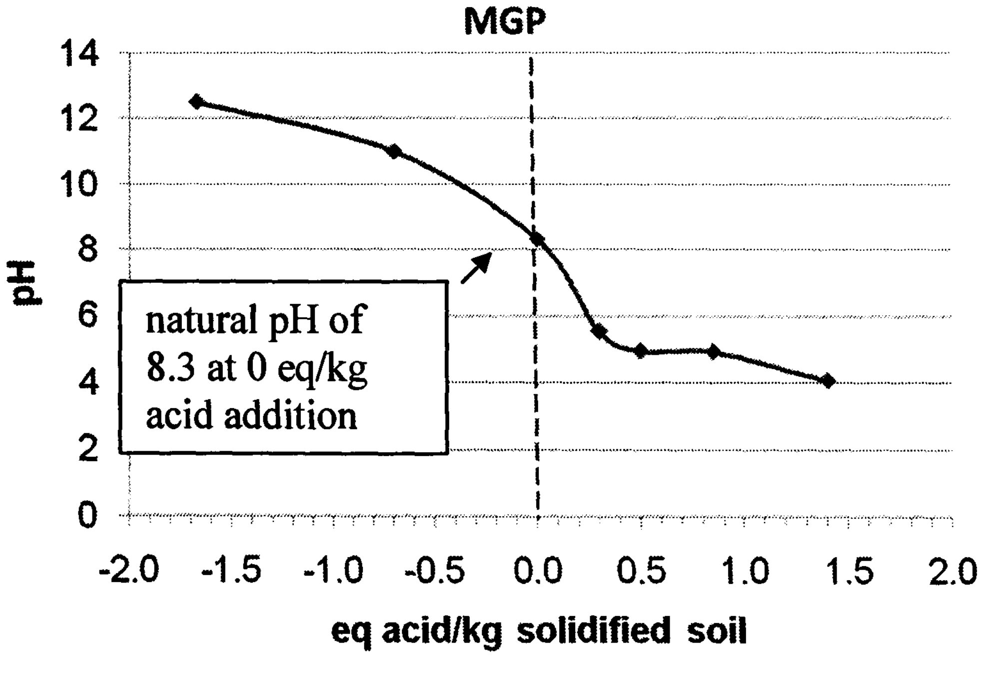


Figure 7.5 – Acid/alkali neutralisation capacity (eq·kg^{-1}) against pH obtained for Columbus MGP

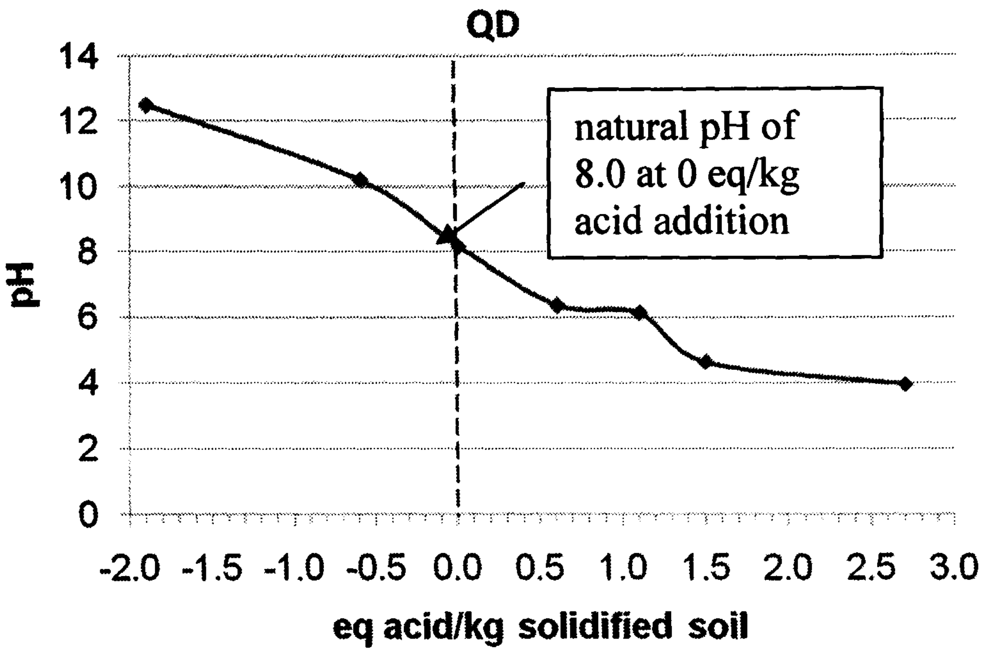


Figure 7.6 – Acid/alkali neutralisation capacity (eq·kg^{-1}) against pH obtained for Quarry Dump

2.3.2.2 Portland cement/PFA formulations

Figs 7.7-7.10 present the ANC curves of the S/S soils treated with Portland cement/PFA formulations. The results indicate that, similarly to the Portland cement formulations, these S/S soils do not exhibit buffering at high pH. The soils containing PFA displayed a variable initial pH, from 9.5 to 11.4.

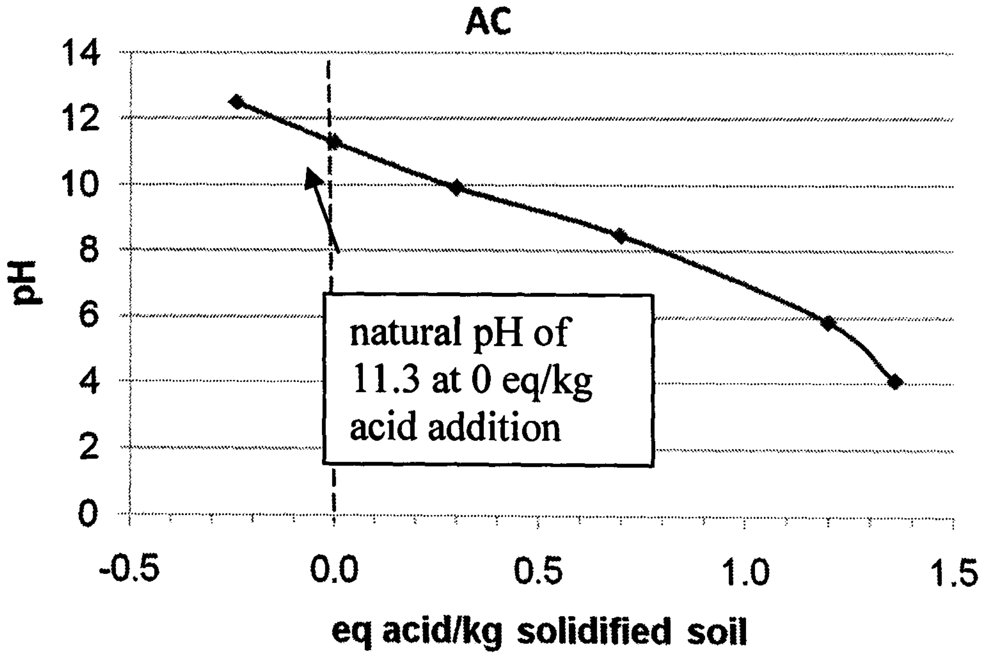


Figure 7.7 – Acid/alkali neutralisation capacity (eq·kg^{-1}) against pH obtained for American Creosote

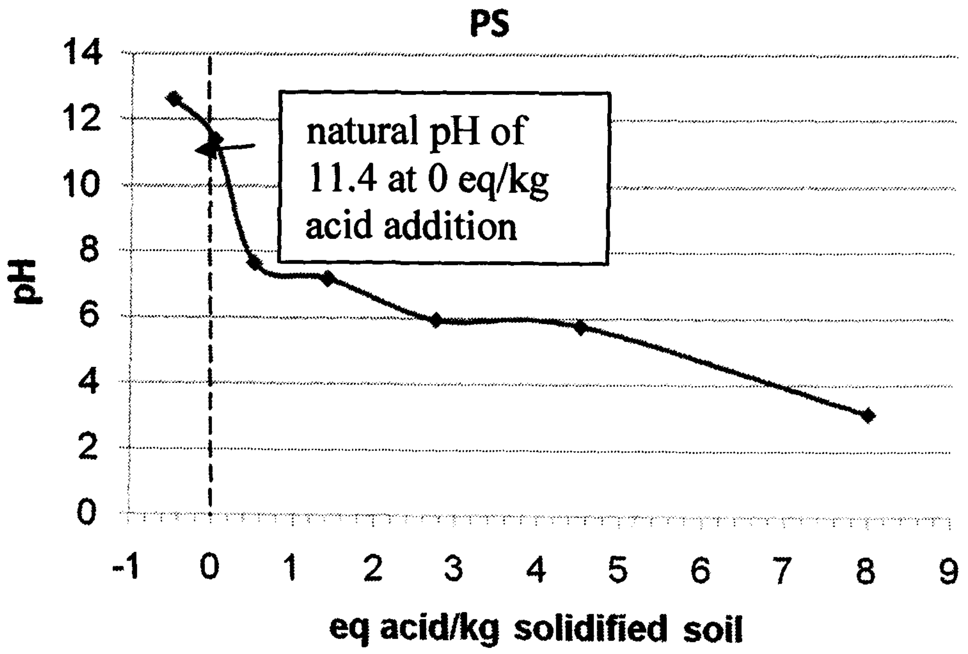


Figure 7.8 – Acid/alkali neutralisation capacity (eq·kg^{-1}) against pH obtained for Pepper Steel

The ANC of AC soil had a gradual decrease on acid addition, from the natural pH of 11.3 to pH 4, without any discernable buffering plateaus. In contrast, the PS soil had two plateaus; the first between pH 7.2-7.6 and a second at pH 6. Work by previous authors have attributed the buffering at pH 5-8 to the presence of carbonates, aluminosilicates or carbonates coexisting with silica gel (Sweeney, 2001; Chen *et al.*, 2009) .

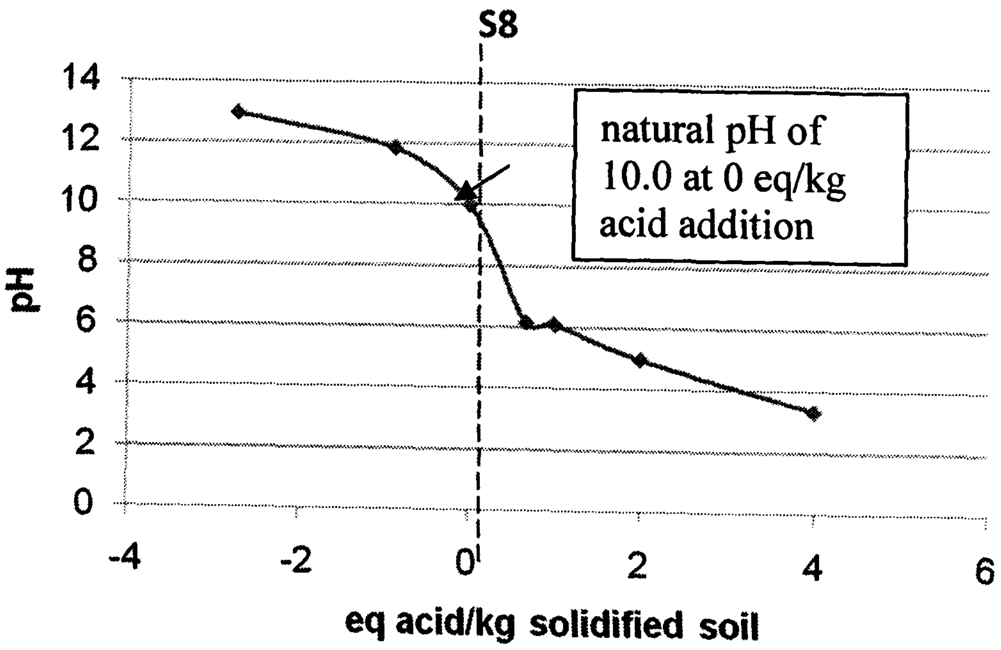


Figure 7.9 – Acid/alkali neutralisation capacity (eq·kg^{-1}) against pH obtained for South 8th Street

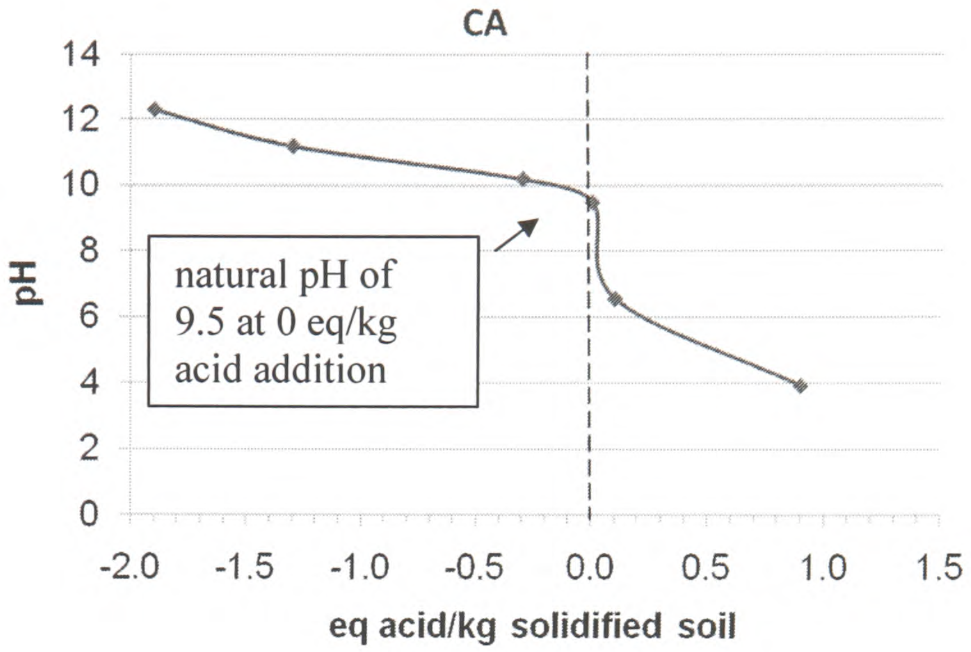


Figure 7.10 – Acid/alkali neutralisation capacity (eq·kg^{-1}) against pH obtained for Caerphilly

The S8 soil had a steep drop from the natural pH of 10.0 to pH 6.0. A plateau which was equivalent to 0.3 eq/kg occurred at pH 6 and was attributed to the presence of carbonates. Between pH 4 and 6, the ANC curve recorded a gradual decrease.

In order to make a comparison of the ANC of the S/S soils, an end point for the acid addition was chosen. Although previous research used ANC to pH 9 ($ANC_{9.0}$) (Stegemann *et al.*, 1997), this could not be used in this work. $ANC_{9.0}$ was an adequate end point for systems that rely on buffering at high pH; however, since the S/S soils were weathered, they lacked any significant buffering at pH >8. For this reason, the ANC to pH 4 ($ANC_{4.0}$) was used as a final point for acid addition.

Based on a typical $ANC_{4.0}$ of a hydrated paste of Portland cement, the $ANC_{4.0}$ for the S/S soils could be calculated by taking into consideration the amount of binder used. This comparison showed that the $ANC_{4.0}$ for the S/S soils of age up to 16 years was equal or higher than the calculated value, except for the soils treated with Portland cement. This finding is contrary to previous work by Sweeney (2001) and Stegemann *et al.* (1997), which reported a decrease of ANC at addition of replacement materials.

The CA soil displayed a sudden drop from the natural pH of 9.5 to pH 6.5, at additions of less than 0.1 eq/kg of acid (Figure 7.10). The pH decline continued to the end of the acid addition, at pH 4, without any discernable plateaus.

The S/S soils had low (<2 eq/kg) to high (>5 eq/kg) $ANC_{4.0}$ (Jing *et al.*, 2004). At the low end of the spectrum was CA with an $ANC_{4.0}$ equal to 0.9 eq/kg and the high end the PS soil with $ANC_{4.0}$ of 8.0 eq/kg. Since all S/S soils were treated with Portland cement-based formulations, a comparison of the $ANC_{4.0}$ measured values with hydrated Portland cement pastes could be carried out. Sweeney (2001) reported an $ANC_{4.0}$ value of 20 eq/kg, for pure Portland cement pastes cured for 28 days under nitrogen. This was used to calculate the $ANC_{4.0}$ for the S/S soils, considering the amount of binder used for remediation. The results of this comparison are presented in Table 7.2.

Table 7.2 – Comparison between calculated and measured $ANC_{4.0}$ for the S/S soils

Soil	ANC (eq/kg)	
	Calculated	Measured
AC	1	0.9-1.4
PS	2.4	3.4-8.0
S8	4	3.0-4.0
QD	5	2.1-2.7
MGP	2	1.0-1.5
HA	1.2	3.3-4.0
CA	0.8	0.9-1.4

The measured $ANC_{4.0}$ was lower than the calculated value for the S/S soils treated with Portland cement (QD and MGP) and equal or higher for those containing blended formulations (AC, PS, S8, HA and CA).

2.2.3 Scanning electron microscopy (SEM)

Scanning electron microscopy was used to examine the S/S soils and identify the contaminants of concern. Backscattered electron imaging, X-ray microanalysis and mapping were applied to each S/S soil and the results are summarised below.

2.2.3.1. Lead

Although lead was a contaminant of concern in a number of S/S soils, it was not easily observed by means of SEM. However, X–ray microanalyses or elemental mapping of the cement matrix positively identified lead. This was associated with calcium silicates, organic compounds, barium and sulfur, and in isolated cases with ettringite.

An interesting association of lead was with organic compounds, observed solely in the S8 soil. Figure 7.11 is a backscattered electron micrograph of an organic inclusion, separated from the surrounding S/S matrix as a result of exposure to the high vacuum conditions inside the SEM. The X-ray map group of the inclusion shows metallic lead interdispersed with barium, sulfur and organics. Lead was also observed in the structure of ettringite. This fact is illustrated in Figure 7.12, in the X-ray elemental map of a cluster of radiating ettringite crystals formed in a void in the matrix. The white dots in the lead map represent the distribution of submicron particles of lead in the ettringite crystals.

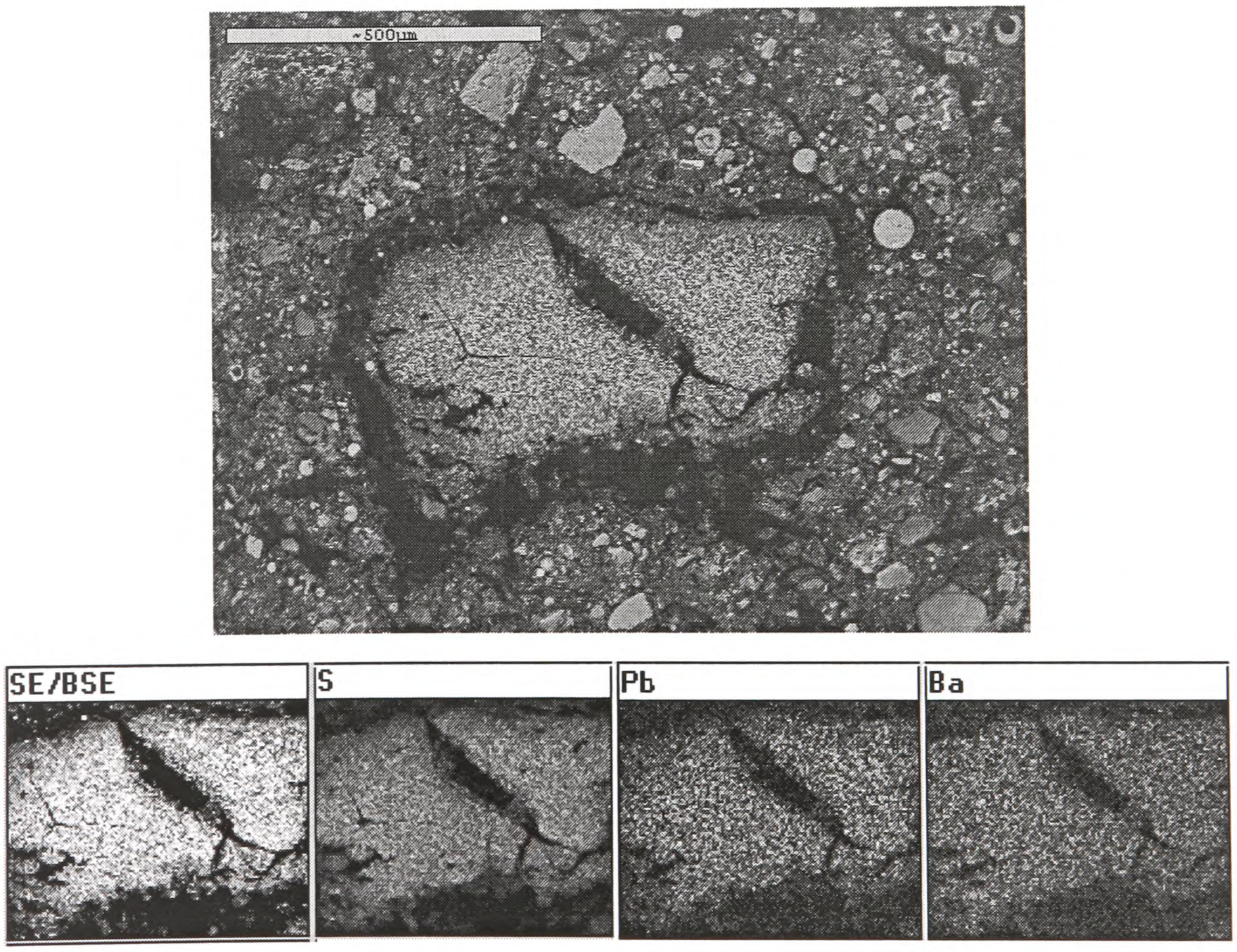


Figure 7.11– X-ray elemental maps of the S8 soil showing lead incorporation into organic compounds and the elements distribution

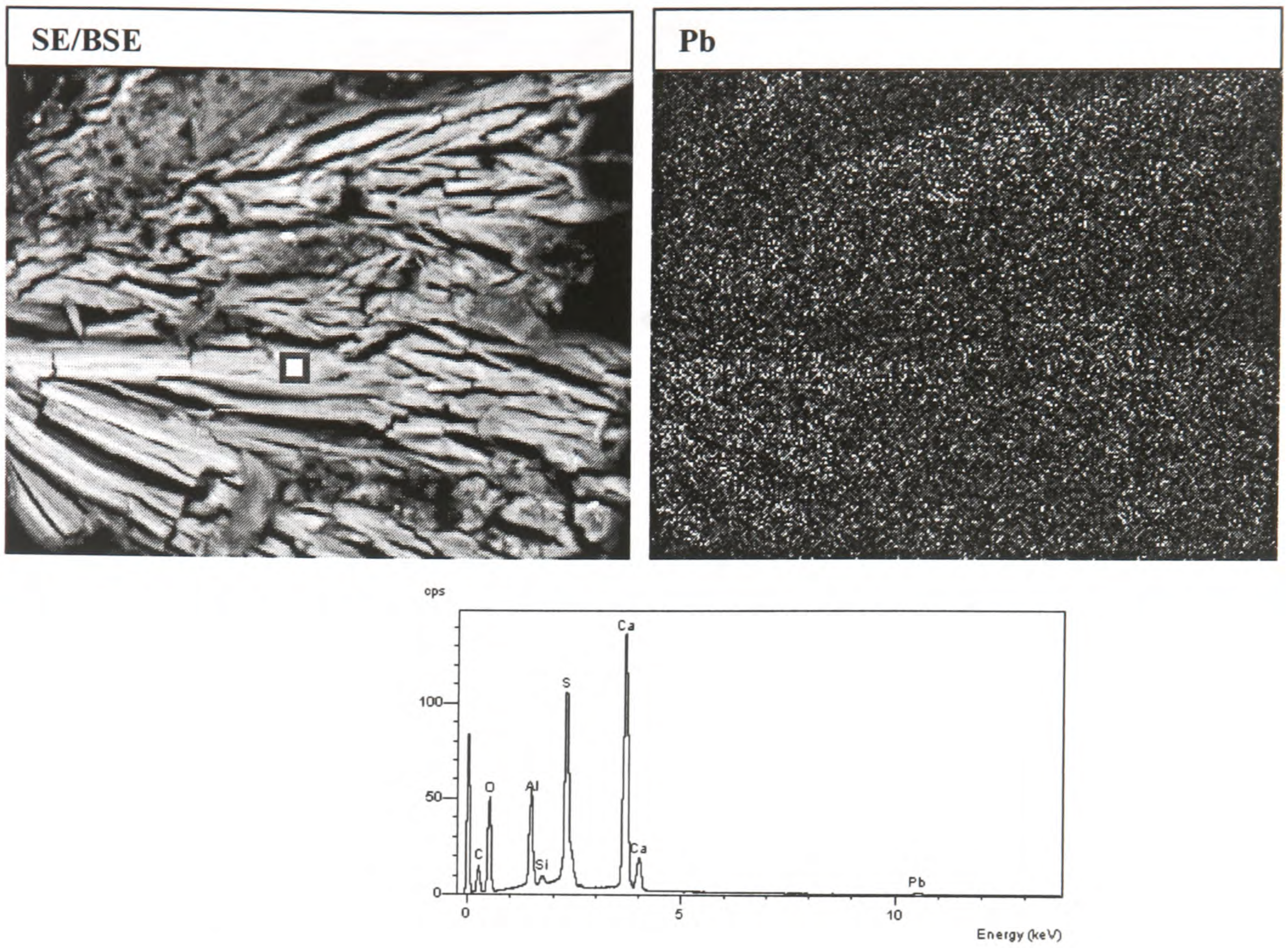


Figure 7.12 – X-ray maps showing lead incorporation in ettringite, in S8 soil and the EDS spectrum of the marked area

Figure 7.13 shows a backscattered electron micrograph of an area in the HA soils obtained at high magnification. This illustrates the distribution of the lead, but also copper and zinc in an area containing calcium silicate.

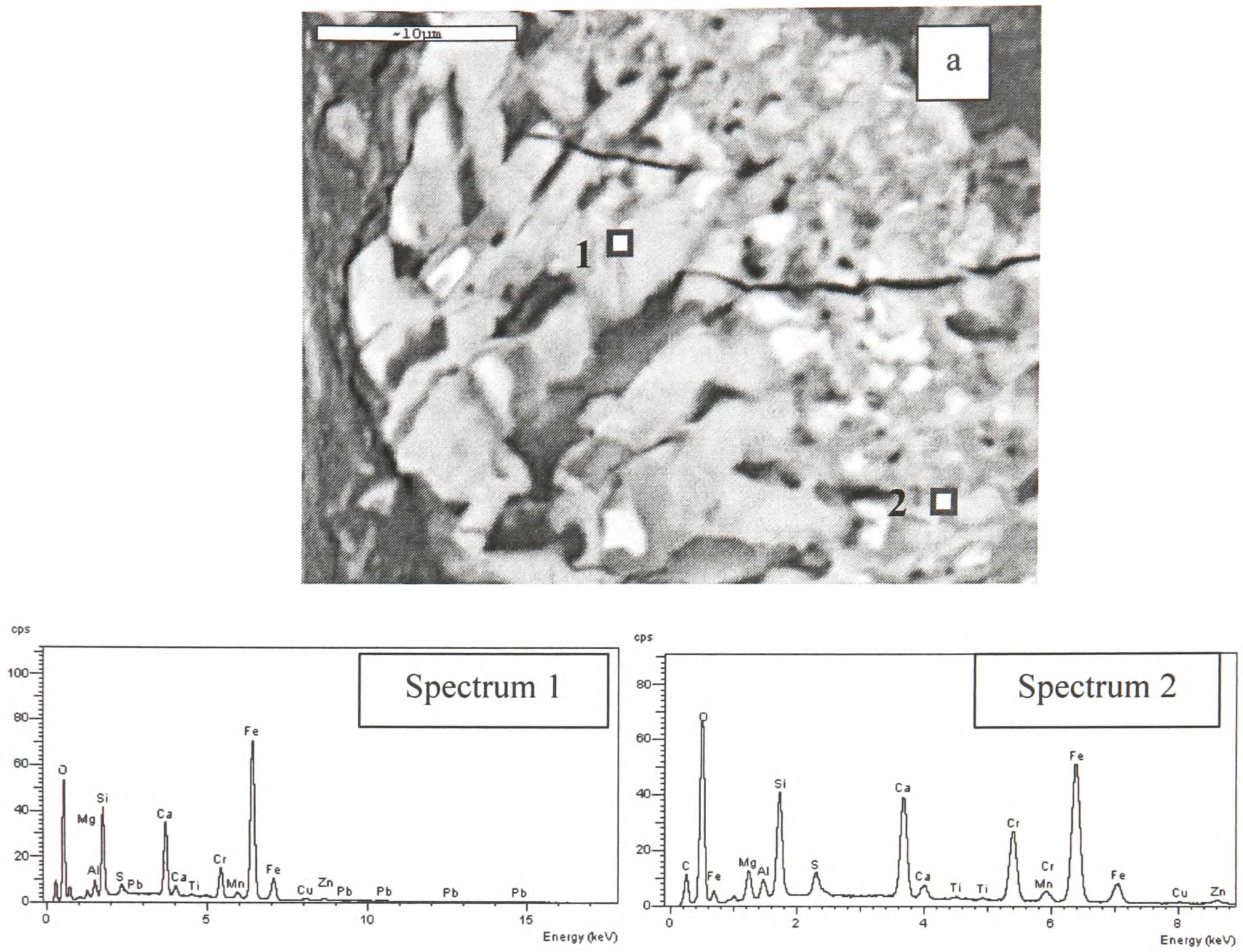


Figure 7.13 – Backscattered electron micrograph showing the distribution of lead, copper, zinc in the HA soil and corresponding EDS spectrum of marked areas.

2.2.3.2. Arsenic

Arsenic was rarely observed, although was a contaminant of concern in more than a half of the S/S soils. Generally, arsenic was dispersed within the matrix and was associated with zinc, copper and potassium. Figure 7.14 shows amorphous masses of arsenic, iron and zinc as haloes around a waste particle, which may indicate the outward migration of the contaminants.

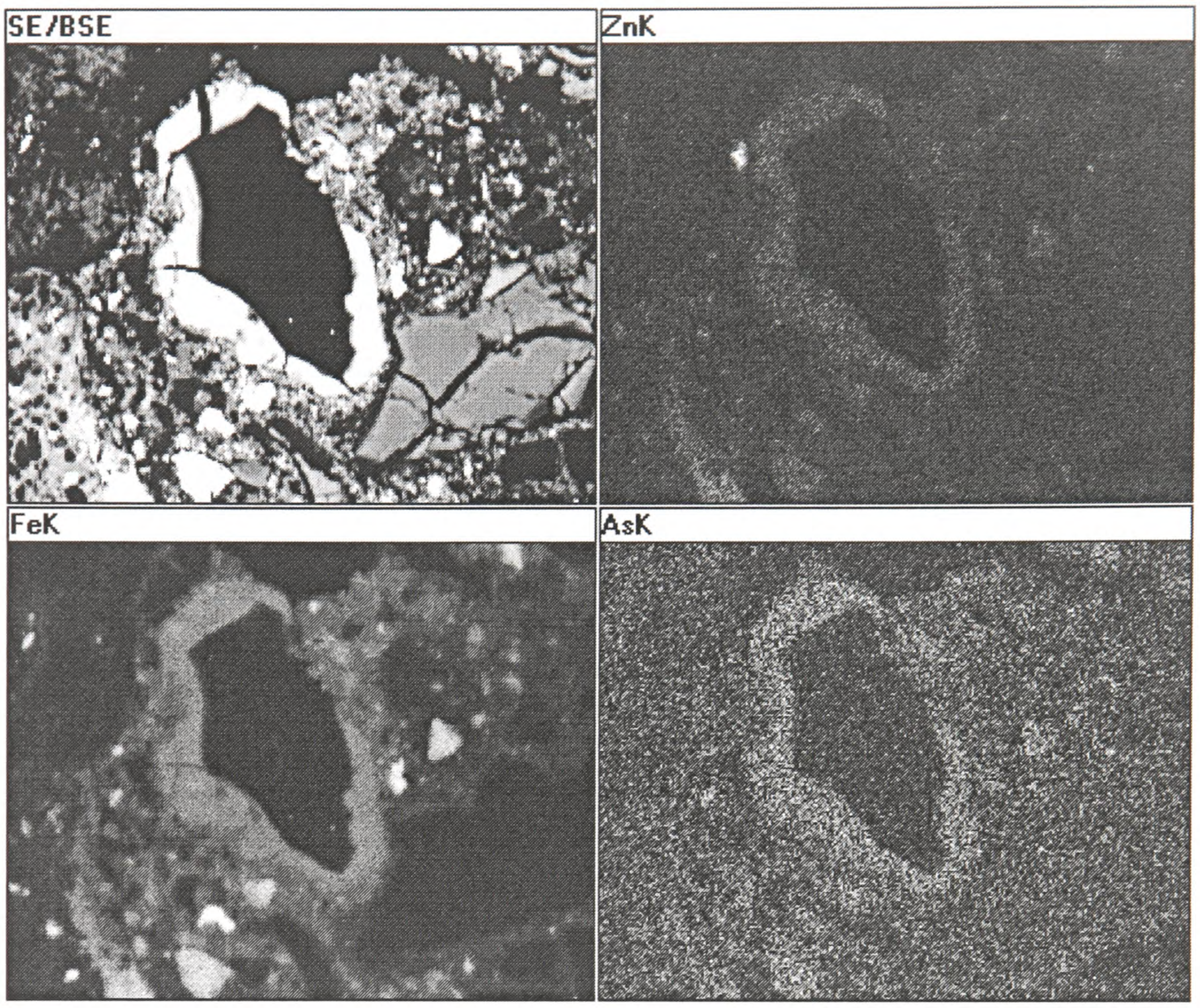


Figure 7.14 – X-ray elemental map showing the distribution of arsenic and zinc in the matrix of the HA soil

2.2.3.3. Copper

Copper was one of the contaminants of concern in the HA soil. This was frequently observed as metallic fragments, precipitates or as disperse fine particles in the cement matrix. Fragments of metallic copper were noted in the porosity of the S/S soil matrix, which was being filled with crustiform calcium carbonates (zone 1), during episodes of wetting and drying (Figure 7.15). Carbonation resulted in the physical entrapment of the metallic copper as indicated by the arrows; however there was some evidence of the dissolution of copper at the contact zones with the calcium carbonate i.e. zone 2.

X-ray mapping showed copper alone or in association with sulfur, oxygen, potassium, magnesium, arsenic and zinc (Figure 7.16). Copper was also observed as a precipitate in the matrix, noted in the centre of the SEM micrograph from Figure 7.17. The EDS point analysis of the precipitate indicated the presence of copper sulfide (Cu_2S).

2.2.3.4. Zinc

Figure 7.14 shows the distribution of the zinc within the S/S soils from HA. This metal appears dispersed in the matrix, but also concentrated around a carbon rich particle, seen here as a dark area in the centre of the image, surrounded by a white halo. Similar diffuse distribution can be seen in Figure 7.18, in the same soil, except that they are intermixed with fragments and disperse particles of copper.

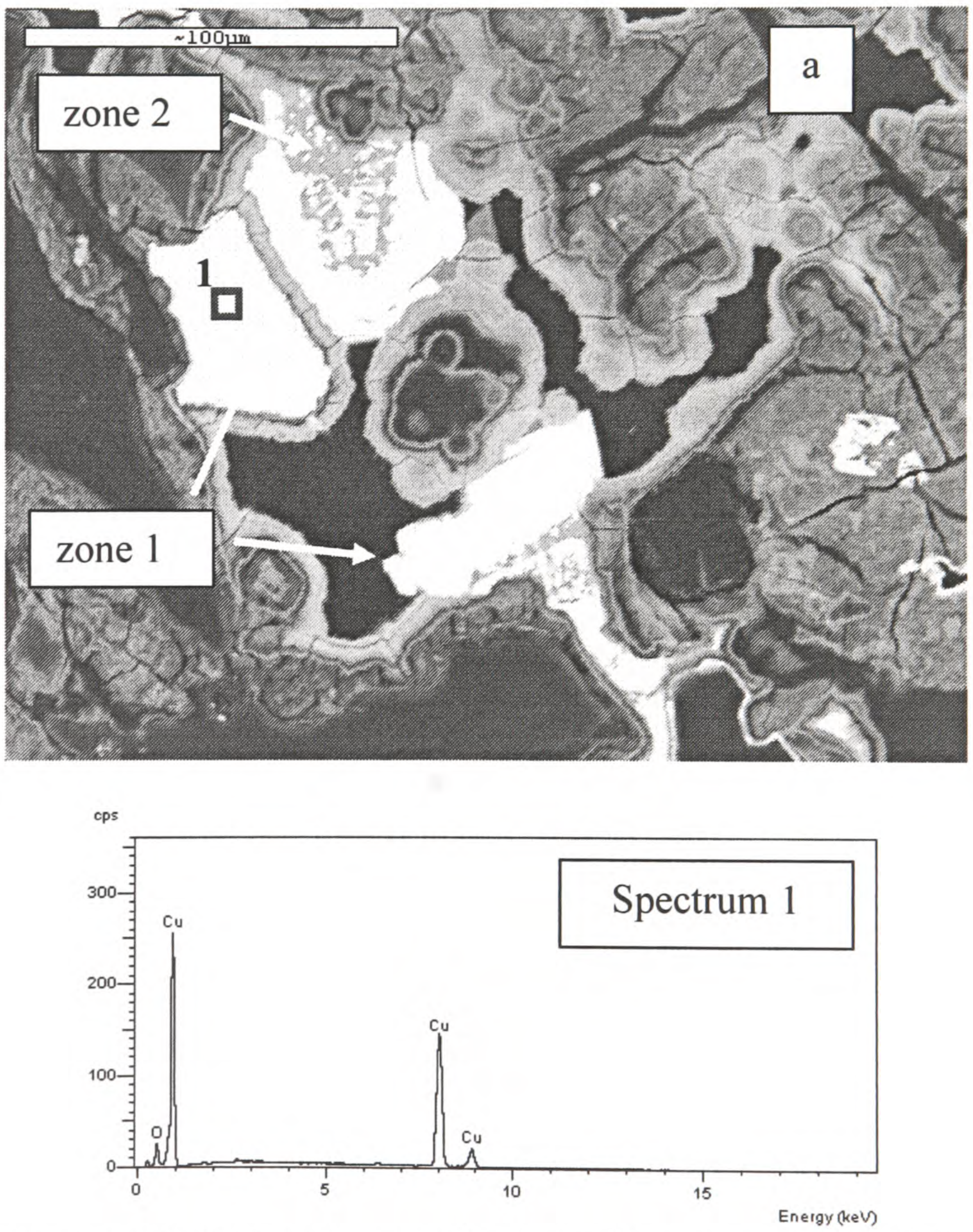


Figure 7.15 – Backscattered electron image of copper fragments becoming physically trapped in the progressively carbonating matrix (a) and (b) the EDS point analysis of the marked area (HA)

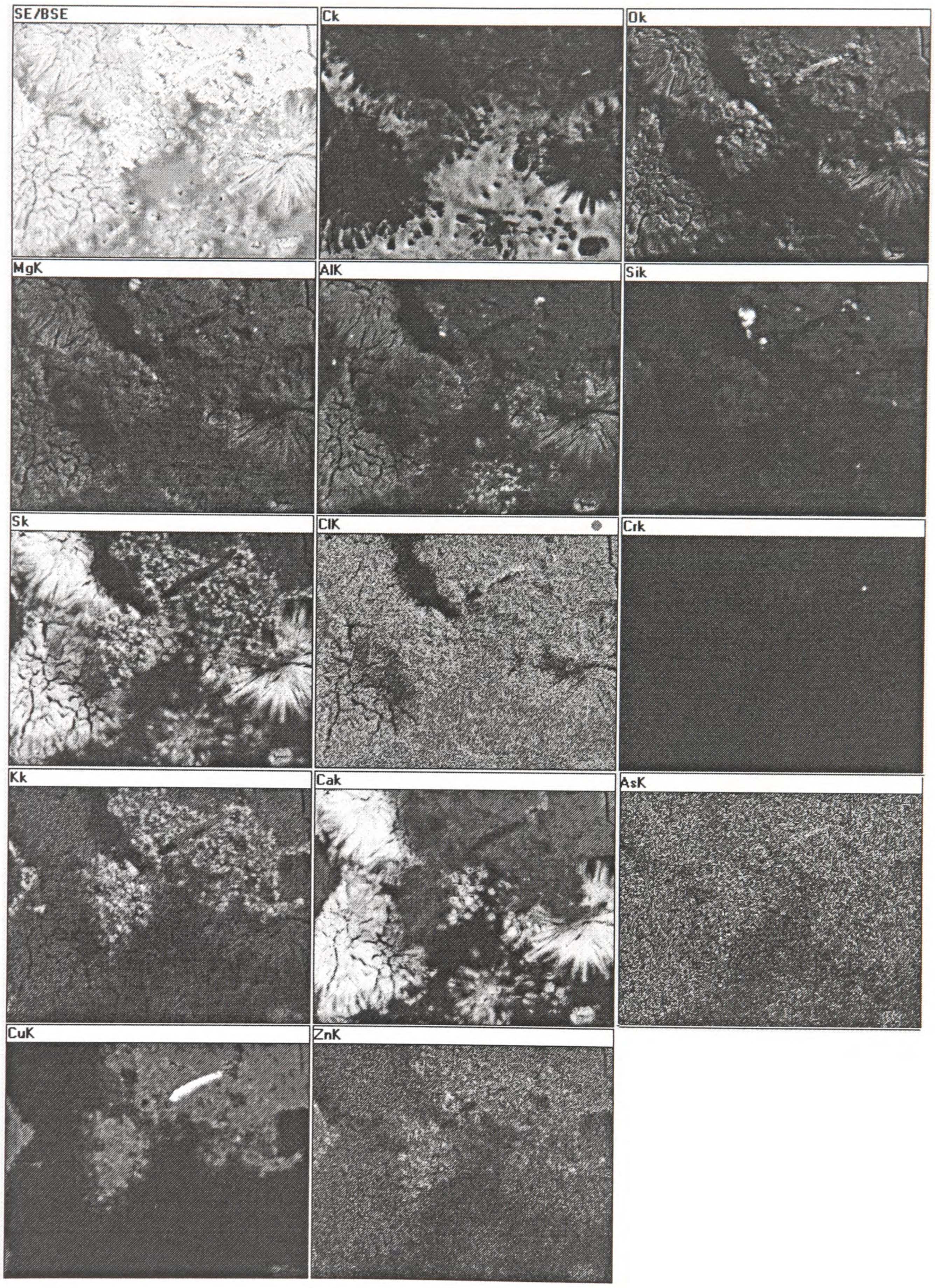


Figure 7.16 – X-ray elemental map of copper, zinc and arsenic in the HA soil, showing the relationship between ettringite and arsenic and the distribution of copper and zinc

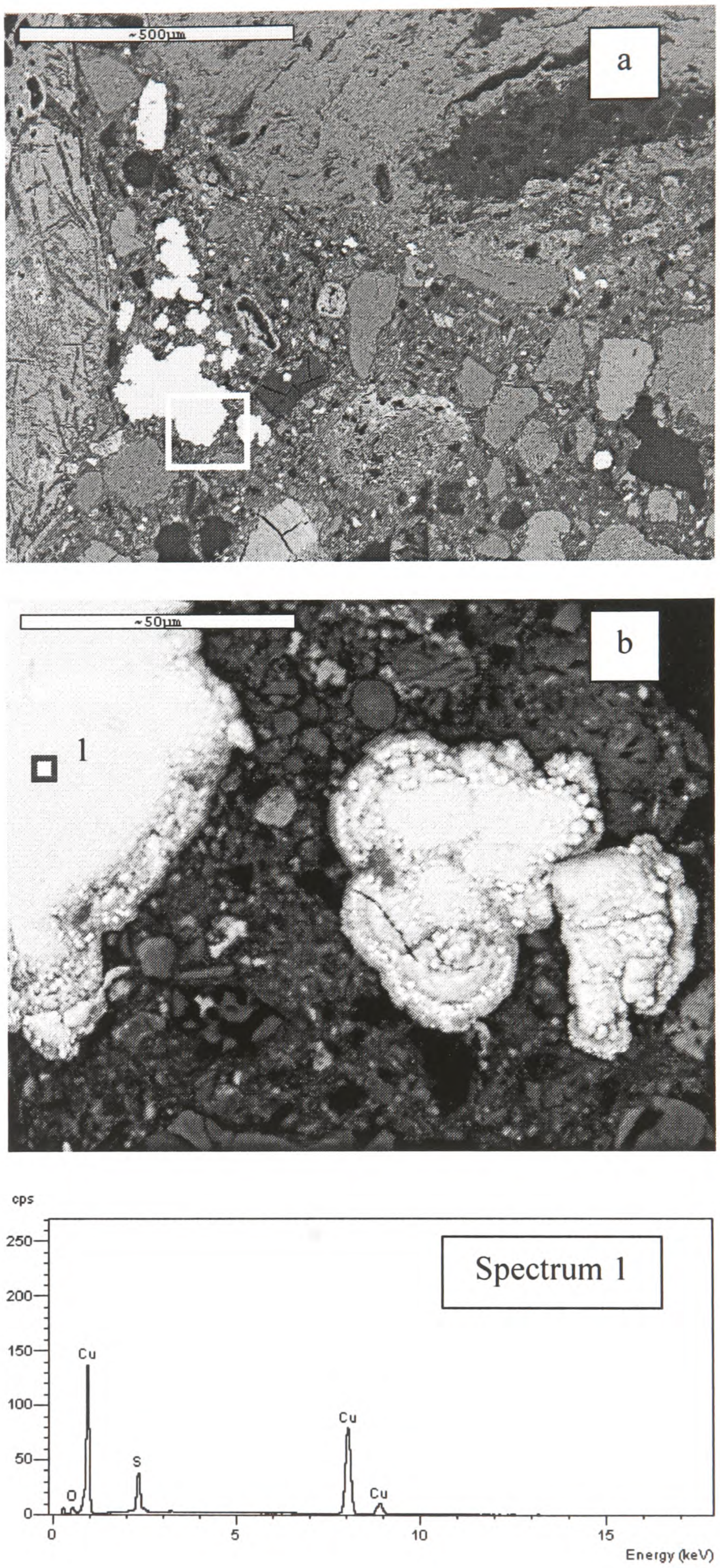


Figure 7.17 – Backscattered electron image showing copper sulfide precipitate in the HA soils (a); higher magnification of the marked area (b); EDS point analysis of the copper sulfide precipitate (spectrum 1)

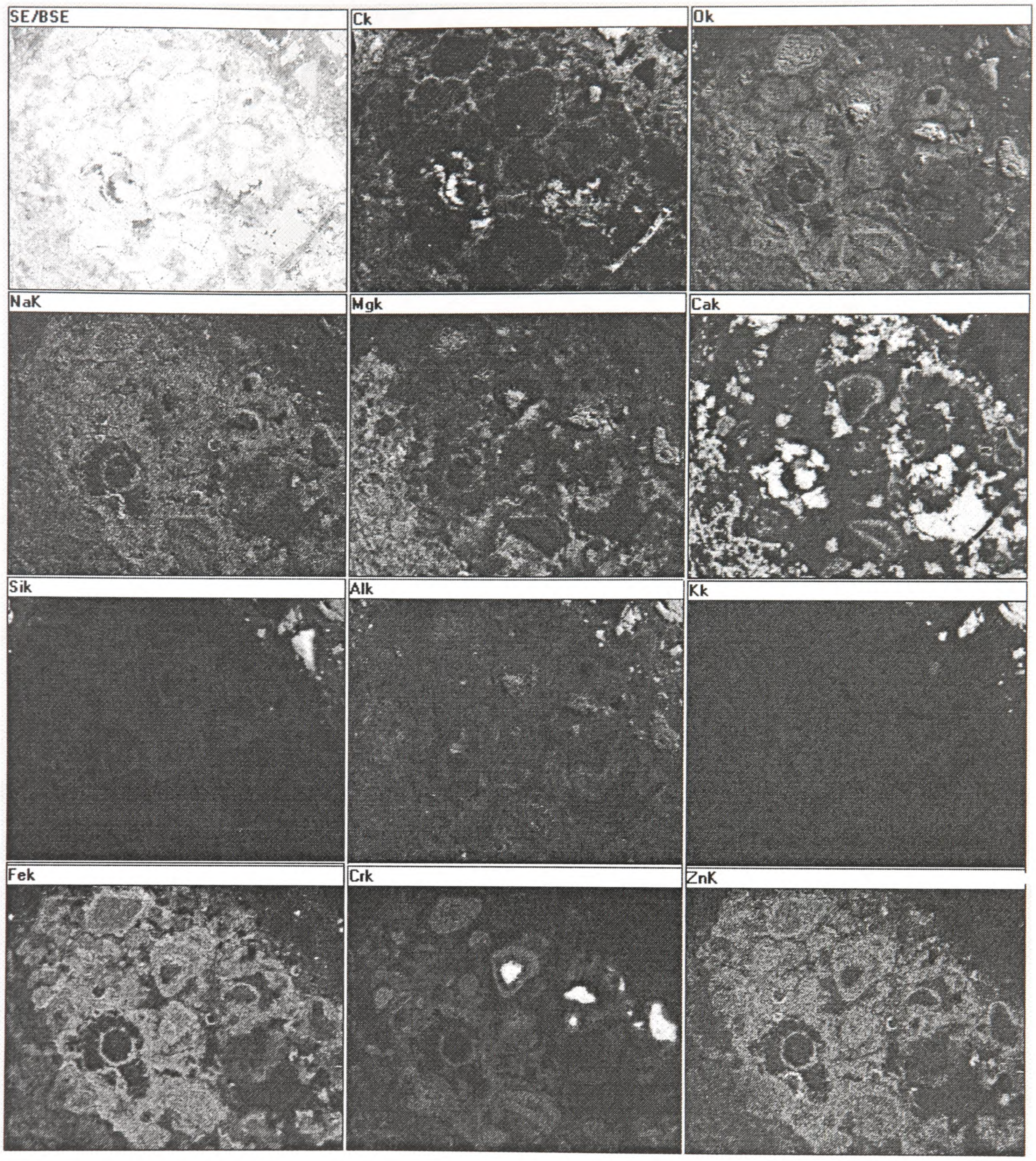


Figure 7.18 – X-ray maps showing the distribution of zinc in relation to other elements, in the soils at HA

2.2.3.5 Organic contaminants

The organic contaminants were observed in the S/S soils with the aid of an optical microscope and confirmed by SEM. Organic residues were trapped within the inorganic matrix and an example is shown in Figure 7.19.

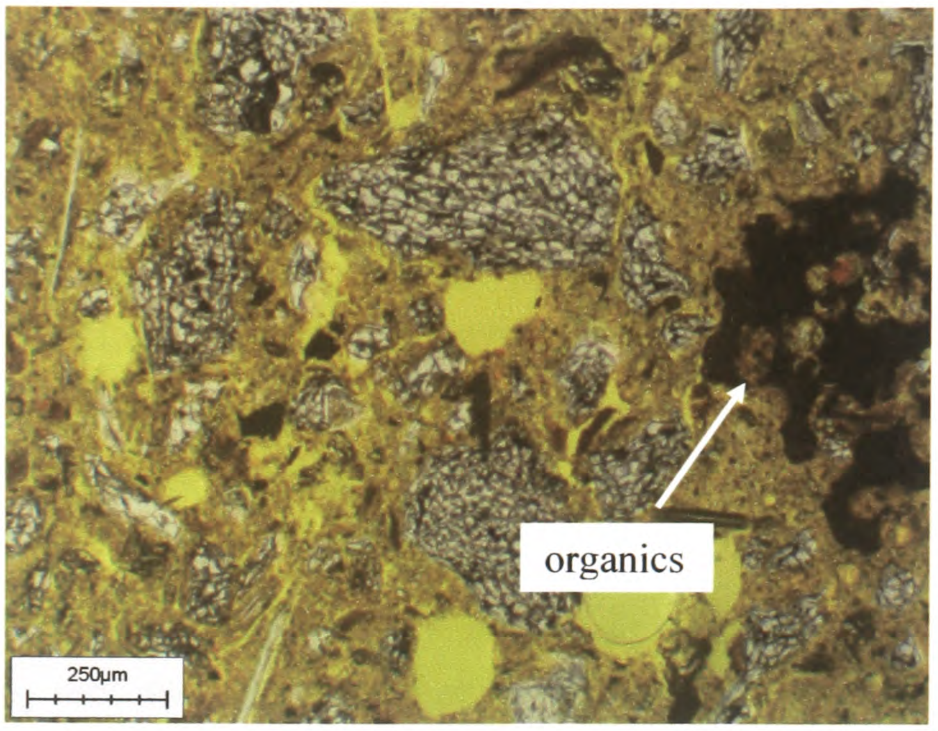


Figure 7.19 – Transmitted light micrograph of organic inclusions in the S/S soil matrix (QD)

4. Discussion

The metal release from S/S soils is influenced by a number of physical and chemical factors. The most important factors determining leaching behaviour come from i) matrix properties (mineralogy, permeability and acid neutralisation capacity); ii) environmental conditions (infiltration, leachant composition, flow regime, groundwater composition) and iii) waste – binder – environment interactions (e.g. carbonation, sulfate attack, alkali silica reaction) (Garrabants and Kosson, 2005).

This chapter focused on the metal leaching from the S/S soils and the acid neutralization capacity.

4.1 Compliance leaching tests

Whether in preparation of a treatment design or for the monitoring of a soil treatment, it is necessary to evaluate the performance of the S/S in relation to the contaminant retention. In this Chapter, the permanence of contaminant immobilisation in the S/S soils was assessed by a number of compliance leaching tests such as SPLP, NRA and NEN and equilibrium based test (pH dependent leaching).

Although not reproducing the true conditions on individual sites, the compliance leaching tests have often been used to evaluate the performance of S/S soils against site specific remedial targets (SSPC). The SSPC were calculated depending on the location and extent of contamination, the potential site reuse and other site specific conditions. However, in the case of HA, PS and CA, SSPCs were not defined. Instead, for comparison with the leaching results, the remediation contractors have used drinking water guidelines (in the UK) and maximum contaminant limits or MCL (in the US).

As shown in Table 7.1, the contaminant release from the S/S soil following various compliance leaching tests was low, but not always within the SSPC or the national drinking water guidelines. Remediation target values equal to drinking water quality limits are somewhat over-specified, since numerous factors contribute to dilution, dispersion and retardation of the contaminant release from the S/S soil. The contaminant concentration in groundwater is determined by the permeability of the S/S matrix, the rate of diffusive release of contaminants to infiltrating water, retardation in the vadose and additional hydrogeological factors i.e. aquifer thickness and hydraulic gradient (Gardner, 2005). Therefore higher levels are allowed in the leaching extract so long as the concentrations will be reduced to the MCL at the site boundary or other points of compliance (USEPA, 2004a).

4.2 Equilibrium tests

The limitations of compliance leaching tests to explain the behaviour of S/S soils have been acknowledged, thus equilibrium tests have also been performed. The results indicated that all metals of concern, Cu, As, Pb, Zn had an amphoteric behaviour, which was expected for an S/S system (Conner, 1990).

In S/S soils the expected speciation of heavy metals is as hydroxides (Conner, 1990). However, the solubility of these phases in the S/S soils was much lower than the theoretical hydroxide solubility, indicating that the contaminants may be immobilised by incorporation into more stable combinations involving the cement hydrates. The chemistry of the S/S systems is complex and the leaching behaviour cannot be explained by the presence of single compound. The SEM observations indicated that the contaminants of concern were precipitated as sulfides, incorporated in ettringite or organic compounds, or were associated with the C-S-H.

Despite carbonation of all S/S soils, there was no evidence of carbonates acting as solubility controlling phases for the metal leaching, as indicated in the PASSiFy report (2010). At the natural pH of the soils, which was between 10 and 11.4, most metals had values above their minimum solubility. As shown in Figure 7.1-7.3, it is expected that the metal leaching would improve as the matrix will continue to carbonate and the pH decrease to near neutral values. Below this pH value a sharp increase of the metal leaching is expected.

4.3 Acid neutralisation capacity

Acid neutralisation capacity is an intrinsic property, which characterises the ability of the S/S matrix to resist pH decrease caused by external factors. In the case of S/S soils, which are placed underground, the interaction with acidic groundwater and rainfall is likely to affect the ANC.

The acid neutralisation test performed on the soil samples was considered a worst-case scenario of exposure, since the pH of the leachant used was approximately 1 and the samples were ground to below 1 mm. This test mimics a granular S/S soil not being capped and found in direct contact with acidic water. In real environments, the S/S soils would be exposed to rainwater or groundwater, with a typical pH of approximately 3-4 (Stegemann *et al.*, 1997) and a very low acidity compared to that of the leachant used in our tests. Moreover, the permeability of the S/S soil and the surroundings would determine the interaction of the acidic waters with the contaminants. An extensive study of eight different scenarios of interaction between groundwater or rainfall and cement-based waste forms was carried out by Coté and Bridle (1987). The conclusions were that the S/S soils must not be placed in materials with similar permeability, since this will favor the groundwater flow through the soils, leading to an increase of contaminant leaching.

Since the S/S soils were real life samples, it is necessary to refer to known systems to make interpretations of the ANC. As shown in Chapter 4, all S/S soils were treated with Portland cement binder formulations; therefore this will be used as a reference point.

The chemistry of Portland Cement systems was discussed in detail in Chapter 2. The acid resistance of the S/S soils is normally associated with the binder system and only marginally with the soil components. The main hydration products are the C-S-H accounting for 50 – 60% of the matrix composition, $Ca(OH)_2$ 20-25% and the remainder calcium sulfoaluminates. The pH will be determined by the nature of the C-S-H gel with various Ca/Si ratios, but also by portlandite. The C-S-H does not dissolve in the same manner with crystalline compounds and maintains acid resistance by decalcification in favour of formation of calcium hydroxide and siliceous gel (Garrabants and Kosson, 2005). These phases provide buffering capacity, expected between pH 10 and 12.3.

The study of the behaviour of the seven S/S soils to progressive acid addition did not indicate any buffering potential at high pH, more precisely above pH 8. This could be attributed to portlandite depletion and C-S-H decalcification due to carbonation or as a result of environmental exposure and the use of pozzolanic material. This fact was supported by the XRD and SEM examination, which indicated the presence of calcite in all samples and the absence of portlandite. Moreover, the Ca/Si ratio of the C-S-H determined in the previous Chapter, showed a decalcification of this phase (see section 2.4.1 in Chapter 6). The average Ca/Si ratio varied between 0.5 and 1.0. Although the buffering capacity is lower for the silica rich C-S-H than for its calcium rich counterpart (Ca/Si >1.5), it was reported to exert greater resistance to acid attack over time by creating a silicious protective layer on mineral surfaces (Stegemann *et al.*, 1997).

The ANC of the S/S soils was dominated by the buffering capacity of carbonate, which occurred at much lower pH ranging between 5-7. Most estimates of the durability of S/S materials have been based on the high pH buffering capacity. Atkinson *et al.* (1985) modelled Portland cement treated wastes and showed that, in certain leaching conditions in a nuclear repository, it would take approximately 10^5 years for the pH of the waste to drop from 12.5 to 12, due to lime leaching, and further 10^6 years to decrease to pH 10.5.

However, since the S/S soils studied lacked of any significant buffering capacity at high pH it is necessary to understand the efficacy of carbonates for maintaining the pH. Calcium carbonates are efficient buffers in the neutral to basic pH range and they will provide pH buffering as long as carbonate solids are present and available for dissolution (Bozkurt *et al.*, 2000).

Johnson *et al.* (1999) evaluated the behaviour in a monofill of demolition waste, composed of calcium carbonate in proportion of 30%. Their work concluded that between 20,000 and 30,000 years were necessary in order for the calcium carbonate, from a 1 m deep deposit of demolition waste, to be uniformly depleted. A similar study this time on the durability of a waste in a landfill was conducted by Bozkurt *et al.* (2000). The 10 m thick landfilled waste contained 10% calcium carbonate and was assumed to be in equilibrium with rainwater with approximately pH 4. The estimates of the duration before all the buffering capacity of the carbonates was exhausted, was in the range of thousands of years (> 3000 years).

5. Conclusions

This chapter assessed the chemical performance of the S/S soils exposed to real environments and their efficacy for retaining the metal contaminants when subjected to a number of pass/fail leaching and ANC tests. The conclusions of this chapter are:

- The S/S soils have not always met their site specific performance criteria or the guideline values for contaminant leaching.

- The choice of leaching test will influence the concentration of contaminants in leachate. Therefore in order to obtain meaningful results, a suitable test must be chosen according to the nature of the S/S soils (monolithic or granular) and the soil exposure conditions.

- The use of drinking water guideline values for contaminant leaching from the S/S soil is inappropriate, since numerous other factors contribute to the contaminant dilution and dispersion prior to reaching the receptor e.g. the groundwater. In addition, in the

USA the drinking water limits were lowered after the remediation was carried out, therefore it should not be expected to meet those limits.

- Despite S/S soils high metal loading, leaching after up to 16 years of service, was less than 0.1 mg/l, and in some cases below the instrument detection limits. This observation supports previous data from the literature, which shows that the release of metals from the S/S soils is gradual. Hence S/S is a good risk management method.

- The metal contaminants were immobilised in cement hydrates, such as C-S-H and ettringite, and were also associated with organic contaminants.

- The microstructural investigation showed organic compounds being physically entrapped in the inorganic matrix.

- Despite carbonation being observed in all S/S soils studied, no metal carbonates formed. This was confirmed by the geochemical modeling, which did not identify carbonates as solubility controlling phases for the metal leaching.

- The S/S samples examined lacked any buffering capacity at high pH. The acid neutralisation capacity was low to moderate and was maintained by calcium carbonates. Based on previous estimates, the buffering capacity of these systems is likely to persist for thousands of years.

A summary and the conclusions of this work are presented in the next chapter.

Chapter 8 Summary and conclusions

The work presented in this thesis investigated the performance with time of Stabilised/Solidified soils, exposed to their environments of service for up to 16 years.

The literature showed that there is an important gap in the knowledge of the performance of applied S/S. Current knowledge of the performance of these systems is based on the laboratory simulations or pilot scale studies and not on real applications of S/S. Prior to this study, investigators have concentrated on certain aspects of the performance of S/S soils i.e. contaminant leaching behaviour and not on a holistic approach.

In this work, conceptual models were developed from the individual site literature to gain an understanding of the environments in which the S/S soils were placed, and the loads which were likely to influence their performance with time. This information was used to inform the choice of appropriate analytical techniques and tests for the study of S/S samples and interpret the observations made following the study. As a result, optical and electron microscopy, x-ray methods, leaching tests and standard physical tests were applied.

Sampling and sample preparation

Samples were obtained from seven S/S remedial operations by using a variety of coring techniques. Intact cores were difficult to obtain due to the nature of the soil. Most notable was the amount of fracturing induced during sample retrieval, including both macro and micro fracturing, and this impacted upon the measured properties recorded in the laboratory. At some of the sites, a water-based lubricant was used during coring and it is possible that this may have had an impact upon the leaching of contaminants during subsequent testing.

A great deal of method development was necessary for the SEM sample preparation, in order to preserve the sample integrity. Since some S/S soils were not monolithic in nature, the preparation of polished blocks and thin sections was difficult.

S/S soil characterization

The chemical composition indicated that the S/S soils comprise of silicates, silica, aluminium, calcium and iron. Despite the addition of cement up to 25% by weight of soil, the composition was similar to that of concrete, PFA and clayey soil.

Mineralogically, the S/S soils were a mixture of soil-derived phases (e.g. clays, feldspars, micas) and minerals originating in the binder system applied during remediation. Moreover, secondary phases were identified depending on the environmental exposure and the metastability of each S/S soil.

Physical properties and microstructure

The current practice is to apply the same tools used in evaluating the performance of concretes to S/S soils. The results of this study indicated that the S/S soils are dissimilar to concrete from the point of view of their unconfined compressive strength and permeability, but are subjected to the same degradation processes characteristic of cementitious systems.

The S/S soils were weaker than concretes by design, and not because a degradation over time has occurred. All S/S soils, except one, have met their design criteria for strength.

According to their permeability, the S/S soils could be compared to soils composed of sand, silt and clay, rather than concrete. Thus, the transport mechanism through S/S soils will be different to concrete.

The microstructure of retrieved S/S materials was complex and involved interactions between all three system components; soil, contaminants and binder, and this relationship was subject to modification as a result of exposure in their service environment. This study showed that there is no relationship between the age of the S/S soil and the changes observed. Carbonation and sulfate reactions took place in all soils investigated and were the main identifiable reactions.

All the S/S soils were found to be carbonated to a lesser or greater degree. Since the prime location of carbonation was in pre-existing voids and cracks, the main effect was matrix densification.

Although ettringite and gypsum were present in the S/S soils microstructure, to this point there has been no damage associated with them. However, some soils were naturally alkali sensitive and reacted when solidified with the cement binder leading to ettringite formation. This reaction is potentially deleterious in monolithic S/S soils since it takes place with a volume change.

Contaminant immobilization

The contaminants are well immobilized in the S/S soils and this was likely to continue as long as the pH remained above neutral.

The acid resistance of the aged S/S soil was low to moderate, which was mainly assured by carbonates and not by cement hydrates, as previously anticipated. Estimates available for carbonated materials indicate that S/S systems acid resistance may persist over thousands of years.

The metal contaminants were bound into cement hydrates e.g. C-S-H, ettringite, but also clay minerals. Physical encapsulation may be responsible for the organics immobilization; therefore the maintenance of the structural integrity of the S/S soil is critical for the long-term retention of organics.

Testing

A number of risk indicators for the performance of S/S soils were identified following mineralogical and microstructural investigation. They included: reactions involving sulfates, carbonation, microcracking and the presence of weathered minerals. Since the impact of these minerals is mainly related to the dimensional stability of the S/S soils, their physical properties and microstructure are fundamental. The use of microstuctural investigation, in addition to mineralogical analysis was key to understanding the behaviour of the S/S soils, since it has shown that the presence of potentially expansive minerals did not necessarily equate to damage. Hence neither one of these techniques should be used in isolation.

The aim of the treatment of soil by S/S is to immobilize key contaminants through physical encapsulation and chemical stabilization. Although the strength, hydraulic conductivity combined with mineralogy and microstructure are important in assessing the physical performance of the S/S soil, they are not sufficient for evaluating the permanence of contaminant immobilization; as such, leaching tests must be performed.

This work provided an assessment of the efficacy of contaminant immobilization in the S/S soils, over time, by applying a number of compliance and specialist tests. The compliance tests showed that the S/S soils were not always performing according to the design criteria/regulatory limits. This non-conformance was in some cases due to the tightening of the regulatory limits, after the treatment was designed and applied.

The type of leaching test yielded different results, even when performed on the same sample. Therefore, the choice of an appropriate test must be sought. Since S/S soils are generally unique, the site specific conditions and loads must be identified prior to assessing the leaching behaviour. Also, the leaching values should be compared against limits, derived based on site specific risks, and not arbitrarily.

Recommendations from the current work:

- since the majority of potentially deleterious processes require water to take place, the durability of soils could be improved by isolating them from moisture by using secondary containment systems;
- a less rigid S/S soil, with low hydraulic conductivity is likely to be more durable than a rigid soil, in the eventuality that secondary reactions take place;
- the characterization of soil prior to remediation should include mineralogical and chemical testing to ensure the design of a robust treatment. Although the extrinsic loads were impacting most on the S/S soil durability, intrinsic factors e.g. pyrite oxidation and weathered minerals were also critical and should not be neglected.

- the use of pozzolana or forced carbonation should be considered if secondary reactions are likely to occur in the treated soils.

Further work

A number of suggestions for further work are indicated below:

- **long-term performance**. The investigation of the S/S soils revealed a series of risk phases in their microstructure. Although at this point, for some of them 16 years after remediation, there was no physical damage observed, the soils could be sampled again in 5-10 years to re-assess their performance.

- **environment of service**. The current work covered S/S soils with wide range of contaminants, different ages, different mix formulations and varied climates. However, not all S/S soil placement scenarios were addressed. Freeze/thaw was identified as a factor which might affect S/S soils, but apart from one site in this work, they were all located in temperate, subtropical climates where this phenomenon was not an issue. Sampling and examination of sites from northern latitudes, e.g. northern United States, may bring new insights on the performance of S/S.

- **sampling**. Since the recovery of intact samples from the S/S sites constituted one of the main drawbacks in this work, more investigation is needed to improve the sampling techniques or in situ methods of investigation. This is a fundamental issue since all interpretation of the microstructural features observed and the laboratory results on performance are heavily influenced by the sampling.

- **binder systems**. The current work evaluated Portland cement based S/S soils due to the limitation on the sites which could be accessed and sampled. Since Portland cement is not the sole binder used in S/S, soils treated with other binders such as lime-based systems should be investigated.

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Appendix 1 X-ray Diffractograms of S/S soils

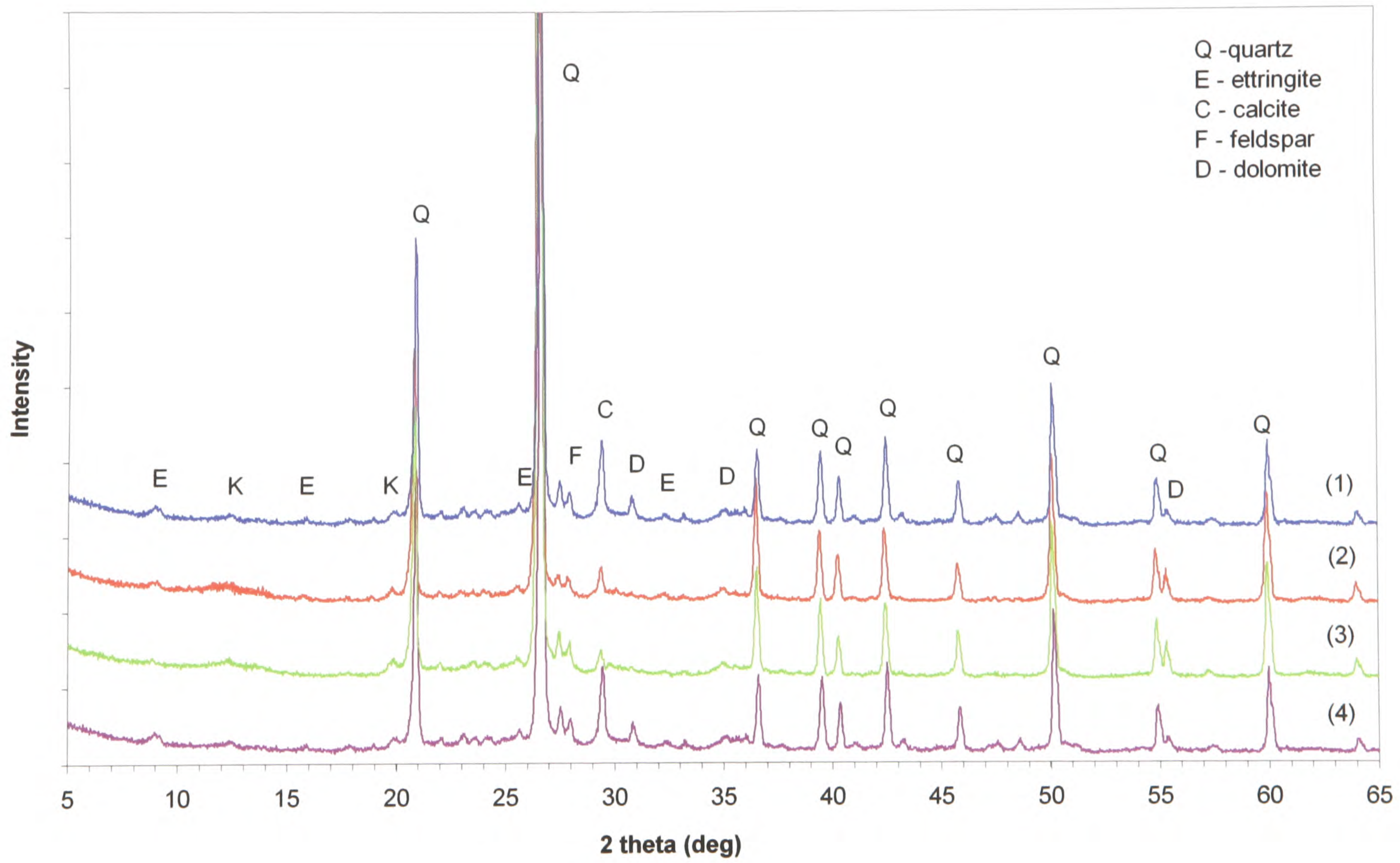

Figure 1 – XRD of American Creosote soil

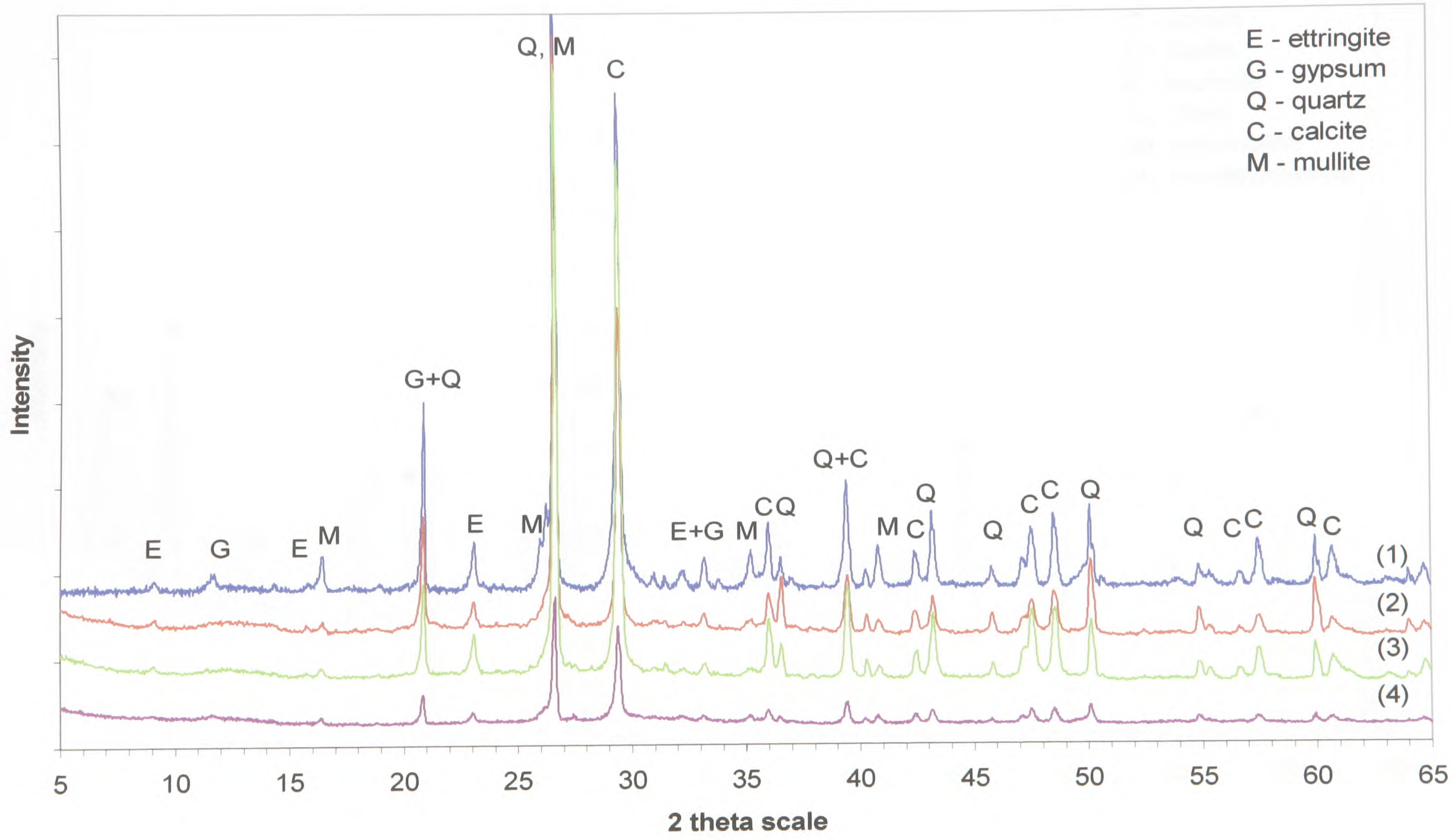

Figure 2 – XRD of Pepper Steel soil

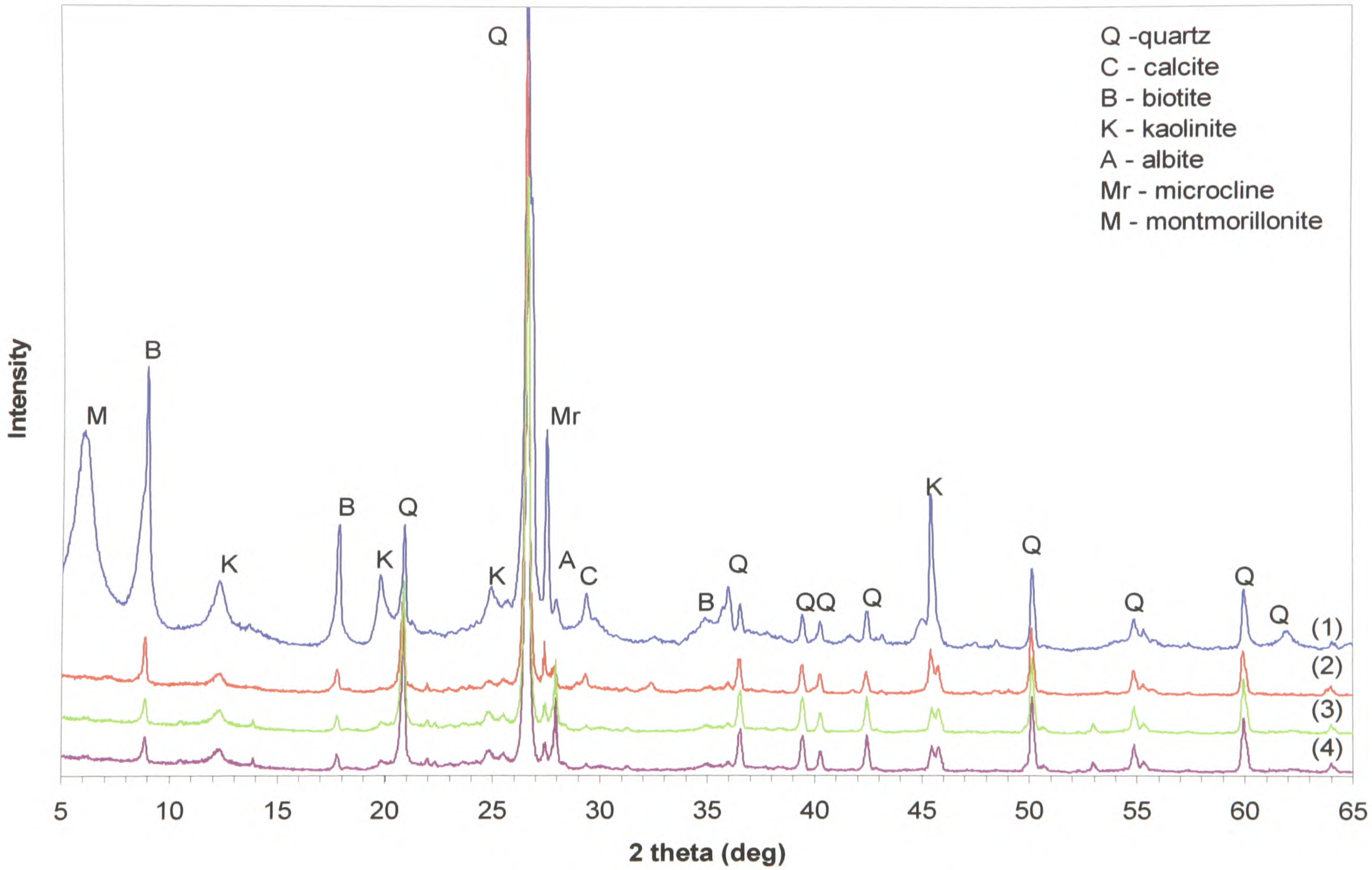

Figure 3 – XRD of Columbus MGP soil

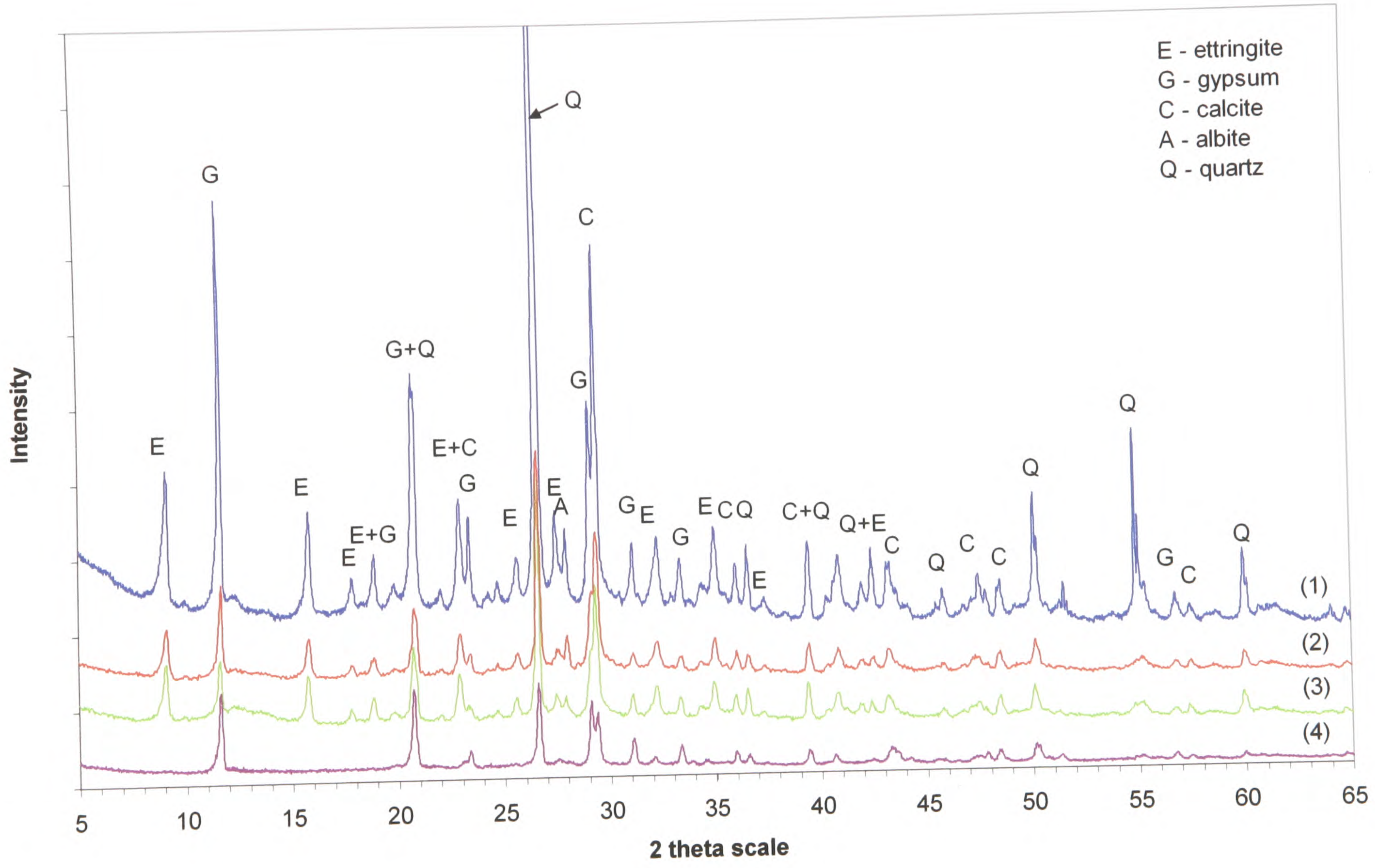

Figure 4 – XRD of South 8th Street soil

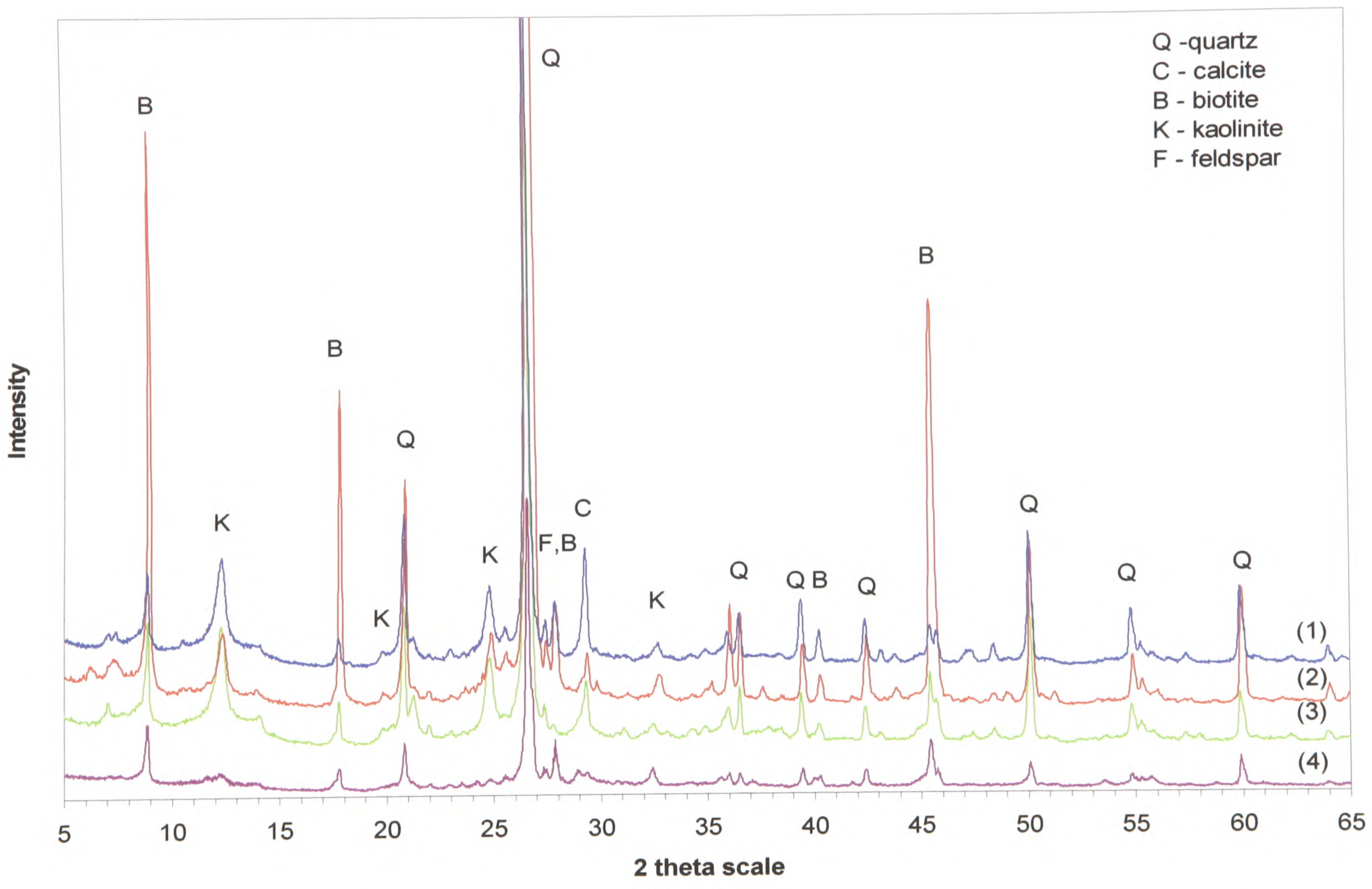

Figure 5 – XRD of Quarry Dump soil

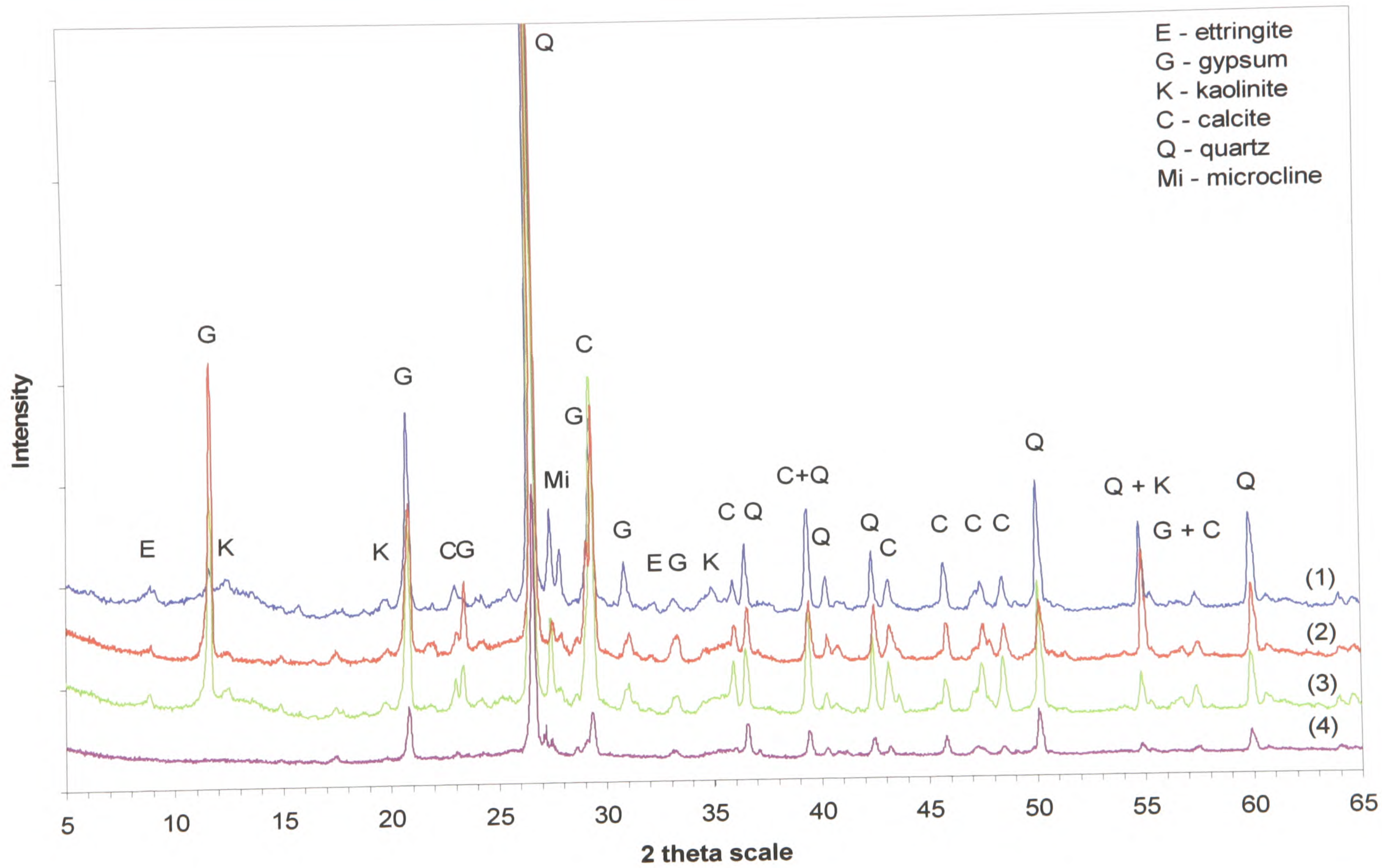

Figure 6 – XRD of Halton soil

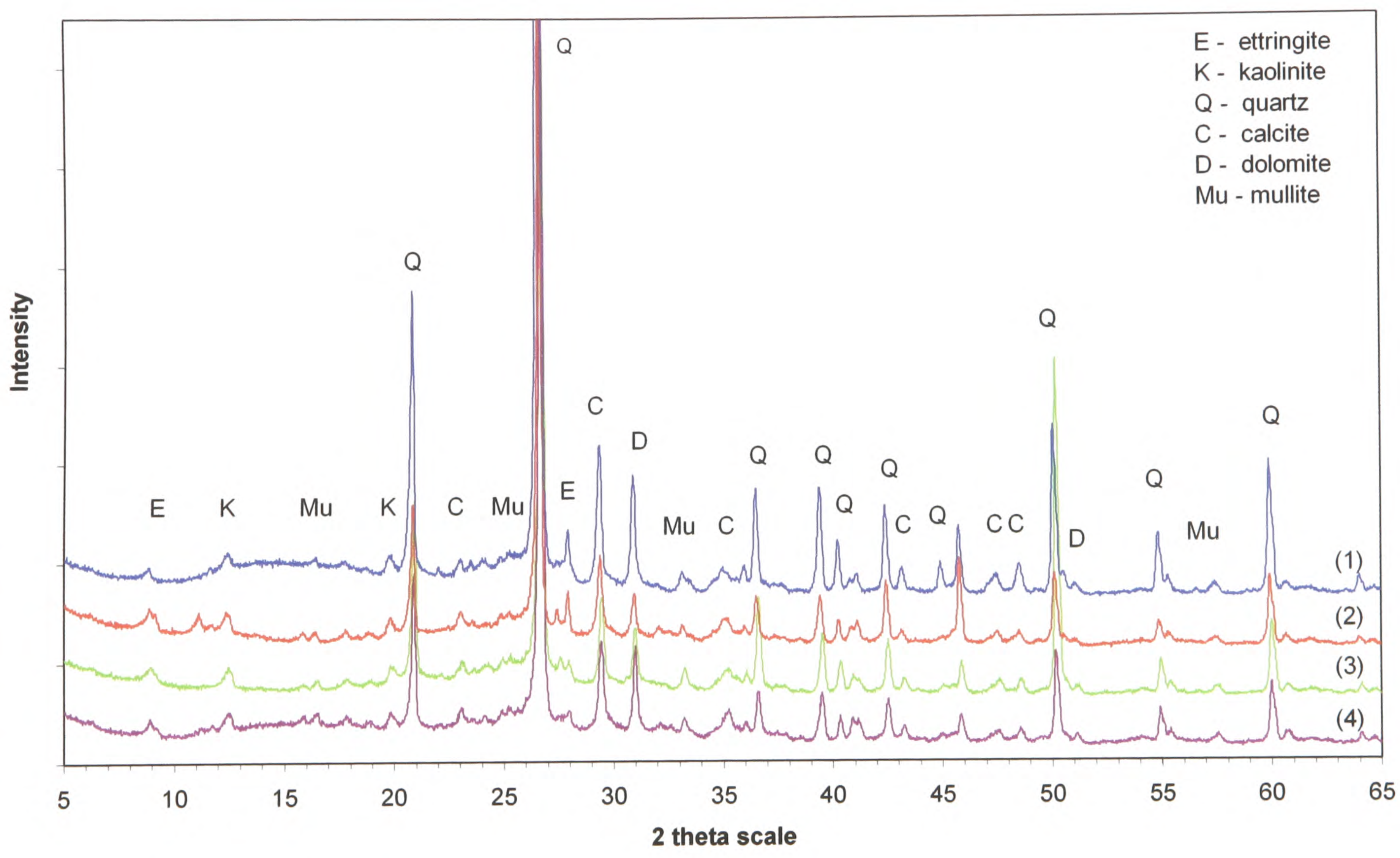

Figure 7 – XRD of Caerphilly soil

Appendix 2 List of publications

Antemir. **A**, Hills, C.D., Carey, P.J., Magnie, M-C, Polettini, A. (2010a) Investigation of 4-year old stabilised/solidified and accelerated carbonated contaminated soil. Journal of Hazardous Materials 181:543-555

Antemir, A., Hills, C.D., Carey, P.J., Gardner, K. H., Bates, E.R., Crumbie, A. (2010b) Long-term performance of aged waste forms treated by Stabilization/Solidification. Journal of Hazardous Materials 181:65-73

Antemir, A., Hills, C.D., Carey, P.J. (2008). Performance of pilot scale soils treated by Accelerated Carbonation. 2nd International Conference on Accelerated Carbonation for Environmental and Materials Engineering. Rome (Italy), 1-3 October 2008

Aubry, M.A., Magnie, M.C., Urso, P., Hills, C.D., Carey, P.J., Gardner, K. H., **Antemir, A.** (2008) Stabilisation/Solidification for treatment of hazardous waste and polluted soils: a first large scale assessment study. Proceedings of the WasteEng 08 International Conference, Patras, Greece, June 3-5, 2008

Urso, P., Magnie, M-C, Aubry, **Antemir, A.**, Yvon, M-A, Jdid, J. E.A, Martin, I. (2008) Stabilisation/solidification (S/S) of hazardous waste : feedback on real site based study. Proceedings of the WasteEng 08 International Conference, Patras, Greece, June 3-5, 2008

Antemir, A., Hills, C.D., Carey, P., Cutter, S. (2006) Weathering of accelerated carbonated contaminated soil – review of results from five-year exposure. 1st International Conference on Accelerated Carbonation for Environmental and Materials Engineering, London, UK

Antemir, A., Hills, C.D.; Carey, P. (2006) A Preliminary Evaluation of the Performance of Stabilised/Solidified Soils Using Two Different Binder Systems. The sixth International Conference on the Environmental and Technical Implications of Construction with Alternative Materials "WASCON 2006" Belgrade, Serbia and Montenegro

Antemir, A., Hills, C.D.; Carey, P.; A.K. Crumbie, Gardner, K.; Boardman D., (2005) Microstructural and chemical evolution of exposed cement stabilised soil contaminated with pyrotechnics waste 25th International Cement and Concrete Science Conference, September 14 – 15, 2005, Royal Holloway, London, UK

Antemir, A., Hills, C.D.; Carey, P.; Spear, J.; Gardner, K.; Boardman, D.; Rogers, C. (2005) Performance assessment of stabilised/solidified waste-forms: initial results from site characterisation, sampling and testing. Proceedings of the International Conference on Stabilisation/Solidification Treatment and remediation. Advances in S/S for Waste and Contaminated Land, 12-13 April 2005, Cambridge University, England, UK

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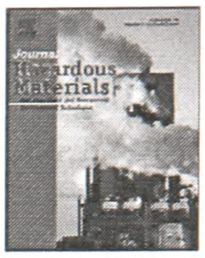

Investigation of 4-year-old stabilised/solidified and accelerated carbonated contaminated soil

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ABSTRACT

The investigation of the pilot-scale application of two different stabilisation/solidification (S/S) techniques was carried out at a former fireworks and low explosives manufacturing site in SE England. Cores and granular samples were recovered from uncovered accelerated carbonated (ACT) and cement-treated soils (S/S) after 4 years to evaluate field-performance with time. Samples were prepared for microstructural examination and leaching testing. The results indicated that the cement-treated soil was progressively carbonated over time, whereas the mineralogy of the carbonated soil remained essentially unchanged. Distinct microstructures were developed in the two soils. Although Pb, Zn and Cu leached less from the carbonated soil, these metals were adequately immobilised by both treatments. Geochemical modeling of pH-dependent leaching data suggested that the retention of trace metals resulted from different immobilisation mechanisms operating in the two soils examined.

1. Introduction

Approximately 1.2% of the total land surface in the UK is contaminated and poses a threat to human health and the environment [1]. Traditionally, contaminated soils have been landfilled, but as void space declines and costs soar, alternative techniques for soil remediation are being adopted. These include containment (physical, encapsulation or vitrification) and in situ (soil flushing, phytoremediation) and ex situ (physical separation, soil washing, thermal treatments, electrokinetics) extraction techniques [2,3].

Stabilisation/solidification (S/S) and accelerated carbonation (ACT) are containment methods used for the remediation of metal contaminated soil, which allow soil re-development. Stabilisation/solidification decreases the bioavailability/mobility of contaminants in soils, by isolating the contaminants within an impervious mass at a pH at which many contaminants are practically insoluble [4].

Accelerated carbonation (ACT) incorporates another step into S/S. This consists of introducing carbon dioxide (CO_2) during the soil mixing with the cementitious binder, which induces activation of poorly hydraulic cementitious compounds, high early strength and a reduction of pH [5].

The treatment by S/S or ACT does not eliminate the contamination, and therefore the long-term durability and performance of the soils is critical [6,7]. Although ACT has been extensively studied, for the treatment of industrial hazardous wastes [8,9,10,11], it has had limited use for contaminated soil treatment [12]. No full scale treatments have been carried out using ACT, although several pilot-scale trials and laboratory investigations were conducted [13,14]. However, limited data exist on the behaviour of ACT-treated soils over time. Similarly, despite the widespread use of S/S, there is still a lack of field-data pertaining to commercially treated soils [6,7,15].

The present work discusses the findings of a study into a pilot-scale remedial application of accelerated carbonation and traditional cement-based S/S on the same site after 4 years of exposure in the field. The stability of the S/S treated soil and the efficacy of the metal immobilisation by the two treatments is evaluated.

2. Materials and methods

2.1. Site description

The former 8.5 ha Astra Fireworks site in the SE England was used until the early 1990s for the manufacture of low-grade

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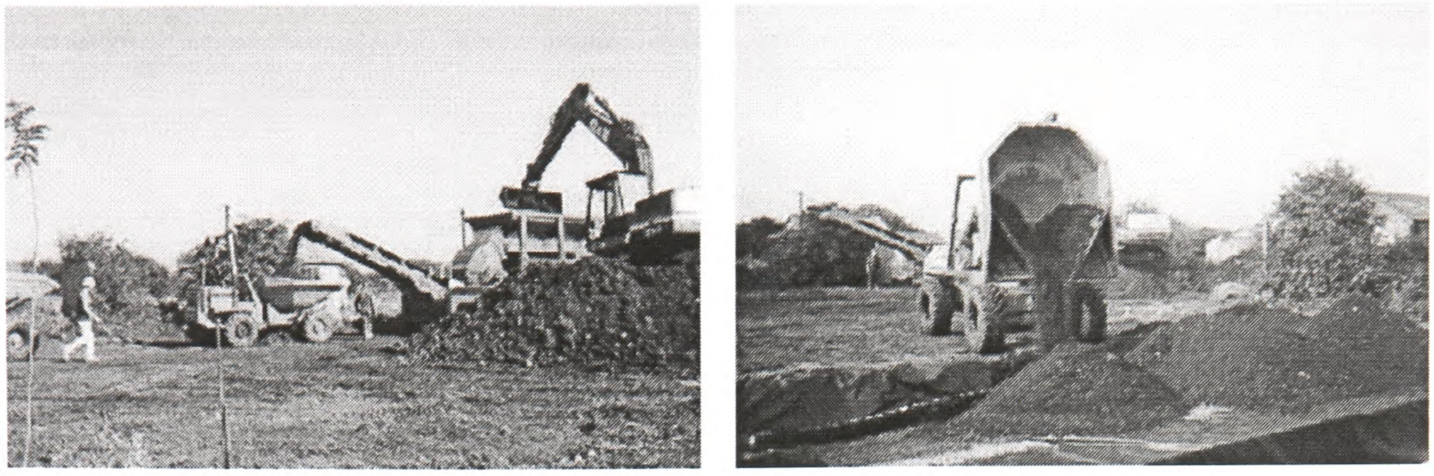

Fig. 1. Soil screening (left) and backfilling in the specially designed cells (right) at the Astra site.

military explosives and fireworks. A hotspot of metals contamination, containing up to 96 000 mg/kg copper, 81 000 mg/kg zinc and 750 mg/kg lead was pilot-treated by excavating, homogenizing and shredding the soil prior to mixing it with cement [16]. A dosage of 20% (w/w) EnvirOceM™, a superfine sulphate-resisting Portland cement, was added to the excavated soil at a 0.2–0.3 w/c ratio. Three cells of 5 m × 10 m were dug and lined with a high density polyethylene (HDPE) membrane (Fig. 1). One was filled with untreated soil, the second with soil treated with EnvirOceM, further referred as the S/S soil. The third cell contained soil mixed with EnvirOceM, which was dynamically carbonated in a closed chamber for 20 min. The maximum depth of soil in the cells was 0.6 m. Soils were left uncompacted and uncovered to allow the effects of weathering (and rain infiltration) to be maximised.

2.2. Sampling

Core samples of 100 mm diameter were obtained from the untreated, S/S and ACT soils, using a hand driven core cutter, 4 years after treatment. No cores could be recovered from the untreated soil due to the lack of strength and instead granular material was obtained.

The granular samples were quartered, dried and crushed and were used for bulk mineralogy (XRD), chemical characterisation (XRF), pH and metal leaching, as described in Sections 2.2, 2.3 and 2.5. Fragments of core were prepared for microstructural investigation according to the method indicated in Section 2.4.

2.3. X-ray diffraction

Bulk X-ray analyses were performed on powder samples (Siemens D500 X-ray Diffractometer) with a Cu Kα radiation, between 5 and 65° 2θ, a step size of 0.02° and step time of 1.2 s. Clay tiles were prepared for the identification of the clay minerals, according to the method described in Moore and Reynolds [17]. The analysis of the clay was performed using the same instrument and the scanned angles were 2–30° 2θ, step size 0.02° and step time 2.4 s.

2.4. X-ray fluorescence and acid digestion

Bulk chemical analyses of the cement-stabilised soils were carried by the Materials and Engineering Research Institute, Sheffield Hallam University. The oxide composition (major elements) was determined on glass beads, prepared by fusion with lithium tetraborate, using a Philips PW2440 Wavelength Dispersive Spectrometer.The total concentration of minor elements was determined by acid digestion according to the USEPA 3050B method.

2.5. Leaching and geochemical modeling

Granular samples obtained from the untreated, S/S and ACT soil were leached using the TCLP 1311 [18], DIN 38141-S4 [19] and pH-dependent leaching tests, prCEN/TS 15364 [20]. The conditions and key parameters of each leaching test are summarized in Table 1.

The eluates were analysed for major and trace contaminants by ICP-OES (VARIAN Vista MPX) and ion chromatography (Dionex). The pH-dependent leaching data was processed using Visual MINTEQ to predict the equilibrium leachate compositions. The default database was augmented by the solubility constants of minerals available from the literature [21–26], which are listed in Table 2 with reference to the corresponding dissolution reaction. In some cases it was required to rearrange the dissolution reaction to fit with the type of components used by Visual MINTEQ and recalculate the stability constant accordingly. The application of the geochemical speciation code initially involved using the measured concentrations and pH values as input data while suppressing precipitation for all solid phases. Potential solubility-controlling minerals were then chosen in a second step from those displaying saturation indices (SI) in the range $-1.5 \leq \mathrm{SI} \leq +1.5$ and on their potential for incorporation in soils and in S/S materials. The predicted equilibrium concentration of each element/species in solution was then calculated using the following equation:

$$C_{pred,i} = C_{meas,i}(\ 10^{-SI_j})^{1/n_{i,j}}$$

where $C_{pred,i}$ and $C_{meas,i}$ are the theoretical and measured concentrations of the ith element/species in solution, SI_j is the saturation index for the jth mineral, and $n_{i,j}$ is the molar coefficient of the ith element/species in the jth mineral.

2.6. Scanning electron microscopy

The specimens were prepared from intact cores recovered from the S/S soils. Fragments of core with dimensions of approximately 30 mm × 30 mm were cast into epoxy resin (Epoxy 301 by Struers).

Table 1
Parameters used in the leaching tests.

	TCLP 1311	DIN 38414-S4	prCEN/TS 15364
Grain size	<10 mm	<9.5 mm	<1mm
L/S ratio	20:1	10:1	10:1
Leachant	Fluid 1 Sodium acetate pH = 4.93 ± 0.05 Fluid 2 Acetic acid pH = 2.88 ± 0.05	Deionised water	HNO_3-0.5M
Leachant renewal	0	0	0
Contact time	18 h	24 h	48 h
Rotation speed	30 rpm	NA	30 rpm

Table 2
Stability constants of the new mineral phases added to the standard thermodynamic database in Visual MINTEQ, based on the dissolution reactions reported.

Mineral	Dissolution reaction	log K	Ref.
Sulphate minerals			
K_2SO_4	$K_2SO_4 \rightarrow 2K^+ + SO_4$	−1.87	[26]
Pentasalt	$(CaSO_4)_5{\cdot}K_2SO_4{\cdot}H_2O \rightarrow 5Ca^{2+} + 2K^+ + 6SO_4 + 6H_2O$	−29.3	[26]
$PbSO_4{\cdot}PbO$	$PbSO_4{\cdot}PbO + 2H^+ \rightarrow 2Pb^{2+} + SO_4 + H_2O$	−0.19	[24]
Syngenite	$K_2Ca(SO_4)_2 \rightarrow Ca^{2+} + 2K^+ + 2SO_4$	−7.45	[26]
C–S–H phases			
Afwillite	$3CaO{\cdot}SiO_2{\cdot}3H_2O + 6H^+ \rightarrow 3Ca^{2+} + 2H_4SiO_4 + 2H_2O$	46.90	[26]
C–S–H(0.8)	$0.8CaO{\cdot}SiO_2{\cdot}2.2H_2O + 1.6H^+ \rightarrow 0.8Ca^{2+} + H_4SiO_4 + H_2O$	11.08	[26]
C–S–H(1.1)	$1.1CaO{\cdot}SiO_2{\cdot}3.9H_2O + 2.2H^+ \rightarrow 1.1Ca^{2+} + H_4SiO_4 + 3H_2O$	16.72	[26]
C–S–H(1.8)	$1.8CaO{\cdot}SiO_2{\cdot}5.2H_2O + 3.6\ H^+ \rightarrow 1.8Ca^{2+} + H_4SiO_4 + 5H_2O$	32.60	[26]
Jennite	$[Ca(OH)_2]_{1.5}{\cdot}(SiO_2)_{0.9}{\cdot}0.9H_2O + 3H^+ \rightarrow 1.5Ca^{2+} + 0.9H_4SiO_4 + 2.1H_2O + 0.485Mg^{2+}$	26.40	[22]
Tobermorite	$[Ca(OH)_2]_2{\cdot}(SiO_2)_{2.4}{\cdot}2H_2O + 4H^+ \rightarrow 2Ca^{2+} + 2.4H_4SiO_4 + 1.2H_2O$	27.81	[22]
AFm phases			
C_4AH_{13}	$2CaO{\cdot}Al_2O_3{\cdot}13H_2O + 14H^+ \rightarrow 4Ca^{2+} + 2Al^{3+} + 20H_2O$	104.42	[22]
C_4FH_{13}	$2CaO{\cdot}Fe_2O_3{\cdot}13H_2O + 14H^+ \rightarrow 4Ca^{2+} + 2Fe^{3+} + 20H_2O$	99.50	[22]
C_2AH_8	$2CaO{\cdot}Al_2O_3{\cdot}8H_2O + 10\ H^+ \rightarrow 2\ Ca^{2+} + 2Al^{3+} + 13H_2O$	60.43	[22]
C_2FH_8	$2CaO{\cdot}Fe_2O_3{\cdot}8H_2O + 10H^+ \rightarrow 2Ca^{2+} + 2Fe^{3+} + 13H_2O$	55.51	[22]
C_2ASH_8	$2CaO{\cdot}Al_2O_3{\cdot}SiO_2{\cdot}8H_2O + 10H^+ \rightarrow 2Ca^{2+} + 2Al^{3+} + H_4SiO_4 + 11H_2O$	49.35	[22]
C_2FSH_8	$2CaO{\cdot}Fe_2O_3{\cdot}SiO_2{\cdot}8H_2O + 10H^+ \rightarrow 2Ca^{2+} + 2Fe^{3+} + H_4SiO_4 + 11H_2O$	44.44	[22]
$C_4AS^*H_{12}$	$3CaO{\cdot}Al_2O_3{\cdot}(CaSO_4){\cdot}12H_2O + 12H^+ \rightarrow 4Ca^{2+} + SO_4{}^{2-} + 2Al^{3+} + 18H_2O$	74.29	[22]
Cr-monosulphate	$3CaO{\cdot}Al_2O_3{\cdot}(CaSO_4){\cdot}15H_2O + 12H^+ \rightarrow 4Ca^{2+} + CrO_4{}^{2-} + 2Al^{3+} + 21H_2O$	71.62	[25]
$C_4FS^*H_{12}$	$3CaO{\cdot}Fe_2O_3{\cdot}(CaSO_4){\cdot}12H_2O + 12H^+ \rightarrow 4Ca^{2+} + SO_4{}^{2-} + 2Fe^{3+} + 18H_2O$	69.37	[22]
$C_4AC^*H_{11}$	$3CaO{\cdot}Al_2O_3{\cdot}(CaCO_3){\cdot}11H_2O + 12H^+ \rightarrow 4Ca^{2+} + CO_3{}^{2-} + 2Al^{3+} + 17H_2O$	70.52	[22]
$C_4FC^*H_{11}$	$3CaO{\cdot}Fe_2O_3{\cdot}(CaCO_3){\cdot}11H_2O + 12H^+ \rightarrow 4Ca^{2+} + CO_3{}^{2-} + 2Fe^{3+} + 17H_2O$	65.60	[22]
$C_4AC^*{}_{0.5}H_{12}$	$3CaO{\cdot}Al_2O_3{\cdot}[Ca(OH)_2]_{0.5}{\cdot}(CaCO_3)_{0.5}{\cdot}11.5H_2O + 13H^+ \rightarrow 4Ca^{2+} + 0.5CO_3{}^{2-} + 2Al^{3+} + 18.5H_2O$	86.23	[22]
$C_4FC^*{}_{0.5}H_{12}$	$3CaO{\cdot}Fe_2O_3{\cdot}[Ca(OH)_2]_{0.5}{\cdot}(CaCO_3)_{0.5}{\cdot}11.5H_2O + 13H^+ \rightarrow 4Ca^{2+} + 0.5CO_3{}^{2-} + 2Fe^{3+} + 18.5H_2O$	85.63	[22]
Fiedel's salt	$3CaO{\cdot}Al_2O_3{\cdot}(CaCl_2){\cdot}10H_2O + 12H^+ \rightarrow 4Ca^{2+} + 2Al^{3+} + 2Cl^- + 16H_2O$	72.04	[26]
Kuzel's salt	$3CaO{\cdot}Al_2O_3{\cdot}(CaCl_2)_{0.5}(CaSO4)_{0.5}{\cdot}12H_2O + 12H^+ \rightarrow 4Ca^{2+} + 2Al^{3+} + Cl^- + 0.5SO_4{}^{2-} + 18H_2O$	71.94	[26]
AFt phases			
Cl-ettringite	$Ca_6Al_2Cl_6(OH)_{12}{\cdot}24H_2O + 12H^+ \rightarrow 6Ca^{2+} + 2Al^{3+} + 6Cl^- + 36H_2O$	56.84	[26]
Cr-ettringite	$Ca_6Al_2(CrO_4)_3(OH)_{12}{\cdot}26H_2O + 12H^+ \rightarrow 6Ca^{2+} + 2Al^{3+} + 3CrO_4{}^{2-} + 38H_2O$	60.54	[25]
Fe-ettringite	$Ca_6Fe_2(SO_4)_3(OH)_{12}{\cdot}26H_2O + 12H^+ \rightarrow 6Ca^{2+} + 2Fe^{3+} + 3SO_4{}^{2-} + 38H_2O$	51.98	[22]
Tricarboaluminate	$Ca_6Al_2(CO_3)_3(OH)_{12}{\cdot}26H_2O + 12H^+ \rightarrow 6Ca^{2+} + 2Al^{3+} + 3CO_3{}^{2-} + 38H_2O$	60.69	[22]
(Hydro)garnets			
C_3AS_3	$3CaO{\cdot}Al_2O_3{\cdot}(SiO_2)_3 + 12H^+ \rightarrow 3Ca^{2+} + 2Al^{3+} + 3H_4SiO_4$	52.55	[26]
C_3AH_6	$3CaO{\cdot}Al_2O_3{\cdot}6H_2O + 12H^+ \rightarrow 3Ca^{2+} + 2Al^{3+} + 12H_2O$	79.528	[22]
$C_3AS_{0.5}$	$3CaO{\cdot}Al_2O_3{\cdot}(SiO_2)_{0.5}{\cdot}5H_2O + 12H^+ \rightarrow 3Ca^{2+} + 2Al^{3+} + 0.5H_4SiO_4 + 10H_2O$	74.12	[26]
C_3ASH_4	$3CaO{\cdot}Al_2O_3{\cdot}SiO_2{\cdot}4H_2O + 12H^+ \rightarrow 3Ca^{2+} + 2Al^{3+} + H_4SiO_4 + 8H_2O$	69.37	[26]
C_3FH_6	$3CaO{\cdot}Fe_2O_3{\cdot}6H_2O + 12H^+ \rightarrow 3Ca^{2+} + 2Fe^{3+} + 12H_2O$	74.61	[22]
CAH_{10}			
CAH_{10}	$CaO{\cdot}Al_2O_3{\cdot}10H_2O + 8H^+ \rightarrow Ca^{2+} + Al^{3+} + 14H_2O$	38.51	[22]
Mg phases			
Hydrotalcite	$Mg_4Al_2(OH)_{14}{\cdot}3H_2O + 14H^+ \rightarrow 2Al^{3+} + 4Mg^{2+} + 17H_2O$	73.96	[22]
CO_3-hydrotalcite	$Mg_4Al_2(OH)_{12}{\cdot}CO_3{\cdot}2H_2O + 12H^+ \rightarrow 4Mg^{2+} + CO_3{}^{2-} + 2Al^{3+}$	50.85	[22]
Other phases			
Akermanite	$Ca_2MgSi_2O_7 + 6H^+ + H_2O \rightarrow 2Ca^{2+} + Mg^{2+} + 2H_4SiO_4$	46.08	[23]
Anorthite	$CaO{\cdot}Al_2O_3{\cdot}(SiO_2)_2 + 8H^+ \rightarrow Ca^{2+} + 2Al^{3+} + 2H_4SiO_4$	25.31	[23]
C_3A	$3CaO{\cdot}Al_2O_3 + 12H^+ \rightarrow 2Al^{3+} + 3Ca^{2+} + 6H_2O$	113.05	[26]
C_4AF	$4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3 + 20H^+ \rightarrow 2Al^{3+} + 2Fe^{3+} + 4Ca^{2+} + 10H_2O$	140.51	[26]
Ca oxychloride	$3CaO{\cdot}CaCl_2{\cdot}16H_2O + 6H^+ \rightarrow 4Ca^{2+} + 2Cl^- + 19H_2O$	68.75	[26]
Ca zincate	$CaZn_2(OH)_6{\cdot}2H_2O + 6H^+ \rightarrow Ca^{2+} + 2Zn^{2+} + 8H_2O$	43.90	[21]
Ca-zeolite P	$CaO{\cdot}Al_2O_3{\cdot}(SiO_2)_{2.6}{\cdot}3.2H_2O + 8\ H^+ \rightarrow Ca^{2+} + 2\ Al^{3+} + 2.6\ H_4SiO_4 + 2\ H_2O$	20.20	[26]
Chabazite	$CaO{\cdot}Al_2O_3{\cdot}(SiO_2)_4{\cdot}6H_2O + 8H^+ \rightarrow Ca^{2+} + 2Al^{3+} + 4H_4SiO_4 + 2H_2O$	13.63	[26]
Forsterite	$Mg_2SiO_4 + 4H^+ \rightarrow 2Mg^{2+} + H_4SiO_4$	28.60	[23]
Gehlenite	$2CaO{\cdot}Al_2O_3{\cdot}SiO_2 + 10H^+ \rightarrow 2Ca^{2+} + 2Al^{3+} + H_4SiO_4 + 3H_2O$	55.23	[23]
Leucite	$KAl(SiO_3)_2 + 2H_2O + 4H^+ \rightarrow K^+ + Al^{3+} + 2H_4SiO_4$	6.42	[21]
Merwinite	$Ca_3Mg(SiO_4)_2 + 8H^+ \rightarrow 3Ca^{2+} + Mg^{2+} + 2H_4SiO_4$	69.28	[23]
Na-zeolite P	$Na_2O{\cdot}Al_2O_3{\cdot}(SiO_2)_{2.6}{\cdot}3.2H_2O + 8H^+ \rightarrow Ca^{2+} + 2Al^{3+} + 2.6H_4SiO_4 + 2H_2O$	26.40	[26]
$ZnFe_2O_4$	$ZnFe_2O_4 + 8H^+ \rightarrow Zn^{2+} + 2Fe^{3+} + 4H_2O$	9.85	[24]
$ZnSiO_3$	$ZnSiO_3 + H_2O + H^+ \rightarrow Zn^{2+} + H_4SiO_4$	2.93	[21]
Wairakite	$CaO{\cdot}Al_2O_3{\cdot}(SiO_2)_4{\cdot}2H_2O + 2H_2O + 8H^+ \rightarrow Ca^{2+} + 2Al^{3+} + 4H_4SiO_4$	18.87	[21]
Wollastonite	$CaSiO_3 + H_2O + H^+ \rightarrow Ca^{2+} + H_4SiO_4$	12.99	[21]

The blocks were ground by hand to expose the surfaces to be analysed, using successive SiC paper with decreasing grit sizes (30, 15 and 10 μm). The resin blocks were polished on an Engis polishing machine, with progressively decreasing grit size diamond pastes (3, 1 and 0.25 μm), supplied by Struers. Between each stages of grinding and polishing, the resin blocks were cleaned in absolute ethanol.

Prior to the SEM analysis the blocks were carbon coated and analysed with an SEM (JEOL JSM 5310-LV) equipped with a LaB_6 filament and Energy Dispersive Spectrometer (EDS). Backscattered electron images (BSE) were collected using a 20 kV accelerating voltage. X-ray microanalysis provided qualitative and semi-quantitative compositional information.

Table 3
Mineral phases identified by XRD in Astra soil at different ages.

Sample	Age (months)	Mineral phases												
		Quartz	Kaolinite	Montmorillonite	Muscovite	Hematite	C_2S	C_3S	Calcite	Aragonite	Portlandite	Ettringite	Bassanite	Pyrite
Untreated	0[a]	•	•	•	•									•
	16[a]	•	•	•	•									•
	48	•	•	•	•									
S/S	0[a]	•	•	•	•		•	•						
	16[a]	•	•	•	•		•		•	•				
	48	•	•	•	•	•			•		•	•	•	
ACT	0[a]	•	•	•	•		•	•	•	•				
	16[a]	•	•	•	•		•		•	•				
	48	•	•	•	•				•					

[a] From [16].

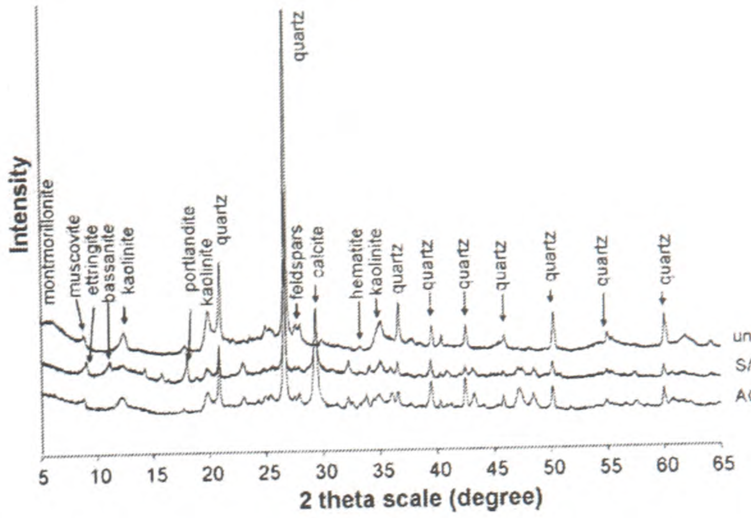

Fig. 2. Diffractograms from the 4-year-old, weathered treated and untreated soils.

3. Results

3.1. Mineralogical composition

Examination of the Astra soil mineralogy was carried out at different ages and the findings are shown in Table 3. The main minerals found in the three soils were quartz (SiO_2), montmorillonite ($(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$), kaolinite ($Al_2Si_2O_5(OH)_4$), muscovite ($(KAl_2AlSi_3O_{10}(OH)_2$, hematite ($Fe_2O_3$), pyrite ($FeS_2$) and feldspars. Portlandite ($Ca(OH)_2$), ettringite ($Ca_6Al_2(SO_4)(OH)_{12} \cdot 26H_2O$), calcite ($CaCO_3$), bassanite ($CaSO_4 \cdot 1/2H_2O$) and anhydrous cement phases such as calcium di/tri silicates (C_2S and C_3S) were observed in the treated soils. Initially, the treated soils contained calcium silicates, soil derived minerals and calcium carbonates, in the case of the ACT soil; however subsequently secondary minerals such as ettringite and bassanite formed in the S/S soil (Fig. 2).

3.2. Microstructure of soils

Representative samples from untreated, S/S and ACT soils were prepared in thin section and analysed by SEM. Prior to the SEM analysis, photographs of the thin section were taken. These show the distinct structures observed in the untreated and treated soils, as shown in Fig. 3.

The resin-impregnated untreated clayey soil is bisected by desiccation cracks (yellow-coloured resin-rich areas) and contains fragments of brick and opaque slag (Fig. 3a). The S/S soil was finer-grained and contained dark brown clay agglomerations, of up to 0.5 cm in size, (Fig. 3b). In contrast to the cement-treated soil, the carbonated soil contained 'pebble-like' formations, consisting of spherical soil agglomerates enveloped in a carbonate coating (Fig. 3c). The microstructure of the two treated soils was found to be distinct (Fig. 4c–f). The less porous S/S soil contained stratified precipitates in pore space which could be seen with the unaided eye. The formation of these was facilitated by periodic wetting and drying episodes over the 4 years of field exposure during time of lower than average rainfall.

Fig. 4c shows a typical clay agglomerate, surrounded by light grey-coloured crustiform calcium carbonate. The circled area (Fig. 4d) shows the calcium carbonate matrix bordered by clay (top right). The ACT soil contained clay coated by carbonated decalcified cement, up to 100 μm thick (Fig. 4e and f). The carbonated rim in Fig. 4f is sandwiched between clay intermixed with quartz and cement grains. An examination of the rim showed persistent anhydrous cement grains co-existing with highly decalcified cement grains, characterised by a Si-rich pseudomorph enveloped in calcium carbonate.

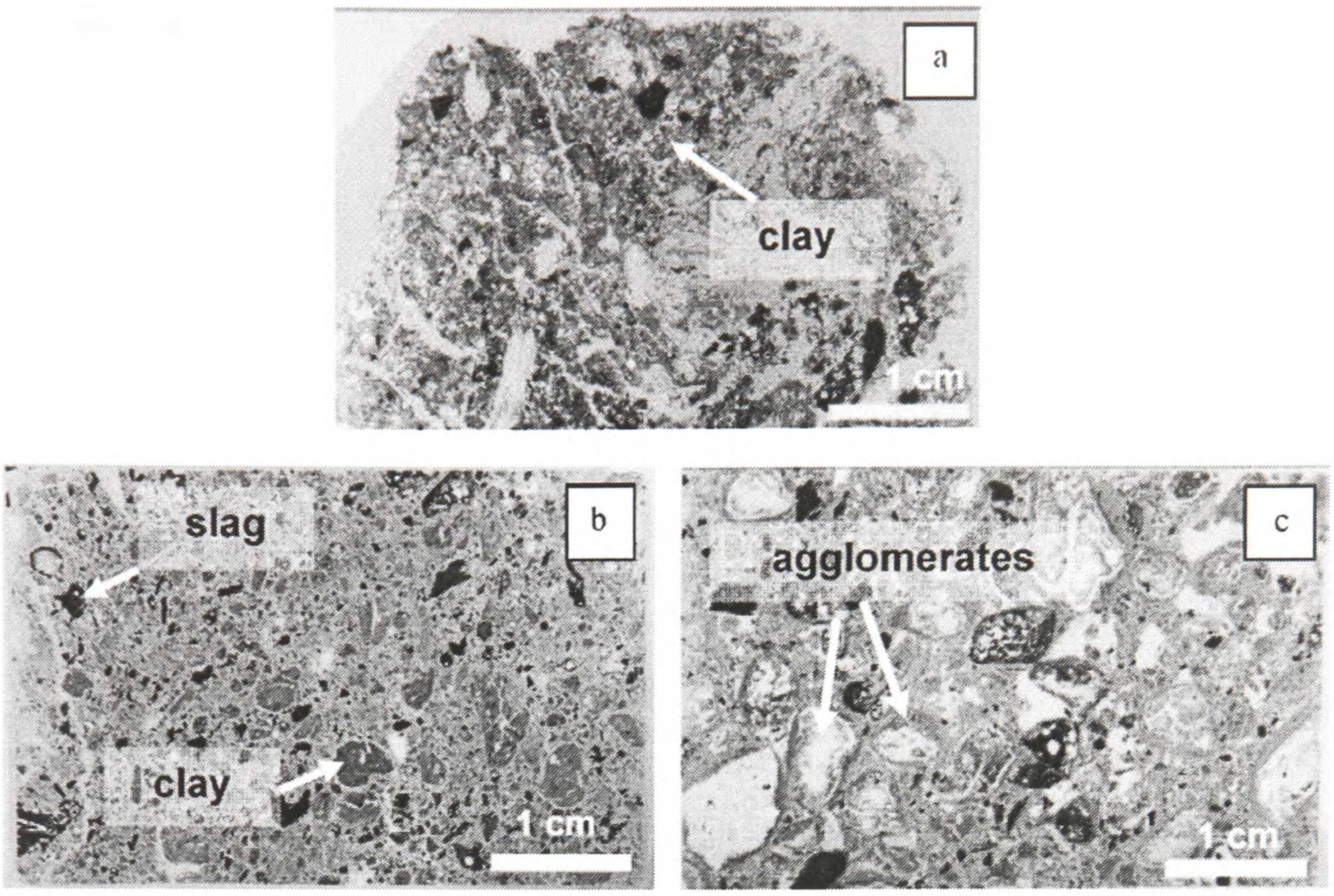

Fig. 3. The thin sections prepared from 4-year-old (a) untreated, (b) S/S and (c) ACT soil.

Ettringite was abundant in the S/S soil. Fig. 5 shows radiating clusters of ettringite infilling void space within the matrix, or intermixed with the outer C–S–H hydration product and portlandite (not shown here).

Metal contaminants were identified in the untreated soil, which were not observable in the S/S and ACT soils, resulting from dilution by cement addition, physical comminution, or by the dissolution/dispersion of particles during initial mixing at high pH.

The contaminants were present as sub-rounded fragments of individual metals of up to 50 μm in size or as grains of mixed metals up to 200 μm dispersed in the clay matrix. Zn was in particular associated with Fe and montmorillonite, as shown in Fig. 6. This clay mineral was identified by XRD and confirmed by the EDS point analysis (spectrum 2).

3.3. Chemical characterisation

The pH of the untreated soil was neutral, whilst that of the ACT and S/S soils was mildly to highly alkaline and equal to 8.9 and 12.3, respectively.

Table 4 presents the oxide composition obtained from the untreated and treated soils. These were composed of SiO_2, Al_2O_3, Fe_2O_3 and CaO, comprising up to 70% of the total weight of sample. The metal contaminants were Cu, Pb, Zn and Cr. As seen from Table 5, the concentration of these heavy metals was generally higher in the untreated than in the treated soils. This difference was ascribed to the dilution effect by the addition of cement binders.

Table 4
Oxide analysis of the 4-year-old Astra soils.

Oxide	Composition (%)		
	Untreated soil	S/S soil	ACT soil
SiO_2	49.7	34.4	41.3
Al_2O_3	14.5	12.5	12.1
Fe_2O_3	6.7	6.4	6.1
Na_2O	0.3	0.3	0.3
CaO	1.4	16.5	12.7
MgO	1.2	1.2	1.2
K_2O	2.0	1.4	1.7
P_2O_5	0.2	0.2	0.1
BaO	0.1	0.1	0.1
SO_3	0.2	0.2	0.7
LOI	22.7	25.9	23.4

3.4. Metal leaching

3.4.1. Regulatory leaching tests

When the remedial trial was conducted at the Astra site, the leaching testing methods across Europe were not yet harmonized and this is reflected in the methods chosen at that time.

Three samples for each type of soil were leach tested immediately after remediation and after 4 years, according to two pass/fail tests (DIN 38414-S4 and TCLP 1311) and the results are presented in Table 6. These show that the leaching from the S/S and ACT soils remained below the set thresholds for all four metals of concern. The untreated soil exceeded the limit for Zn, using the TCLP 1311 leaching test. It should be noted that although historically the S/S treated soils leached Zn and Cu above the set threshold, this decreased with time by more than one order of magnitude.

3.4.2. pH-dependent leaching test and modeling of leaching data

Fig. 7 shows the pH-dependent leaching results for the four metal contaminants of concern (Cr, Cu, Pb and Zn). It was observed that the shape of the leaching curves changed dramatically upon

Table 5
Total contaminant concentration in the 4-year-old Astra soils.

Element	Concentration (mg/kg)		
	Untreated soil	S/S soil	ACT soil
Zinc	1324 ± 144	735 ± 79	696 ± 185
Lead	138 ± 15	85 ± 29	100 ± 13
Chromium	35 ± 7	18 ± 2	26 ± 1
Copper	543 ± 142	228 ± 58	146 ± 27

Errors represent the standard deviation of three replicate samples.

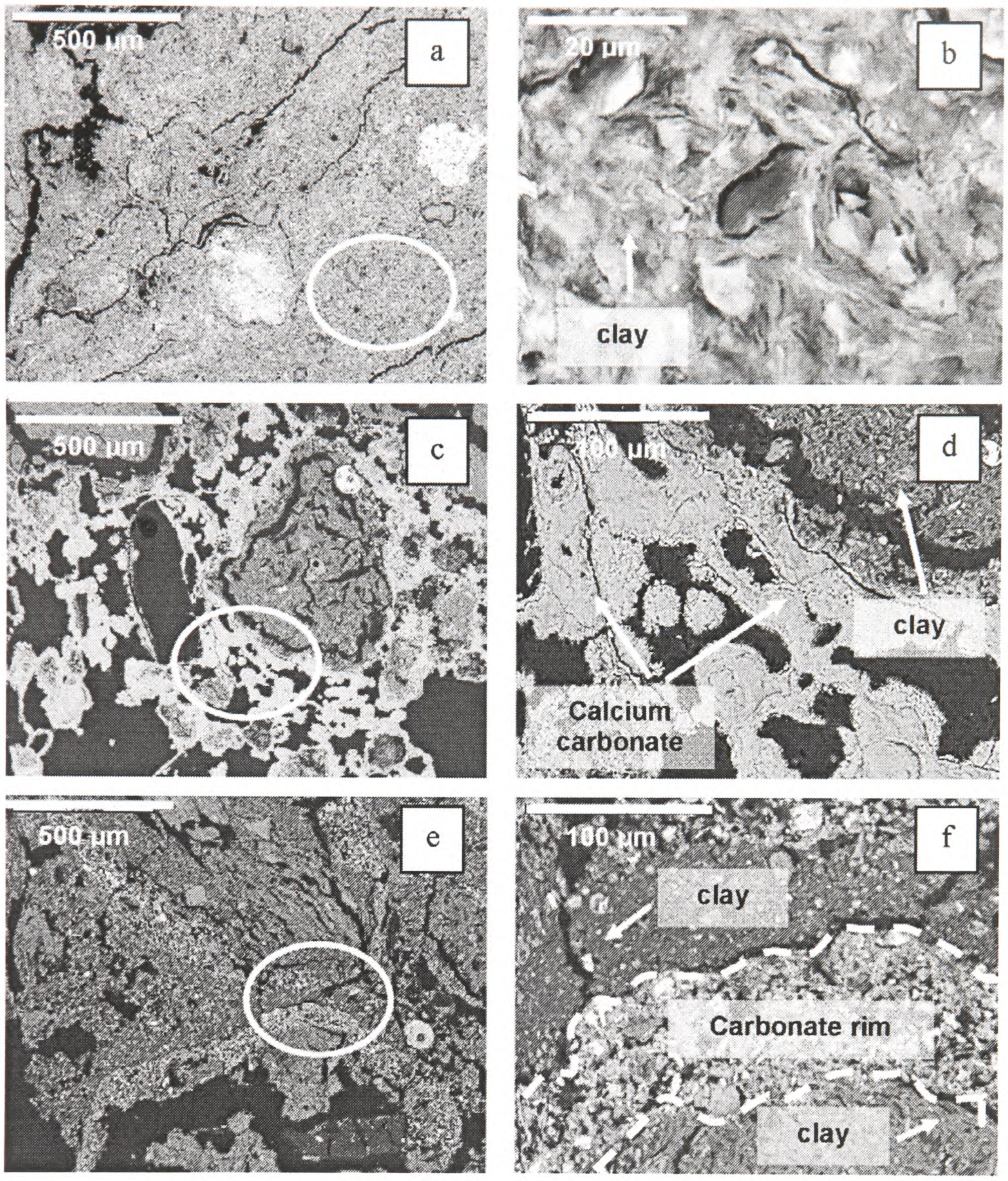

Fig. 4. Backscattered electron micrographs showing clay in the untreated soil (a and b); calcium carbonate infilling voids in the matrix of the S/S soil (c and d); pebble-like formations in the ACT soil and magnification of the circled area (e and f).

Table 6
Metals leached from untreated, S/S and ACT soil after remediation and 4 years later (mg/l).

	Leaching limit	Untreated soil		S/S soil		ACT soil	
		Historical[a]	After 4 years	Historical[a]	After 4 years	Historical[a]	After 4 years
DIN							
Zn	5	0.20	1.17 ± 0.26	0.03	0.01	n.d.	0.04 ± 0.02
Pb	0.05	0.02	0.04 ± 0.01	n.d.	n.d.	n.d.	n.d.
Cr	0.1	0.01	n.d.	0.05	0.03	0.03	0.01 ± 0.01
Cu	5	0.05	0.39 ± 0.04	0.94	0.61 ± 0.02	0.04	0.33 ± 0.13
TCLP							
Zn	5	391	9.02 ± 1.64	82	n.d.	3.13	0.35 ± 0.07
Pb	5	0.18	0.14	0.02	n.d.	n.d.	n.d.
Cr	5	n.d.	0.12	0.02	0.01	0.02	0.01
Cu	1	152	0.55 ± 0.02	11	0.9	0.14	0.15 ± 0.01

Errors represent standard deviations of three replicate samples.
n.d. signifies elements not detected.
Note historical data were not reported with associated errors.
[a] [16].

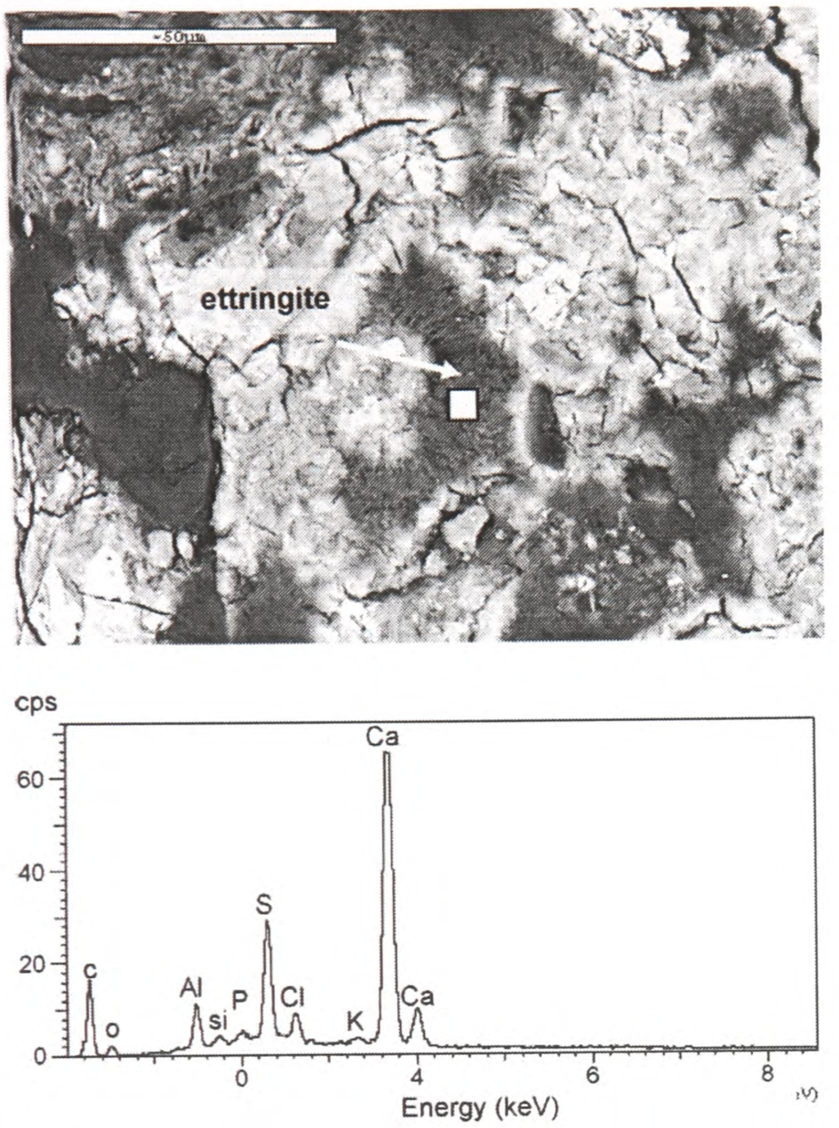

Fig. 5. Backscattered electron micrograph showing radiating clusters of ettringite growing in voids in the S/S soil and the characteristic EDS point analysis of the ettringite taken from the marked area.

treatment, providing a strong indication of different chemical phenomena governing the release of contaminants from the treated material. Differences in the pH-dependent release of heavy metals were also observed between the S/S and the ACT soils, suggesting that the metal immobilisation mechanisms changed when accelerated carbonation was applied to the soil/binder system.

However, irrespective of this heavy metal leaching was reduced by one to two orders of magnitude in comparison to the untreated soil, particularly in the alkaline pH range. However, in the S/S soil, the metal leaching data correlated with the major element concentrations (Ca, Al and Si) in solution (indicating either encapsulation or incorporation in the alumino-silicate hydration phases), whereas for the ACT-treated soil this relationship was much less evident.

The results of the modeling using Visual MINTEQ are reported in Figs. 8–10 for the untreated, S/S and ACT soils, respectively. The measured concentrations in the leachates, as a function of pH, are compared with the predicted solubility curves of candidate solid phases for the solubility control for the element/species of concern. Since it is typical for materials of different nature that the mineral phases which govern the leaching of a given element/species change depending on the pH conditions, different pH domains can be identified on the basis of the most probable candidate phase for solubility control. The overall theoretical solubility curve for a certain element is thus derived as the envelope of the theoretical curves for solubility-controlling minerals in different pH regions, which are plotted individually in Figs. 8–10.

For the untreated soil (see Fig. 8) the most probable solubility-controlling phases for Al included leucite ($KAlSi_2O_6$) at pH values below 7.4 and amorphous $Al(OH)_3$ above this value. Leucite may also control the solubility of Si in the same pH range as for Al. At higher pHs amorphous silica was the best fit with the Si leaching data. Although quartz was identified by XRD (see Fig. 2) no evidence for solubility control by this phase was obtained by modeling the leaching solutions.

For Ca and SO_4, the model predictions described the data well over a limited pH range. In particular, the phases identified for Ca and SO_4 in the pH range 7.4–8.6 were calcite ($CaCO_3$) and barite ($BaSO_4$), respectively. At other pHs, however, modeling indicated that complex solid phases not included in the expanded database were important.

For the metals of concern, leaching as a function of pH was not attributed to any mineral present in the thermodynamic database used for modeling; the only exception was Cu under alkaline conditions, with tenorite (CuO) describing the solubility of this metal at pH > 8. The absence of key phases for trace metals suggests that metal contaminants were present in the soil in complexes that are difficult to describe as pure solids. Such a hypothesis appears to be supported by the findings from microstructural observations, where, for example, Zn was associated with the Al-bearing soil minerals and clay particles.

For the S/S soil (see Fig. 9), Al leaching appeared to be dominated by the hydrous oxides $Al(OH)_3$ or boehmite (AlOOH) at low pH values and possibly by gehlenite hydrate/strätlingite (an AFm phase with the composition: $2CaO{\cdot}Al_2O_3{\cdot}SiO_2{\cdot}8H_2O$). With respect to this phase, however, it should be noted that in the range where gehlenite hydrate was found to fit the experimental data, Al concentrations were in the order of magnitude of the analytical detection limit, and this was taken as the input value for the modeling calculations. It may also be probable that other less soluble phases may have controlled the (trace) level-leaching of Al in solution at pHs > 10.

The alkaline release of Ca and Si from the S/S soil appeared to be controlled by Ca-rich C–S–H phases, including jennite (Ca/Si = 1.7) and C–S–H (Ca/Si ≈ 1.8). In the same pH range, leachates were found to be slightly oversaturated in ettringite. At acidic pH values, the leaching of Ca and Si was dictated by gypsum and leucite, respectively. Although carbonated phases were described in the S/S soil (see above for details), none informed the leaching behaviour of major elements in the treated material.

As a consequence of the effects of accelerated carbonation on the hydration process, the solubility-controlling minerals were predicted to be different from those in the S/S soil. Upon carbonation (Fig. 10), the leaching of Al decreased by approximately two orders of magnitude (and even more in the acidic pH range), so that the very soluble Al hydrous oxide phases could no longer describe the release of this metal. In the acidic pH range, the less soluble hydrous oxide, diaspore (AlOOH), broadly fit the experimental data, but could not explain the overall leaching data obtained for Al. For pH values > 8 either microcline ($KAlSi_3O_8$) or chabazite, ($CaAl_2Si_4O_{12}{\cdot}6H_2O$, a zeolite) were identified as potential solubility-controlling phases for Al and Si.

As the leaching solutions were always found to be strongly (> than one order of magnitude) undersaturated with respect to common cement hydrates, including C–S–H (irrespective of the Ca/Si ratio considered), AFm and AFt phases, other phases must have been important. For Ca for example, in the limited pH range (pH = 5.3–6.7), gypsum and the mono-hydrated Ca carbonate ($CaCO_3{\cdot}H_2O$) also known as monohydrocalcite (at higher pH values) may have been involved. The latter is recognised as being more soluble than its respective unhydrated polymorphs and is preferentially formed in the presence of Mg. As such, some other seawater constituent ions, organic material and microorganisms (see e.g. [27,28]) were involved. It is noteworthy that the Ca^{2+} and $CO_3{}^{2-}$ ions released by calcite dissolution from the ACT soil during the pH-dependent leaching test and the high con-

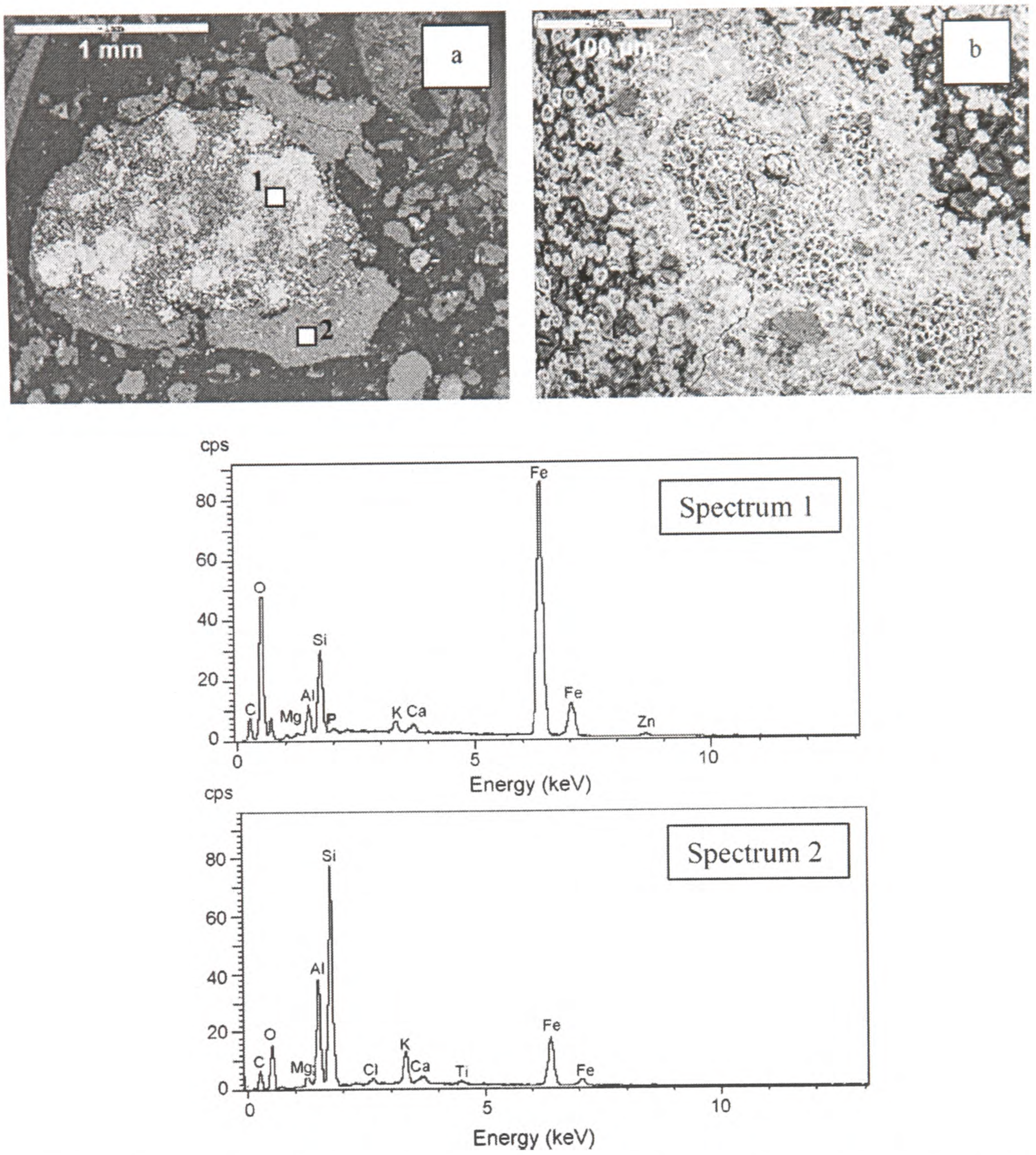

Fig. 6. Backscattered electron micrographs showing contamination of the untreated soil. (a) Soil particle contaminated with Fe and Zn and (b) magnification of the contamination area. EDS spectrum 1 corresponds to the contaminated area containing Fe and Zn and spectrum 2 to the clay soil.

centrations of major cations were favorable to the formation of $CaCO_3{\cdot}H_2O$.

As mentioned, the leachate concentrations of Cr, Cu, Pb and Zn were significantly decreased by S/S and ACT. It was also found that the accelerated carbonation treatment was more effective than the conventional S/S process towards trace metal immobilisation. Furthermore, in the treated soils, the heavy metals of concern leached at appreciably lower levels than predicted for their respective oxide, hydroxide and silicate mineral-forms included in the expanded Visual MINTEQ database. In the S/S soil, this may indicate encapsulation or incorporation of these metals in the mineral structure of the hydration phases formed, while no evidence for this was gained from the ACT soil. It is thus hypothesized that the formation of carbonate minerals during ACT treatment may explain the observed metal release. However, only in the case of Zn was some evidence gained of the formation of pure metal carbonates, with smithsonite ($ZnCO_3$) being a possible candidate in the pH range 5.3–8.3, typical of carbonate stability. For the other metals investigated, it may be argued that precipitation of complex carbonate phases or sorption onto the surface of neo-formed minerals may have determined the actual mechanisms of metal immobilisation within the matrix.

3.4.3. Acid neutralisation capacity (ANC)

Fig. 11 describes the variation of pH with acid addition for the untreated, S/S and ACT soils. The untreated soil displayed a low $ANC_{4.0}$ of 0.1 mequiv./g, whilst the treated soils required additions of up to 4.6 meq/g to reduce the pH from the natural value to 4. Although both treated soils showed an improved ANC compared to the untreated soil and had distinct shaped ANC curves. The ANC curve for the S/S soil was characterised by plateau between pH 12 and 10, followed by a steep drop to pH 5 and another plateau at pH 4.

The most significant difference of the ACT soil compared to the S/S soil was the lack of buffering capacity at high pH (>10). This was due to the consumption, during accelerated carbonation, of portlandite, the main phase controlling the equilibrium pH around 12.3 [29]. The ANC curve displayed a steep gradient from pH 6.3 to 8.8 with low acid additions (<0.5 meq/g), followed by a plateau between pH 5 and 6.7 and a steady drop below pH 5. Fig. 11 shows

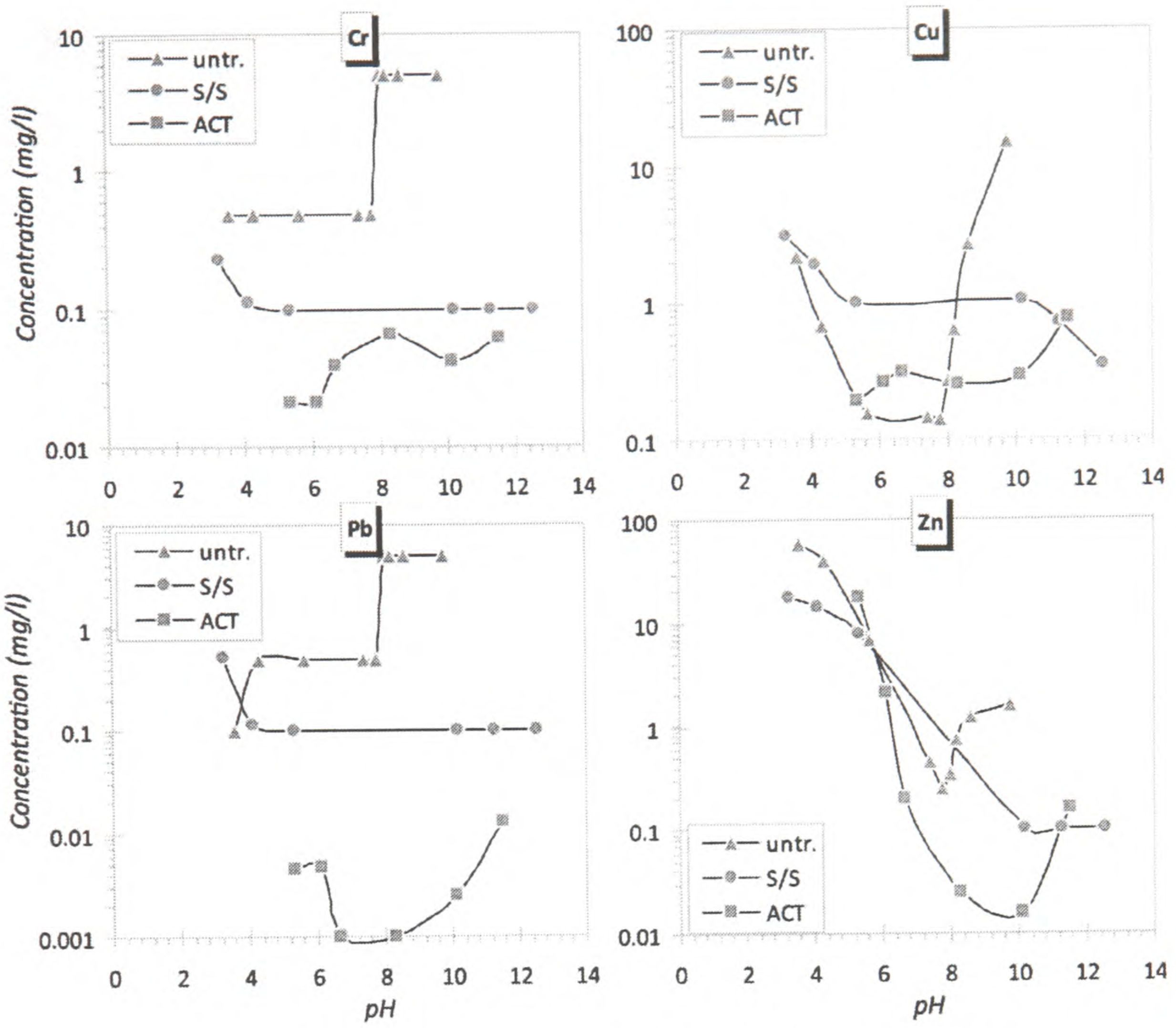

Fig. 7. pH-dependent leaching of Cr, Cu, Pb and Zn for the untreated, S/S and ACT soil.

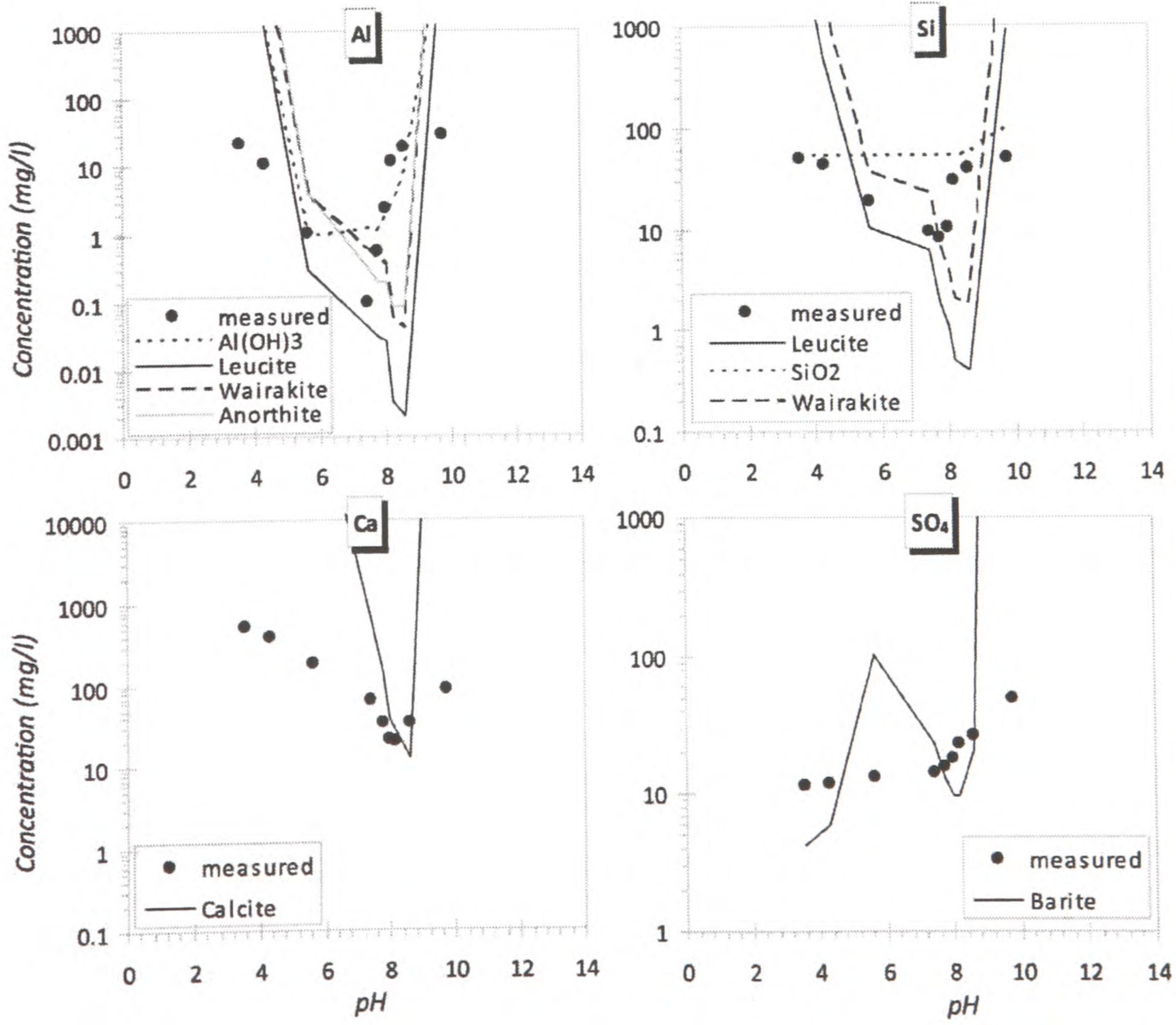

Fig. 8. Experimental data (black dots) and model predictions (continuous lines) for Al, Si, Ca and sulfate leaching from the untreated soil.

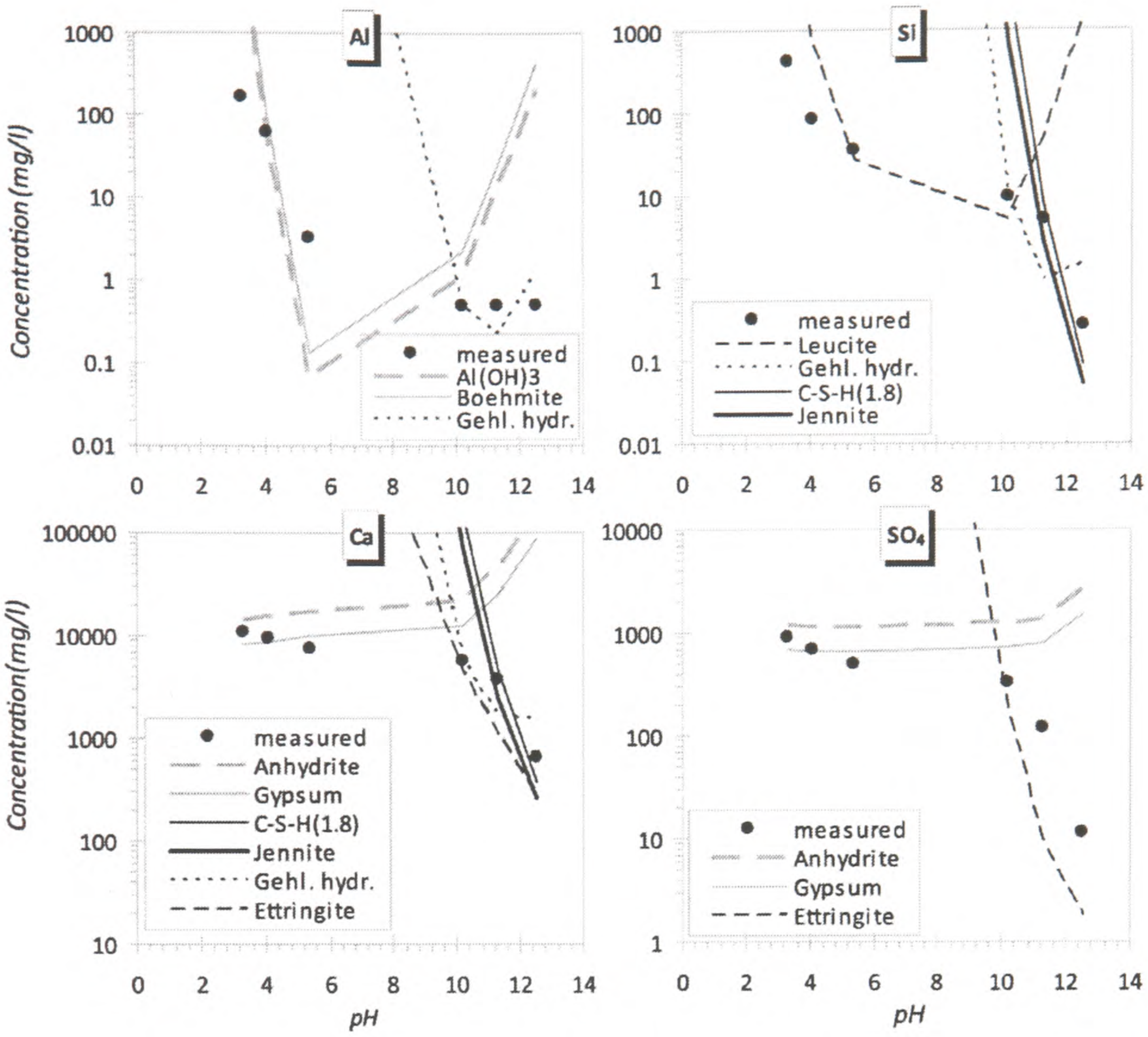

Fig. 9. Experimental data (black dots) and model predictions (continuous lines) for Al, Si, Ca and sulfate leaching from the S/S soil.

that the $ANC_{4.0}$ of the ACT soil was 3.5 meq/g, slightly lower than that of the S/S soil equal to 4.6 meq/g.

4. Discussion

This work has provided an insight into the effect of weathering upon 4-year-old soils treated by stabilisation/solidification and accelerated carbonation. The soils were left uncompacted and exposed to the atmosphere in a 'worse-case' exposure scenario. The data suggest that the two treatments behaved very differently to identical environmental loads over time-scale investigated.

4.1. Microstructure

Mineralogical change was observed in both the treated soils, as indicated in Table 1. At 0 and 16 months the ACT soil contained observable calcium carbonate (calcite and aragonite) and occasional anhydrous cement grains. The S/S soil had a similar mineralogy to the ACT soil at early age, but secondary minerals like ettringite ($Ca_6Al_2(SO4)_3(OH)_{12}\cdot 26H_2O$) formed at about 48 months of age. Despite the extreme exposure environment, portlandite ($Ca(OH)_2$) was observed in the 4-year-old S/S soil.

In the S/S soil, atmospheric carbonation proceeded due to the exposure environment. It is widely accepted that carbonation is deleterious to structural concrete [30], but for S/S systems this is not necessarily the case [10,11].

Massive primary carbonate production formed during accelerated carbonation treatment and this was characterised by the formation of carbonate shells around soil particles, whilst in the S/S soil the secondary carbonation of cement hydration products resulted. The effect of this on the microstructure of the S/S soil was significant. Distinct layers of calcium carbonate (up to 500 μm) were visible in the porosity, indicating intermittent precipitation during wetting and drying cycles. In the same way as in exposed concretes, carbonation of the S/S soils is promoted during drying stages and inhibited by wet stages, when the pores are saturated [12,31]. This carbonate resulted from the reaction of portlandite with atmospheric CO_2.

Another mineral formed in the S/S soil was ettringite. This is common in environmentally exposed concretes [31] and can, in some cases, cause disruption to the hardened structure [32]. Ettringite is closely linked to fluid transport in the soil [33] and was identified in the vicinity of portlandite. Many authors have recognised the benign effect of this type of ettringite which freely deposits in available pore space [31,34,35]. Since the Astra soil was granular rather than monolithic in nature it appears able to accommodate any expansive growth. The presence of bassanite (dehydrated gypsum) in the treated soils may indicate that several mechanisms are active: gypsum may result from the decomposition of ettringite at pH below 10.5 [36], or it can form instead of ettringite when the aluminium is depleted and soluble sulfates are present [37]. Bassanite might also be an artefact of sample preparation [38], and as far as this study is concerned, it is unclear which mechanism leads to gypsum formation in the treated soils. In general, sulfate attack is a term to describe the damage caused by sulfate-bearing phases i.e. ettringite, gypsum, thaumasite, but this does not apply to the Astra soils, since there was no damaging effect associated with their presence.

By comparison with the S/S soil, the structure of the ACT soil remained largely unchanged over the 4 years of weathering. Although two calcium carbonate polymorphs (calcite and aragonite) were identified soon after the treatment with CO_2, only calcite

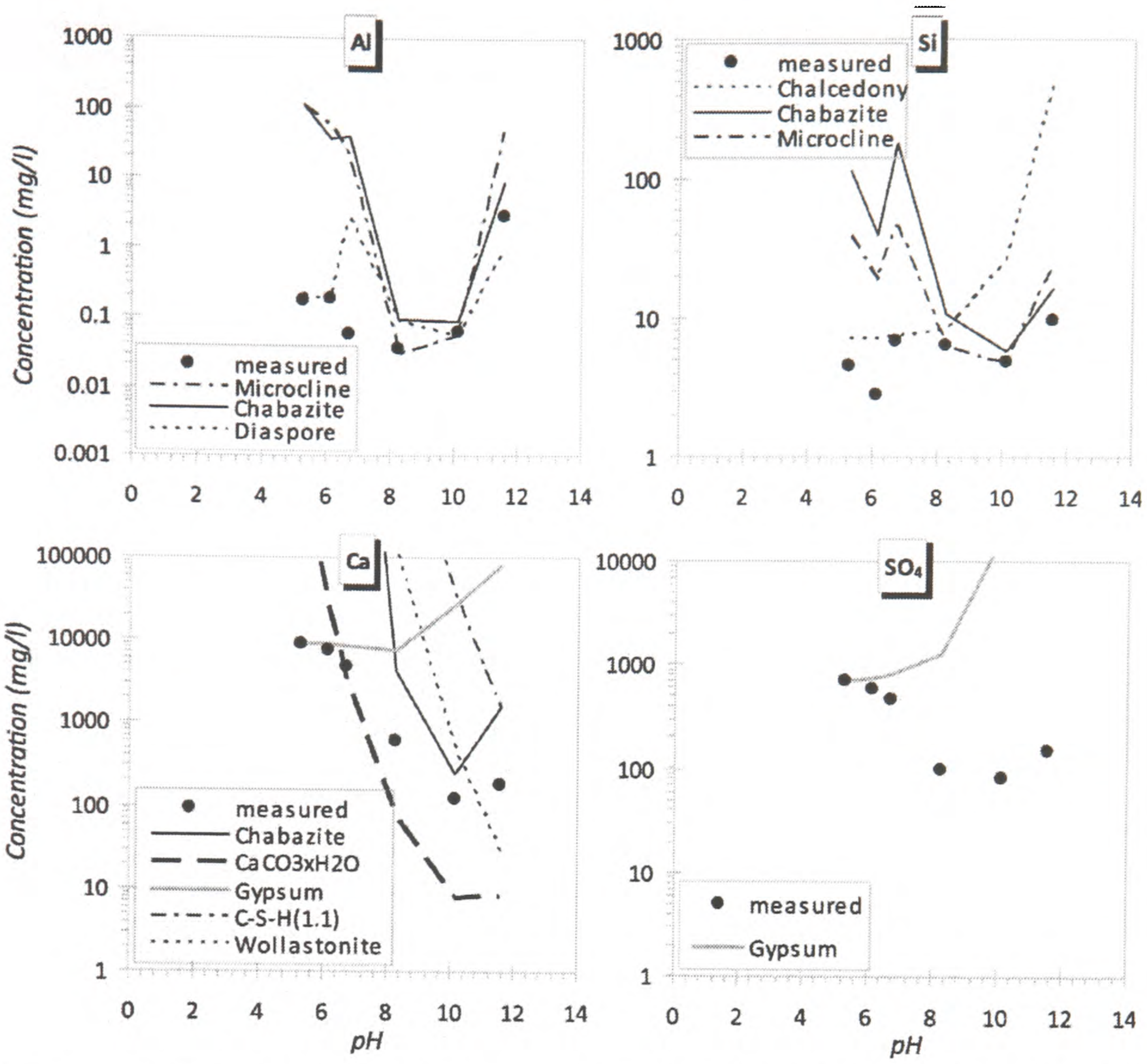

Fig. 10. Experimental data (black dots) and model predictions (continuous lines) for Al, Si, Ca and sulfate leaching from the ACT soil.

was found in the 4-year-old soil. With respect to the microstructure, the ACT soil was characterised by pebble-like structures of clay agglomerations encapsulated in calcium carbonate-rich layers. These structures were a result of the mixing action and the nature of the carbonation reactor utilised in the treatment process.

4.2. Metal leaching

At the time of treatment, the ACT soil had lower contaminant leaching, compared to the freshly treated S/S soils. However, maturation of the S/S soil reduced the metal leaching to levels comparable with the ACT soil, except for Cu. Although in the long term the leaching levels for the metals investigated were comparable for the S/S and the ACT soils at the natural pH of the materials, the analysis of the pH-dependent leaching behaviour showed that the mechanisms governing metal release were significantly different. For the S/S soil, metal release was most likely explained by immobilisation within hydrated alumino-silicate structures whereas for the ACT soil, the precipitation of complex carbonates or sorption onto newly formed minerals may explain the shape of the leaching curves observed. However, further investigation is required to elucidate this matter.

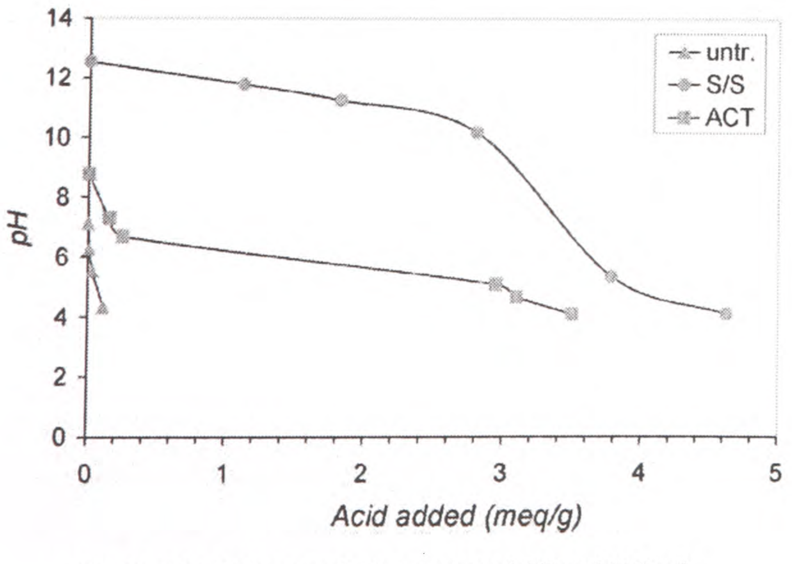

Fig. 11. The ANC curves for the untreated, S/S and ACT soil.

Despite the high concentrations of contaminants in the untreated soil, their availability for leaching was limited. Soil organic matter and clay minerals have strong sorption potential for heavy metals [30], and therefore play an important role in reducing their mobility. The SEM investigation of the untreated soil showed that the contaminants e.g. zinc, were associated with Al-bearing soil minerals, which may have contributed to relatively low leaching even from the untreated soil. The type of interaction between Zn and the clay minerals at the Astra site remains to be established.

4.3. ANC

The durability of a stabilised soil is not entirely represented by resistance to change in pH; nevertheless the acid neutralisation capacity is a key property of the material; therefore ANC is an important measure of a treated soil potential performance indicator. The results have shown that in terms of the ANC, the two treatments were also distinct and this was mainly due to the binder employed. The untreated soil had a negligible ANC, as shown in Fig. 11. The main buffering occurred below pH 7, in the ACT soil, which was due to carbonate minerals [11], which is in good agreement with the SEM and XRD observations. In contrast with the

ACT, the S/S soil displayed the strongest buffering capacity at high pH ($ANC_{9.0}$). The contributing phases within the pH interval 12–10 are portlandite and variable Ca/Si ratio C–S–H, but also ettringite [39,40].

As shown by the SEM examination and the geochemical modeling, the ACT soil was characterised by carbonates, whereas the S/S soil was dominated by hydrated phases, resulting in an overall $ANC_{4.0}$, lower for the ACT soil than that of the S/S soil. In the literature there are conflicting views on the effect of carbonation on the acid resistance; some authors have reported increase of ANC with accelerated carbonation [9,12] and others a decrease [11,41]. However, Chen et al. [41] observed that dissolution processes in cement stabilised systems, which were carbonated, took place at relatively slower rates compared to the non-carbonated counterparts and therefore may still offer good acid resistance over time.

5. Conclusions

The S/S soil is metastable due to the mineralogical changes observed. Over the 4 years in service, secondary minerals such as ettringite, gypsum and calcium carbonate polymorphs formed. However there is no evidence of disruption in the granular S/S soil.

Carbonation was the most widespread phenomenon occurring in the S/S soil, which resulted in densification of the matrix, by precipitation of calcium carbonate in voids. The findings from geochemical modeling indicated that carbonation was not associated with heavy metal or major elements leaching. The heavy metal leaching was appreciably lower than the predicted values from the oxide, hydroxide and silicates solubility; therefore the metals are likely to be incorporated in the cement hydration phases.

The ACT soil minerals and the 'pebble-like' structure persisted with time, remaining largely unchanged over the 4-year monitoring period. Calcite and aragonite were formed early after the treatment, but only calcite was observed after 4 years.

With regard to the metal immobilisation, the ACT treated soil showed better performance over the S/S soil. Both treatments displayed a significantly improved metal retention compared to the untreated soil. The mechanism of metal immobilisation for the ACT soil was different from that of the S/S soil, with accelerated carbonation being responsible for the formation of pure metal carbonates, especially in the case of Zn. For the other metals investigated, precipitation of complex carbonate phases or sorption onto the surface of neo-formation minerals may explain the actual mechanisms of metal immobilisation within the carbonated matrix.

The results from the experimental programme indicated that the acid resistance of the two treated soils was greatly improved compared to the untreated soils. The increasing order was untreated < ACT < S/S. The buffering capacity of the S/S soil was determined by portlandite, C–S–H, ettringite and calcium carbonate, whereas the ACT was totally reliant on the buffering capacity of the carbonate phases present.

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Long-term performance of aged waste forms treated by stabilization/solidification

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ABSTRACT

Current regulatory testing of stabilized/solidified (S/S) soils is based on short-term performance tests and is insufficient to determine their long-term stability or expected service life. In view of this, and the significant lack of data on long-term field performance in the literature, S/S material has been extracted from full-scale remedial operations and examined using a variety of analytical techniques to evaluate field performance. The results, including those from X-ray analytical techniques, optical and electron microscopy and leaching tests are presented and discussed. The microstructure of retrieved samples was found to be analogous to other cement-based materials, but varied according to the soil type, the contaminants present, the treatment applied and the field exposure conditions. Summary of the key microstructural features in the USA and UK is presented in this work. The work has shown that during 16 years of service the S/S wastes investigated performed satisfactorily.

1. Introduction

Solidification/stabilization (S/S) is used to reduce the mobilization of contaminants into the environment. This is achieved by the physical incorporation of contaminants within a hardened mass with lower permeability (solidification), and the chemical conversion of contaminants into less soluble forms (stabilization) [1]. The binders typically used include Portland cement, quicklime, pulverised fly ash (PFA), blastfurnace slag (BFS), natural or modified clays and sometimes waste/by-products with cementitious properties and proprietary additives [2].

The long-term performance of S/S soils is closely linked to both the physical and chemical characteristics developed after binder addition and the exposure conditions in the field. To date, most studies relating to S/S soils longevity focused on understanding their chemical performance by applying a number of accelerated short-term leaching tests to synthetic S/S soils [1], and very limited attention was given to real-life S/S materials [2,3]. The general consensus is that although these tests offer an insight into the behavior of the S/S soils, they do not fully reproduce the conditions in real-exposure environments [4–6]. Therefore it is critical to obtain more field data pertaining to the long-term stability of the S/S soils. For this reason a series of cement-treated soils from full-scale remedial operations in the USA and the UK were obtained and analyzed in order to gain understanding of the long-term behavior of S/S soils.

2. Experimental

Cores of between 30 mm and 100 mm diameter, were extracted from 7 full-scale and 1 pilot scale sites. These sites comprised three Superfund and two private sites in the US, and three private sites in the UK. The key data on each remedial operation, including the binder formulations used, are given in Table 1.

The approach to sampling the sites differed based on availability of equipment, the specific site characteristics and the nature of the stabilized soils, and included wet and dry coring. Approximately half of the recovered cores were well-indurated and monolithic, whilst the other half, were poorly to non-indurated in nature. Consequently, the cores were often cracked, primarily due to sample extraction procedure. The presence of sampling artifacts was noted for each cored sample and this factor was also taken into consideration during the interpretation of microscopic observations.

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Table 1
Characteristics, contaminants and remediation formulation of the cement-stabilized sites studied.

Site and location (abbreviation)	Contaminants of concern	Contaminant concentrations (mg/kg)	Treatment date	Type of remediation and cover system	Depth of remediation	Remediation formulation[a]	Site reuse
Pepper Steel, USA (PS)	Pb, PCBs	2,000; 116	1989	Ex situ S/S (compacted) Capped with limestone	0.6 – 2.4 m	12% PC, 8% PFA	Industrial storage
Columbus MGP, USA (MGP)	PAHs, TPHs	2,400; 5,500	1992	Ex situ and in situ S/S HDPE cap and topsoil	10 m	10% PC (site)	River front park
Quarry Dump, USA (QD)	TPH	1,200	1994	In situ S/S Concrete cap	1.2 – 1.5 m	25% PC	Not known
South Eight Street, USA (S8)	Sulphuric acid, Pb	pH < 1.0; 500	2000	In situ S/S GCL cap and topsoil	5.1 m	25% crushed limestone, 20% PC, 10% PFA	Barge terminal
American Creosote, USA (AC)	As, PAHs, PCPs, Dioxins	225; 335; 3,000; 0.00225	2000	Ex situ S/S (compacted) GCL cap and topsoil	0.6 – 1.5 m	5% PC, 4.5% PFA and 1.3% activated carbon	Storage area for construction materials
Halton, UK (HA)	Pb, As, Zn, Cu	1,550; 825; 980; 639	2000	In situ S/S Permeable membrane, topsoil	0.3 m	6% PC, 0.5% proprietary additive	Football pitch-not in use
Astra Pyrotechnics, UK (AP)	Pb, Cu, Zn	203; 64,089; 17,498	2000	Ex situ S/S (uncompacted) No cover	0.3 – 0.6 m	20% PC cell2; 20% EnvirOceM cell3	Disused
Caerphilly, UK (CA)	PAHs, TPHs	32,960; 27,845	2006	In situ S/S Topsoil	1 -1.5 m	12% proprietary mix	Residential development

[a] Percentage by weight of soil; HDPE: high density polyethylene; GCL: geosynthetic clay liner; PAH: polyaromatic hydrocarbons; PCP: pentachlorophenol; PCB: polychlorinated biphenyls; TPH: total petroleum hydrocarbons; PFA: pulverized fuel ash; PC: Portland Cement.

2.1. X-ray diffraction (XRD)

The XRD analyses were made with a Siemens D500 diffractometer with a CuKα radiation source at 40 kV and 30 mA. The soils samples were ground into powder and scanned between 5° and 65° 2θ, with a step size of 0.02° and a step time of 1.2 s. Peak identification and interpretation of the X-ray diffractograms was assisted by the DIFFRAC^{plus} EVA software (Bruker AXS).

2.2. X-ray fluorescence (XRF)

Bulk chemical analyses of the cement-stabilized soils were determined by X-ray powder fluorescence. The major elements were measured on glass beads prepared by fusion with lithium tetraborate, using a wide range oxide program. The trace elements were measured on pressed pellets using UniQuant® Thermo Scientific software.

2.3. Transmitted light microscopy

Replicate thin sections from the interior regions of the extracted cores were prepared by a specialized laboratory in Denmark, according to the procedure described in [7]. The fluorescent epoxy resin-impregnated thin sections were examined under polarized transmitted light (Optiphot-Pol, Nikon Instruments Inc.), equipped with a digital camera. The soil-derived minerals, pore structure, primary hydration products and secondary products (including carbonate, ettringite and gypsum) were examined.

2.4. Scanning electron microscopy (SEM)

A Jeol JSM 5310-LV Scanning Electron Microscope, equipped with a LINK-ISIS energy dispersive spectrometer (EDS) was used to study the S/S soils. Highly polished thin sections and resin blocks coated with carbon, were prepared from the S/S soils for microanalysis (accelerating voltage 20 kV). The (Ca/Si) elemental ratios of the C-S-H gel were determined using quantitative EDS point analysis on polished blocks.

3. Results and discussion

3.1. Physical characterization of S/S soils

3.1.1. Unconfined compressive strength (UCS)

UCS is a measure of resistance of monolithic or cohesive materials to stress, and can be applied to S/S materials to determine their performance [5]. UCS testing was performed on core samples from each S/S soil and the results are indicated in Fig. 1a together with the remediation targets. These targets were calculated depending on the location and extent of contamination, the potential site reuse and other site specific conditions. However, target UCS values are not always defined, as seen for the UK sites studied. Thus, the values presented in Fig. 1a for the AP and CA sites are not compared with any target values.

The results showed that in all cases but one, the UCS met or exceeded the remediation targets by up to one order of magnitude. This suggested that the S/S soils were still performing to the designed strength, up to 16 years after remediation.

Stabilized/solidified soils are often compared with concrete [3,8], but as seen from the results above, this is not appropriate. The UCS of the S/S soils ranged between 0.1 MPa and 4.2 MPa, which was comparable to stiff soil or very weak to weak rock and not concretes (Fig. 2). Although all S/S soils were treated with Portland cement-based formulations, no correlation was found between the quantity of binder and the strength of the soils. Additions of high percentages (up to 25%) of cement binder did not necessarily equate to high

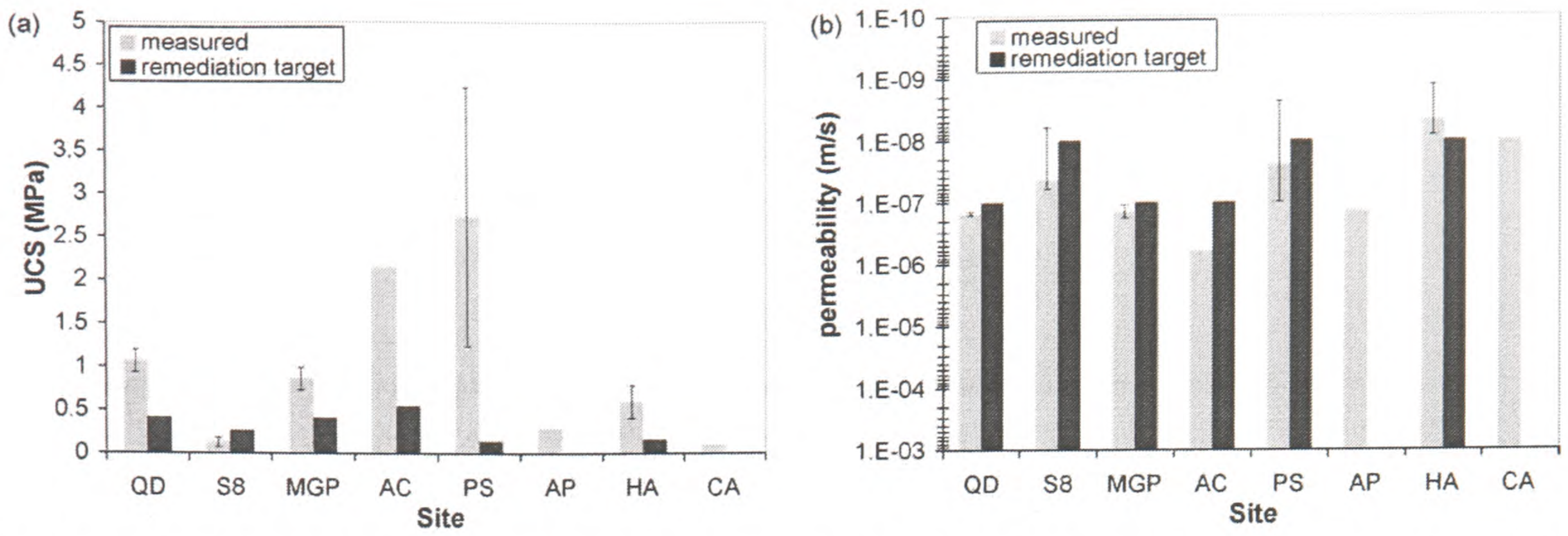

Fig. 1. Physical properties of the S/S soils (a) unconfined compressive strength and (b) permeability of the S/S soils compared with their site specific remediation targets (error bars interquartile range).

strength and this could be attributed to the method of delivery of the S/S or to degradative processes occurring over time.

3.1.2. *Permeability*

Permeability is a key transport property and influences the durability of treated wastes by preventing external agents from entering the S/S soils. The permeability of the S/S soils was in the order of 10^{-7} to 10^{-9} m/s (Fig. 1b), interestingly even for the low strength samples retrieved. This corresponds to the 'very low' permeability range, as described in [9]. Although the S/S soils were within the same order of magnitude with the remediation targets, the permeability materials remains slightly higher. However, according to reports by the USEPA, they remain suitable for the purpose for which they were designed [13].

It is useful to refer to the permeability of natural materials to place S/S soils into context, which shows that they are dissimilar to concrete, but similar to other cement-bound materials such as stabilized structural soil. The permeability of naturally occurring materials was described in Fig. 3. The values cited by [9], are also included, showing some soils have a permeability one order of magnitude lower than those given for S/S soils.

3.2. *Chemical and mineralogical characterization*

3.2.1. *XRF*

The major and trace element composition of the S/S soils was determined by XRF and the results presented in Fig. 4. The S/S soils were silica reach, contained up to 68% SiO_2, 29% CaO, 14% Al_2O_3, and 9% Fe_2O_3.

Other elements identified included magnesium, sodium, potassium, chromium, titanium, zinc, lead and manganese, with concentrations accounting for less than 1% of the S/S soil mass. The loss on ignition had a substantial contribution, up to 31% from the total weight of sample (Fig. 4).

3.2.2. *XRD*

The main crystalline phases identified were ettringite ($Ca_6Al_2(SO_4)_3(OH)_{16}{\cdot}26H_2O$), gypsum ($CaSO_4{\cdot}2H_2O$), calcite and aragonite ($CaCO_3$), mullite ($3Al_2O_3{\cdot}2SiO_2$) and quartz (SiO_2), pyrite (FeS_2), dolomite ($CaMg(CO_3)_2$), clay minerals, mica, feldspars, hence a mixture of cement derived phases and soil minerals, respectively. Since the mineralogy was dependent upon specific site conditions e.g. soil and binder type and the environmental exposure, a list of site specific minerals was complied (Table 2).

All sites contained quartz, calcite and ettringite, whilst gypsum was identified only in the PS, S8, QD and HA derived samples. Although the origin of quartz was entirely from the soil, calcite was present in both the untreated soil and resulted from the atmospheric carbonation of the cement phases. Ettringite and gypsum formed as a result of secondary reactions, which varied from site to site. Mullite, an aluminium silicate formed by burning coal at high temperature, was observed in the soils remediated with PFA mixtures.

Portlandite ($Ca(OH)_2$) resulting from cement hydration was absent in most S/S soils, except for AP. The absence of portlandite could be explained by the use of pozzolanic materials, such as PFA, but also by atmospheric carbonation. With the exception of AP, the pH of the treated soils varied between 7.5 and 10.5. In this pH range most metals of concern have minimum solubility [8]. Portlandite presence in the AP soil is most likely due to slow hydration of the cement binder, which is still present in unhydrous form as shown from the SEM examination.

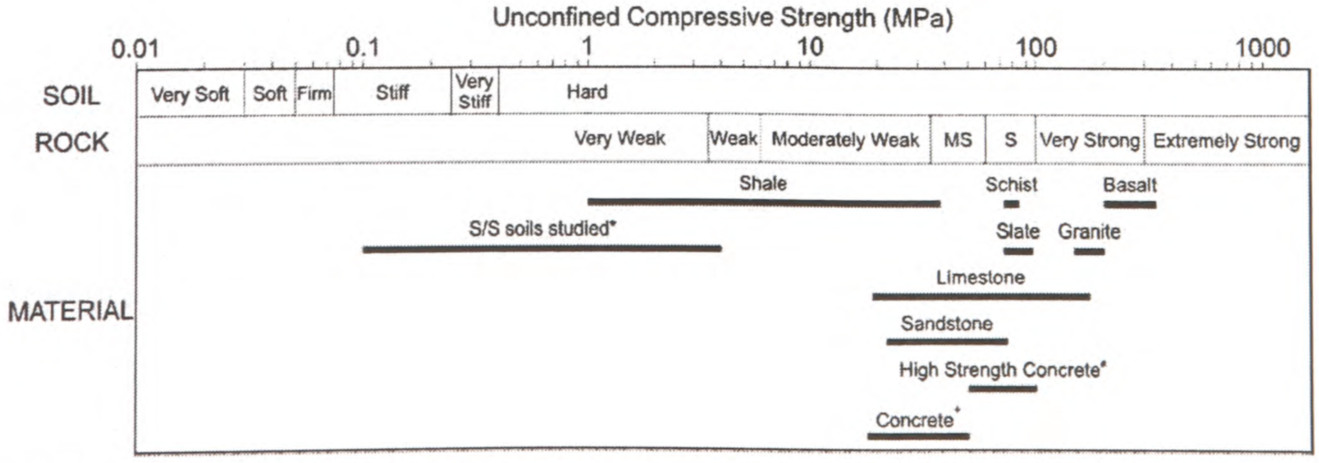

Fig. 2. Comparison between the unconfined compressive strength of S/S soils and various natural and synthetic materials.

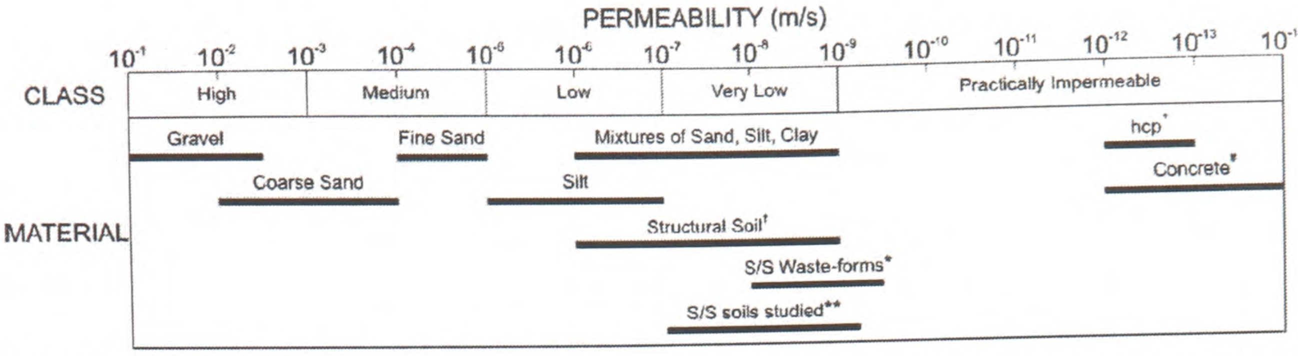

Fig. 3. Permeability of S/S soils in comparison with various materials (modified from [9]) * [10], * hcp: hydrated cement paste [10], # [11], † [12].

3.3. Microstructure

The S/S soils were subject to physical and chemical alteration and the characteristic features observed are shown schematically in Fig. 5. Different polymorphs of calcium carbonate, sulfate minerals (secondary ettringite and gypsum), unhydrated cement grains, remnant secondary binders (PFA) and weathered minerals were amongst the phases observed.

The treated soils, even after years of service, contained isolated residual anhydrous cement grains from the original S/S treatment. These grains are derived from the larger size fractions of the cement, with diameters of 60–100 μm. Previous research has shown that, in concrete, residual unhydrated cement (notably the larger sized grains) is not unusual even after many years of service [14]. In the absence of cement hydration, the main hydration phase, C-S-H, will not form. This hydrate phase plays a key role in metal immobilization and the resistance of cementitious materials to acid attack, as shown by numerous authors [15,16]. The C-S-H gel composition is variable and the incorporation of anions or cations has been linked to the Ca/Si molar ratio. The average Ca/Si ratio for each site is shown in Fig. 6 and varies from 0.5 to 1.0. Glasser [17] showed that at low Ca/Si ratios, the surface charge of C-S-H gel is negative, and thus has an improved cation absorption capacity. A Ca/Si ratio of lower than 1, is ideal for retention of heavy metals [16]. This hypothesis was supported by the data from pH dependent leaching tests performed for the S/S and the MINTEQA2 geochemical modeling of results [18]. In general, the measured concentrations for metal leaching was much lower than the theoretical solubility derived for oxide, hydroxide and silicate mineral forms included in the MINTEQA2 thermodynamic database. This finding suggests that the heavy metals are efficiently retained in the solidified matrix as a result of immobilization mechanisms within cement hydration phases.

Cracking was observed in all cores recovered in this investigation. This could result from drying shrinkage, plastic settlement, freeze–thaw, as well as deleterious chemical reactions such as alkali aggregate reaction, sulfate attack or carbonation [22]. Cracks varying from 1 micron to a few tens of microns were observed, but in many cases the cracks were empty, suggesting they may have occurred during core extraction or may be an artifact of the sampling procedure. However, some cracks were partially or completely filled with secondary products, such as ettringite, or calcium carbonate, indicating that they must have formed in situ, after treatment. It should be noted that some samples contained significant cracks that were not caused by the formation of secondary products such as ettringite [3].

As can be seen from Table 2, all S/S soils were subjected to carbonation. The XRD and SEM results showed that carbonation occurred at all sites, irrespective of their age or placement in the environment. It must be noted that impermeable geomembranes were used to protect the S/S soils from water ingress; however this did not display the same efficacy for carbon dioxide permeation. Calcium carbonate was observed predominantly within voids, but also within microcracks and in the matrix, primarily leading to a densification of the S/S soil. Calcite was common in the S/S soils, and resulted from the carbonation of portlandite. Fig. 7a–c are transmitted light micrographs showing calcium carbonate growth in large voids. Well-formed blade like-crystals between 20 and 30 μm in size were frequently observed indicating that sufficient space was available for their growth [14].

Ettringite was observed in all the S/S soils retrieved. However, using optical techniques it was seen to form predominantly in large voids or within air voids, at aggregate-paste interface, in spaces within porous carbon-rich/coal particles, between mica lamellae, and in the matrix in a limited number of sites (Fig. 8a–d). The mechanisms of expansion and ettringite formation in cementitious systems have been discussed in detail in [23,24]. Klich [25] argue that large ettringite crystals often appear in the available space offered by pre-existing cracks and voids, which is a benign process [14,23,26].

Gypsum was scarcely observed in the S/S soils by SEM/EDS and this may be caused by the similarity between its backscattered coefficient and that of calcium carbonate or the localized distribution of this mineral. Anhedral crystals of gypsum, in the order of 200 μm diameter, were observed to infill an entrapped air void, with no apparent signs of distress of the matrix. In this study the gypsum identified was not necessarily a degradation product following years of environmental exposure, but the result of acidic soil conditioning prior to the S/S treatment (see S8 site).

Altered mica was identified in the S/S soils in the most southerly located two sites, QD and MGP. The alteration of mica may be ascribed to natural weathering of the soil prior to the remediation,

Table 2
Mineral phases identified in the S/S soils.

Site	Quartz	Calcite	Aragonite	Gypsum	Ettringite	Portlandite	C_2S, C_3S	Mullite	Clays	Feldspars	Dolomite	Pyrite	Micas
AC	●	●			●					●	●		
PS	●	●	●	●	●			●					
S8	●	●		●	●					●			
MGP	●	●			●				●	●			●
AP	●	●			●	●	●		●	●		●	
QD	●	●		●	●				●	●			●
HA	●	●	●	●	●				●	●		●	
CA	●	●			●			●	●		●		

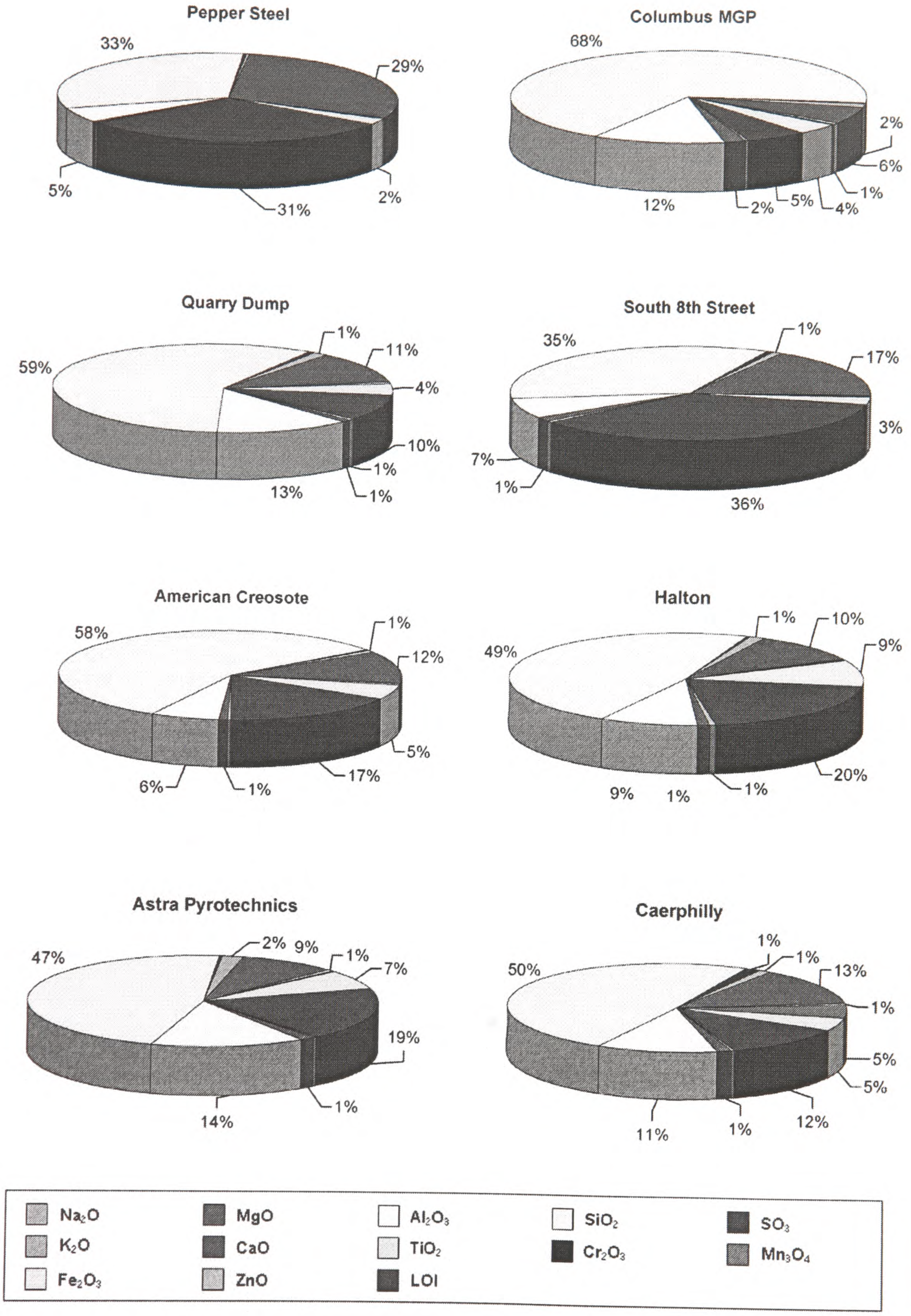

Fig. 4. Elemental oxide compositions of S/S soils and corresponding loss on ignitions (LOI).

rather than degradation in the high pH conditions of a cement-bound system [27]. The soil consists of saprolite, a chemically weathered rock occurring in wet and warm climate [28]. Highly altered alkali-bearing mica and feldspar are known to be potentially deleterious due to the increase risk of alkali release into the pore solution, promoting alkali aggregate reaction [27,29]. However, no evidence of alkali aggregate reactivity was observed in the soils. Instead, a rather interesting reaction within the weathered mica was observed, i.e. ettringite forming between the mica lamellae leading to expansion in the direction normal to the layers (Fig. 9).

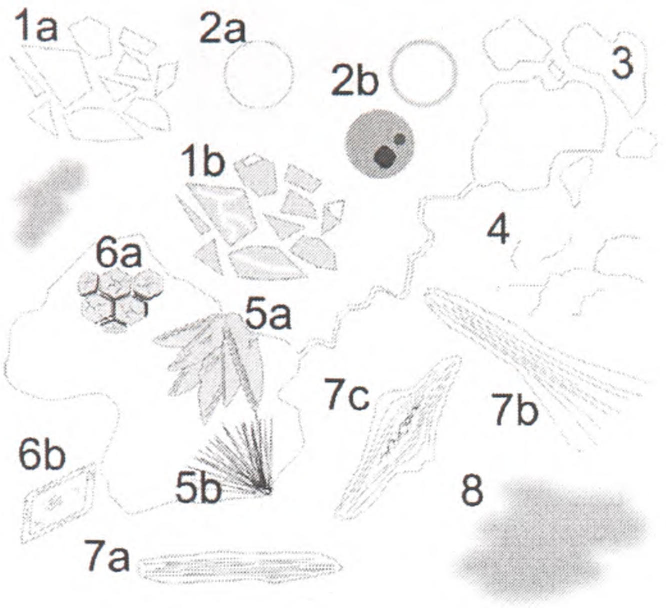

Fig. 5. Schematical representation of the main alteration features in aged S/S soil microstructures based on microscopy studies: 1a, unhydrated cement grains; 1b, hydrated cement grain "relics"; 2a, unreacted fly ash; 2b, partially reacted fly ash cenospheres; 3, voids; 4, microcracks; 5a, calcite; 5b, aragonite; 6a, ettringite; 6b, gypsum; 7a, mica aggregate; 7b, kaolinised mica; 7c, altered mica aggregate and ettringite intergrowth; 8, organic inclusions within soil/cement matrix.

This phenomenon is a type of sulfate attack, which results due to the reaction between sulfate ions and reactive alumina supplied by an aggregate, for example. This occurrence was also reported by Diamond [26] in concrete and is acknowledged to pose a risk for the dimensional stability. A detailed analysis of this phenomenon and the mechanisms involved will be discussed elsewhere.

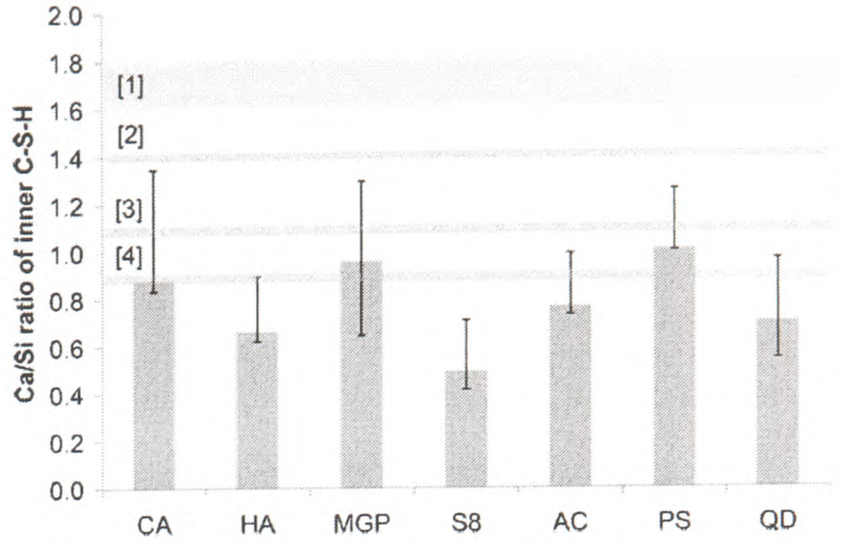

Fig. 6. Average elemental Ca/Si ratios of the inner C-S-H gel from the S/S sites (error bars interquartile range). [1] Portland cement [19,20]; [2], [3], [4] fly ash blended cements [19,18,21].

3.4. Contaminant immobilisation

S/S treatment does not eliminate the contaminants, which remain immobilized within the product. The cementitious component of the S/S-treated soil responsible for encapsulation, is therefore extremely important for contaminant retention over time. However, longer-term chemical reactions and waste binder-interferences may also occur in the S/S soils, and may also reduce the mobilization of contaminants into the environment [2]. To assess these two key aspects of S/S, post remediation monitor-

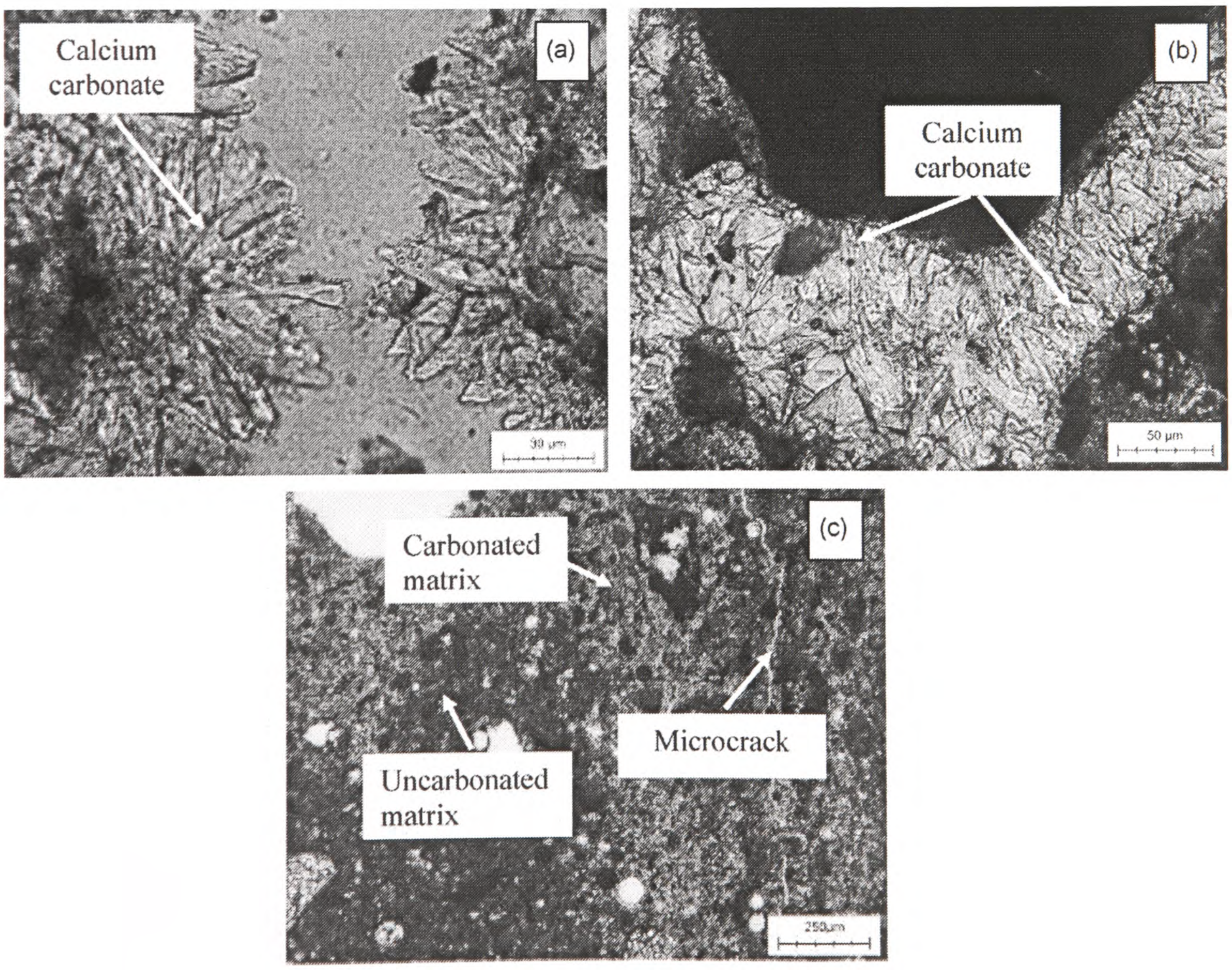

Fig. 7. Transmitted light photomicrographs of well crystallized calcium carbonate infilling large pore spaces in the S/S soil; a) plane polarised light 'dog's tooth' crystals of calcite; b) interlocking crystals of calcite; c) carbonated matrix around microcrack (PS).

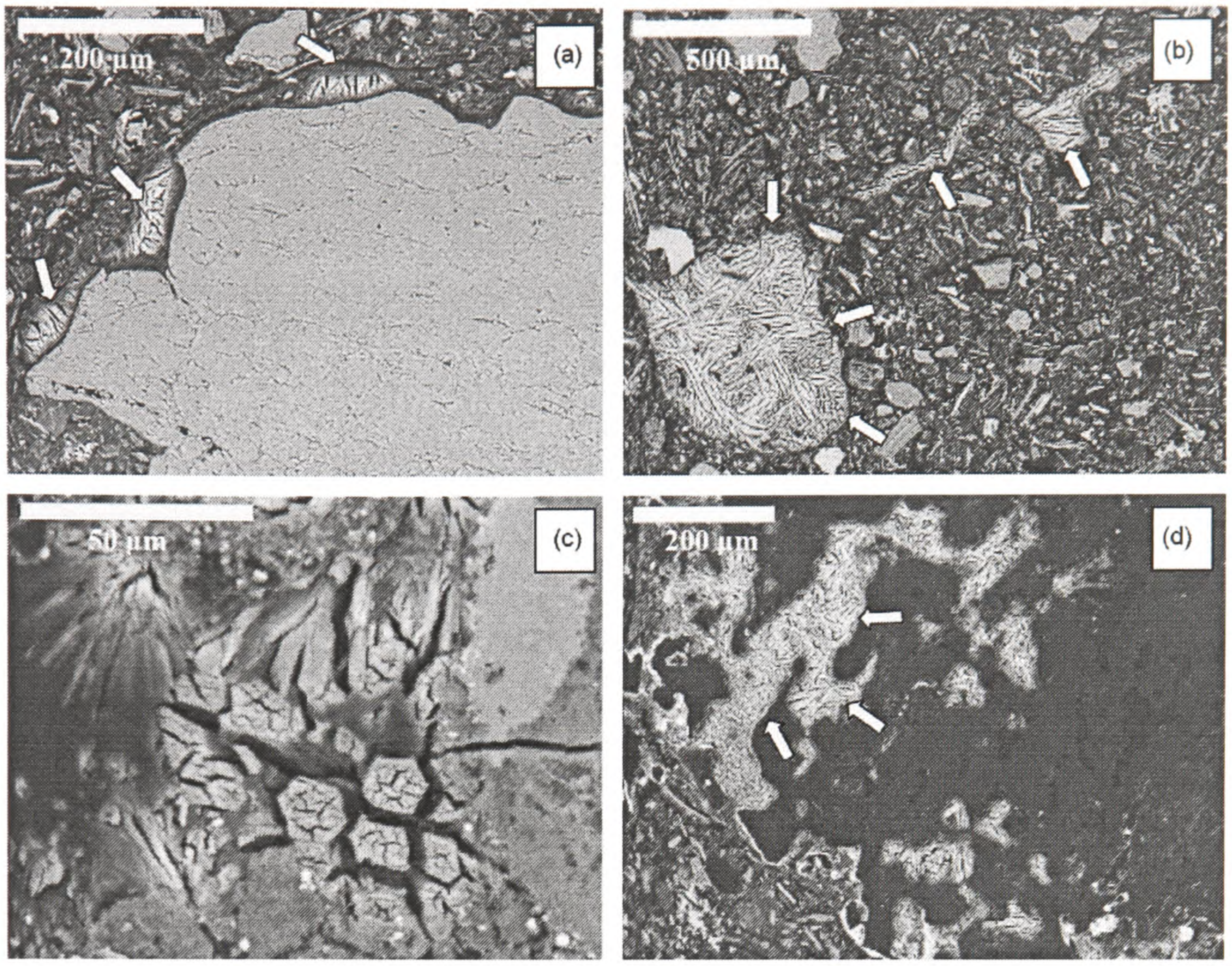

Fig. 8. Backscattered electron images of ettringite formed at: a) the interfacial regions of an aggregate particle (QD site); b) in voids and microcracks (QD site); c) within the matrix (HA site); d) in interconnected voids within a carbon rich/unburnt coal particle (QD site).

ing can be carried out on contaminant release, both within and outside of the treated area [4]. Monitoring depends greatly on the specific contaminants and the conditions prevailing on site; and may include pH, redox, conductivity and contaminant concentration in groundwater. Occasionally, archived samples are tested over time for e.g. unconfined compressive strength (UCS), permeability, California Bearing ratio (CBR) and leaching. The results obtained can be compared against target values set at the time of remediation, and thus can give an indication of the current performance of the cement-treated soil. However, this degree of scrutiny is quite uncommon in practice, hence the lack of strong data relating to field performance of the S/S soils.

The contaminants encountered in the soils were inorganic (lead, zinc, chromium, copper, arsenic) and organic compounds (PAH, PCB, TPH), as indicated in Table 1. The results presented in Table 3 were obtained using different leaching tests, as indicated. It must be noted that, for a number of sites, there are no enforceable limits for metal leaching, but benchmarks for comparing leaching concentrations from the S/S soils. For the US sites (AC, PS, S8, QD and MGP), often the EPA's Maximum Contaminant Level (MCL) for drinking water is used as a benchmark. However, the MCL value is usually

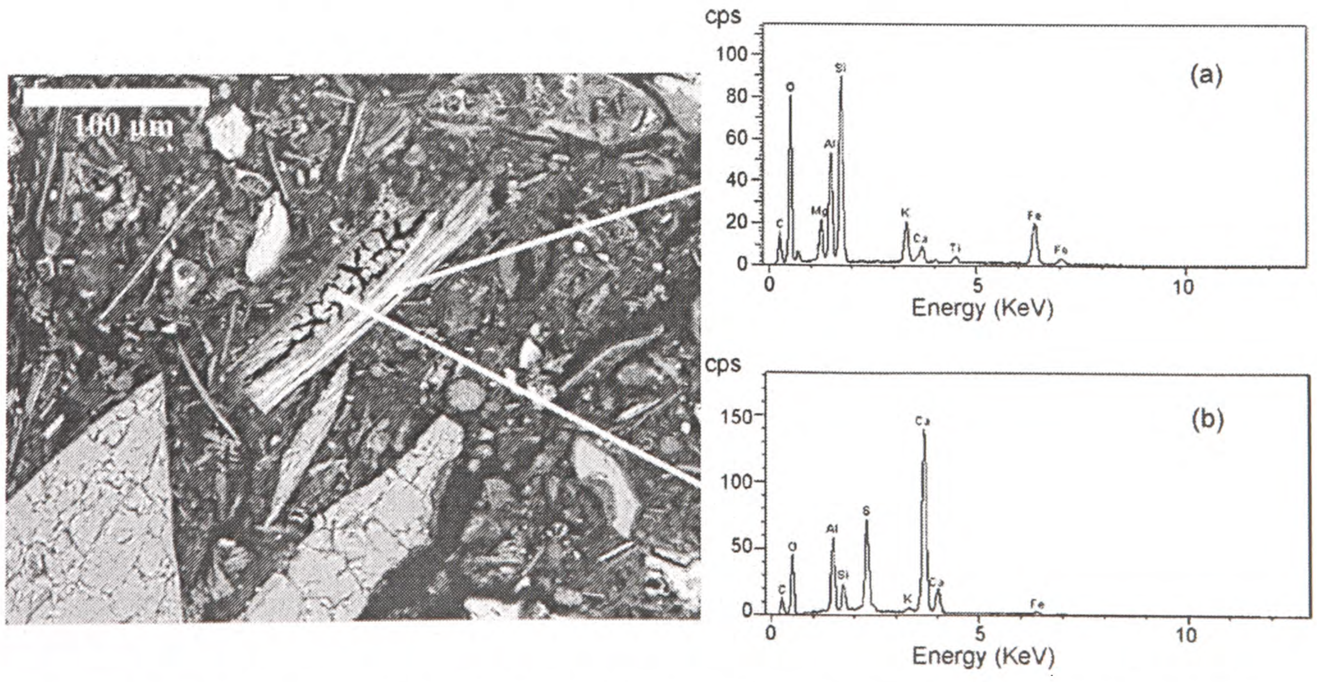

Fig. 9. Ettringite formed between mica lamellae and the corresponding EDS spectra: a) unaltered mica; b) ettringite.

Table 3
Contaminant leaching from the S/S soils up to 16 years following remediation.

Contaminant	Leaching concentration in mg/l (target values in brackets)							
	AC[a]	PS[a]	S8[a]	QD[a]	MGP[a]	AP[b]	HA[c]	CA[d]
Lead		0.029 (*0.050*)[e]	0.04 (0.015)[e]			<0.008 (*0.015*)	0.060 (*0.025*)	
Arsenic	<0.002 (0.050)	0.006 (*0.050*)[e]	<0.002 (0.050)[e]				0.060 (*0.010*)	
Copper						0.06 (*5*)	0.07 (*2*)	
Zinc						0.01 (*5*)	0.01 (*0.8*)	
TPH				bdl (0.001)				0.5 (*0.8*)
PAH	0[f] (0.01)				0.37 (10)			0.2 (*0.1*)
Dioxin	3.6 (30×10^{-3})							
PCP	0.16 (0.2)							

[a] USEPA SPLP 1312.
[b] DIN 38414-S4.
[c] NRA.
[d] NEN 7375.
[e] The State Drinking Water Standards were lowered since the remediation to 0.010 mg/l for arsenic and 0.015 mg/l for lead.
[f] Benzo α pyrene (BaP) equivalent.
bdl signifies values below detection limit.

viewed as a target to be achieved at a point of compliance i.e. monitoring well, at the site boundary, rather than a leaching limit for the metal release from the S/S soil. Therefore the drinking water standards are an indirect means of monitoring the performance of the soil stabilization remedy and its long-term impact on groundwater. Remediation target values equal to drinking water quality limits are over specified, due to the numerous factors which contribute to dilution, dispersion and retardation of the contaminant release. The contaminant concentration in groundwater is determined by the permeability of the S/S matrix, the rate of diffusive release of contaminants to infiltrating water, retardation in the vadose and additional hydrogeological factors i.e. aquifer thickness and hydraulic gradient. Therefore higher levels are allowed in the SPLP extract so long as the levels will be reduced to the MCL at the site boundary or other points of compliance. In Table 3, the benchmark values are presented in italics.

The AP, HA and CA soils did not have enforceable leaching limits, but guideline values derived from Drinking Water Limits [30,31] and site specific risk assessments, respectively.

All contaminants throughout the S/S soils have complied with the guideline or target values, except for lead at S8, as shown in Table 3. The SPLP results for S8 showed that three out of five samples leached lead above the drinking water action level of 0.015 mg/l. However, due to the soil heterogeneity, the USEPA allowed for 20% of samples to be twice the limit, and for 10% of samples to exceed by a factor of 5, provided that the average of all samples tested met the limit [32]. Also, a recent report by the US EPA on the S8 soil performance indicated that despite the lead leaching following the SPLP test, the groundwater concentrations have not reached the action level. Therefore, the treatment is still protective of the groundwater, which was identified as the main risk of contamination [32].

4. Conclusions

This work examined the long-term performance of S/S soils up to 16 years old. The eight Superfund and private sites in the UK and USA were characterized and the main conclusions were:

- The S/S materials retrieved, in general, met their original acceptance criteria for physical performance. The S/S soils were shown to behave like cement-bound materials rather than concretes, as indicated by the physical characteristics and mineralogical and microstructural observations.
- A number of potential key risk indicators for the performance of S/S soils were identified i.e. carbonate minerals, sulfate bearing minerals (ettringite and gypsum) and weathered minerals. Carbonation and ettringite growth are regarded as deleterious processes affecting concrete. The observations made suggest that their role in S/S soils is largely inconsequential.
- The release of contaminants from the S/S soils was within the specified limits. This suggests that the contaminants are likely to be adequately immobilised over a extended period of time.

Acknowledgements

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