Performance Assessment of Solidified/Stabilised Waste-forms

An Examination of the Long-term Stability of Cement-treated Soil and Waste

Final Report

March 2010

www.passify.unh.edu

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CL:AIRE
Environmental Geotechnics Ltd.
Homes and Communities Agency (English Partnerships)
The Welsh Assembly Government
Celtic Technologies Ltd
SITA Environment Fund
Environment Agency
ADEME
United States Environment Protection Agency
Eureka

Acknowledgements

The research partners are indebted to organisations listed above for their financial support and in-kind help, including access to S/S sites, archived data and solidified/stabilised samples. The Passify consortium especially wishes to thank the following individuals: Stephan Jefferis, Rob Sweeney, Christine Mardle, Edward Bates, Andrew Bates, Laurent Chateau, Chuck Wilk and Richard Esposito, Julie Santiago, Femi Akindele, Vincent Mallott for their help on site, their encouragement and considered opinion.

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PASSiFy

1. INTRODUCTION

The past 15 years have seen major changes in the way contaminated land and hazardous waste has been managed in Europe. This partially results from the adoption of risk-based methods for assessing the environmental impact of waste and brownfield land, and the realisation that formerly blighted land represents a potential resource that can generate wealth when re-developed and returned to good use.

The mounting pressure on landfill space and the rising costs of soil removal and disposal have meant that re-use at the site where contaminated land is found is often the preferred management option. Under a risk-based approach it is not always necessary to remove contamination, but to contain it appropriately and a variety of remedial technologies are available to treat both soil and waste.

However, the contaminants of concern that have been retained at a site have the potential to be released into the environment in the longer-term and the risks associated with this are difficult to predict, not least because there may be selective release of pollutants over uncertain timescales. This situation does not inspire stakeholder confidence and needs to be addressed if immobilisation technologies such as stabilisation and solidification (S/S) are to be used confidently to manage the risks associated with contaminated land.

The potential of contaminant release from S/S waste forms with time requires targeted scientific study using methodologies that are appropriate for the prediction of the service life of treated brownfield land. The better understanding of how S/S materials perform in service will provide for the development of tools that will give confidence to regulators, practitioners and customers alike and assure that the risks associated with contamination are properly managed.

For brownfield land to be returned to use with confidence it must be demonstrated that any remaining contaminants are immobilised for a long time and are unable to adversely impact the environment. This is especially important to land (or waste) that has been managed by S/S technologies, employing cementitious-binder systems as huge quantities of contaminated material have been treated in the past. As S/S is one of the few technologies available where contaminants are left in the ground, confidence building for the future application of this risk management technique is required.

Stabilised/solidified materials may be capped or used in association with another barrier system and this approach has been widely used in the USA, but less so in Europe and elsewhere. However, few data exist in the literature on the time-dependent performance of S/S waste forms. This has been considered a major potential impediment to the widespread implementation of S/S, particularly in the UK. Nevertheless, the experience of 50 years of the use of S/S in the USA is, however, encouraging, as there are no reported major failures of S/S waste-forms in that country. Without evidence to the contrary, it appears that S/S is a reliable, relatively easy to use approach to managing the risks associated with contaminated soil.

To date, the most significant research undertaken on the long-term effectiveness of archived S/S materials concluded (Klich et al., 1999):

- The extent of degradation after 6 years is considered slight to moderate, but at these rates the waste form may disintegrate over 50 to 100 years.
- Solidified/stabilised wastes are vulnerable to the same environmental degradation factors as concrete.
- Because the life of concrete products is finite and depends on the local environmental conditions, regulation for on-site burial of S/S treated wastes is needed

In early 2000, the UK Government sponsored a mission to the USA (BCA, 2001) to examine best practice in S/S technology. A number of leading practitioners and on-going remedial operations, primarily in the east of that country, but as far south as Florida were visited. On each occasion the subject of long-term performance was raised and the need to address this important gap in knowledge was highlighted.

During this study mission a number of key contacts were established, which ultimately provided support for a project to access S/S treated sites, examine risk indicators and generate data for a toolbox for the prediction of waste-form performance. The Environment Agency (England and Wales), ADEME (France), the United States Environmental Protection Agency (USEPA) and other key players in each of the three countries gave their support to PASSiFy –Performance Asessment of Stabilised/Solidified Waste forms. PASSiFy also received EU Eureka project status (∑3308!).

Despite the apparent widespread support for PASSiFy, full funding was not forthcoming and the scope of project was scaled down to include 3 major field and laboratory-based operations at the sites of former full-scale remedial operations employing S/S. The approach involved:

- Extraction of samples from sites treated by S/S
- Testing of samples using original acceptance methods
- Evaluation of samples using advanced methods of analysis

The lack of willingness amongst some owners of land treated by S/S to grant permission to sample, in case the project uncovered something ‘sinister’ was largely overcome in the USA by being granted access to a number of completed Superfund S/S remedial operations by the USEPA. In the UK treated sites had often been re-developed and permission to access and sample was often complicated by changes in land ownership. Nevertheless, a total of 10 sites up to 16 years of age were identified for inclusion in the study, and each had different soil/waste types, contaminants (organic and inorganic), and employed different binder systems (Table 1.1).

Table 1.1: Characteristics, contaminants and remediation formulation of the cement-stabilised sites studied under the PASSiFy project

Site and location (abbreviation)	Contaminants of concern	Contaminant concentrations	Treatment date	Type of remediation and cover system	Depth of remediation	Remediation formulation	Site reuse
Pepper Steel, USA (PS)	Lead; PCBs	2,000 mg/kg; 116 mg/kg	1989	Ex situ S/S (compacted) Capped with crushed limestone	0.6 – 2.4 m	12% PC, 8% PFA	Storage for land-sea containers
Columbus MGP, USA (MGP)	PAHs; TPH	2,400mg/kg; 5,500 mg/kg	1992	Ex situ and in situ S/S HDPE cap and topsoil	10 m	10% PC (site) 25% PC (retaining wall)	River front park
Quarry Dump, USA (QD)	TPH	1,200 mg/kg	1994	In situ S/S	1.2 -1.5 m	25% PC ratio to soil	Not known
South Eight Street, USA (S8)	Lead in waste oil residuals, sulphuric acid	22,000 mg/kg pH often less than 1.0	2000	In situ S/S GCL cap and topsoil	5.1 m	25% crushed limestone (pre-treatment of acidic soil) 20% PC, 10% PFA	Redeveloped as an industrial site
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	Ex situ S/S (compacted) GCL cap and topsoil	0.6 – 1.5 m	5% PC, 4.5% PFA and 1.3% activated carbon ratio to soil	Storage area for construction materials

Table 1.1: Characteristics, contaminants and remediation formulation of the cement-stabilised sites studied under the PASSiFy project (continuation)

Site and location (abbreviation)	Contaminants of concern	Contaminant concentrations	Treatment date	Type of remediation and cover system	Depth of remediation	Remediation formulation	Site reuse
Halton, UK (HA)	Lead, Arsenic, Zinc, Copper	1,550 mg/kg 825 mg/kg; 980 mg/kg; 639 mg/kg	2000	In situ S/S Railway ballast, permeable membrane and topsoil	0.3 m	6% PC, 0.5 % proprietary additive	Football pitch-not in use
Astra Pyrotechnics, UK (AP)	Lead, Copper, Zinc	203 mg/kg; 64,089 mg/kg; 17,498 mg/kg	2000	Ex situ S/S (uncompacted) No cover	0.3 – 0.6 m	20% PC cell2; 20% EnvirOceM cell3, ratio to soil	Disused
Caerphilly, UK (CA)	PAHs, TPH	32960 mg/kg 27845 mg/kg	2006	In situ S/S Topsoil	1 -1.5 m	12% PC/PFA ratio to soil	Residential development
Bellegarde, France (BL)*	Lead, Zinc	2,000-3,000 mg/kg 4,000-9,000 mg/kg	1998-2000	Ex situ (plant)	NA	Proprietary formulation	NA
SEDA, France (SD)*	Lead, Zinc	1,000 mg/kg 7,000 mg/kg	1999	Ex situ (plant)	NA	Proprietary formulation	NA

* landfill sites; NA – not applicable; HDPE – high density polyethylene, GCL – geosynthetic clay liner, PAH – polyaromatic hydrocarbons, PCP – pentachlorophenol, PCB – polychlorinated biphenyls, TPH – total petroleum hydrocarbons

One major consideration to be addressed in PASSiFy was how would S/S materials perform in their environment of service over time? Would they behave like concrete as suggested in earlier work or more like rock; and would risk indicators be present and identifiable over such short time scales? An examination of the literature suggested that there was no clear answer and as such, the importance of this omission should not be underestimated. Data from the literature on weathering rates for rock and concrete (Table 1.2), augmented by laboratory and modelling studies suggested that the long-term performance of S/S waste-forms might be significant and extend into geological timescales.

Table 1.2: Service life predictions, for S/S wastes and analogous materials (modified from: EA, 2004)

Timescale (yr)	**Concrete**	**Rock**	**S/S material**	**Other materials**
0-10	Walker, 2000	Bishop, 1998 Emerick, 1995 Fookes *et al,*, 1988a	Read and Clarke, 2001 Board *et al.,* 2000 Baur *et al.,* 2001 Ludwig *et al.,* 2000	
10--50	Hobbs and Taylor, 2000	Sweeting, 1960		
50-100			Klich, 1997 Kosson *et al.,* 1996 Van der Sloot *et al.,* 2000	
100-1000		Mottershead, 2000	Van Zomeren *et al.,* 2003	
>1000	Means *et al.*, 1995 Murdock and Blackledge, 1968	McConnell, 1955 Fookes *et al.*, 1988b	Bozkurt *et al.,* 2000 Catalan *et al.,* 2002	Astrup *et al.,* 2003 Hall *et al.,* 2003 Dole, 1985

2. RECOMMENDATION/ CONCLUSIONS

The sites sampled and evaluated in this study were situated on two continents. They differed widely in respect to their soil types, the contaminants present, and the S/S remedial treatments employed. The time that had elapsed between treatment and sampling varied and a wide spread of aged material was recovered, ranging from 2 to 16 years.

The sampling method employed at the various sites also differed, as local contractors were used to retrieve samples. Where possible, intact cores were taken, stored and transported to the participating laboratories. Nevertheless, because of these factors and the different remedial objectives pertaining to each site, augmented by the regulatory requirements in place in each of the three countries at the time of treatment, the application of acceptance tests was normalised to the maximum extent possible. Acceptance tests were complimented by additional methods that was thought might provide insight into their properties and chemistry.

In most cases, the remedial objectives at the sites involved treatment to substantially reduce the tendency of the soil to leach contaminants and to pass physical property requirements of a minimal allowable strength and a maximum allowable permeability.

In comparing, properties of recently cored samples from monoliths treated as long as 16 years prior, some differences were noted in leaching, strength, and permeability when compared to performance samples evaluated at the time of treatment. It was also noted that a considerable variation in properties between replicate samples was obtained. This was attributed, in part, to the impact of the sampling methodology upon the material extracted, but it was noted that sampling and material had some impact on all the samples evaluated in this study. Most notable was the amount of fracturing induced during sample retrieval, including both macro fracturing 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.

Taking the above factors into consideration, it is the opinion of the authors that treated material from all the sites sampled performed well and met the objectives of the original remedial treatment. This opinion is reinforced by the post treatment 5-year reviews conducted by the USEPA on three of the sites and the 10 and 15-year reviews for one of the sites investigated.

Successful treatment by S/S relies on a combination of reduced leachability and lowered permeability, which combine to minimize the release of contaminants over extended timescales. It was noted that, particularly when acid and other tarry residues were treated by S/S, inclusions of these organic residues were clearly identifiable with the cementitious matrices. Organic residues were seen to have been isolated and trapped within the inorganic matrix by thorough mixing and dispersion.

The study highlighted that a number of risk-indicators were identified in the retrieved samples, but these did not indicate the onset of deleterious reactions. On the contrary, the waste forms were shown to behave much like cement-bound materials and the interactions between soil particles, the waste and the binder systems employed can be readily evaluated and explained. Waste forms were commonly observed to be carbonated, to a lesser or greater degree and ettringite and other phases formed predominantly within pore space. This is an important observation, as cementitious construction and other products are ubiquitous and represent well-understood systems. As such, the behaviour of S/S waste forms over long periods of time should be relatively easy to predict, providing the contaminated S/S soils treated and the binders used are well characterised, and the environmental loads impacting upon a waste form are known.

The authors believe that the results of this study affirm the viability of S/S as an effective long-term treatment, and that they provide the basis for a new approach to the prediction of field performance with time.

The main conclusions of this study are:

- Stabilised/solidified waste forms located in 3 countries and varying in age from 6 months to 16 years, were sampled and evaluated in the laboratory.
- The S/S materials retrieved passed their original acceptance criteria.
- The S/S soil and waste behaved like cement-bound materials and contained mineral phases and microstructural features consistent with this observation.
- The leaching performance of the retrieved samples was evaluated and the release of contaminants was modelled and explained.
- The contaminants varied from site to site and the leaching and modelling data showed that the release of the contaminants was dependent upon the nature of the contaminated soil and the binder system utilised.
- The leaching of contaminants from the S/S soils was generally below instrument detection levels.
- The results indicate that if the nature of the soils/waste are known then a binder system can be developed that will prevent leaching in the long-term
- The microstructure of retrieved S/S materials was complex and involved interactions between all three system components; soil, contaminants and binder, and that this relationship was subject to modification due to aerial and sub-aerial environmental loads, i.e. during treatment and after site closure.
- A number of potential risk-indicators were identified in the materials retrieved and examined. There was no evidence to suggest that degradative processes were occurring and that these were impacting upon the efficacy of contaminant containment.
- Waste forms appeared to be subject to carbonation, which occurred during the remedial operation and/or afterwards.
- Extensive localised carbonation was noted at the microstructural level. This was not a cause of concern as the densification of waste form microstructure resulted, infilling voids and micro-cracks.
- Some soils are naturally alkali sensitive and soil minerals were identified at two sites that were subject to this reaction when solidified by a cement-based binder.

- The development of ettringite, infilling pores and micro-cracks was noted. The presence of ettringite was not associated with any expansive reactions.

3. APPROACH

3.1. Methodology

The approach adopted involved the following key steps:

- Clarification of the history of use of each site
- Determination of site characteristics and the identification of pollutant pathways
- Site sampling and performance testing
- Long term behavioural studies (based on pr ENV 12920)
- Results interpretation and modelling of data
- Reporting and dissemination of results

In Europe, it is established that the conceptual model developed for a particular site can inform the way the testing of samples is carried out. This is covered in pr EN 12920 and promotes a targeted testing regime that is based on the predicted environmental loads to be borne by an S/S waste form. This powerful tool was incorporated in Environment Agency Guidance in 2004 (EA 2004) and was used in the present work to facilitate the objective evaluation of the materials retrieved from the various sites investigated.

It should be noted that the collection of data pertaining to each site was gathered from a variety of sources, including the regulatory authorities, remediation contractors and site owners and from published work. In the USA, the USEPA was the prime holder of data originating from Superfund remedial actions. The openness of the participating remediation contractors and site owners and their willingness to participate in PASSIFY must be acknowledged and applauded.

The following tasks were carried out:

Collection of Historical Information (Task 1)

Site investigation reports and other archived information were used to establish the age and location of each site and the types of wastes that were disposed. The treatment targets at each site and the data quality objectives, sampling methodologies used prior to and during disposal were clarified.

The industrial origins of the residues at each site were determined and the main pollutants identified. The physical characteristics of the hazardous wastes or contaminated soils, and the quantities treated during the remedial operation were recorded. The regulatory testing regime in place during remediation and specific compliance criteria pertaining to each site, including the results of leachability studies were evaluated. The reagents employed during S/S and method of application used (e.g. in situ or ex-situ treatment) were established and the data collected was placed in a database that was specially constructed for this purpose.

Site Characteristics and Pollutant Pathways (Task 2)

This task involved the collection of data to determine the characteristics of the disposal scenario. Historical data collected in Task 1 above, provide information on each site:

- The geological setting
- Hydrological environment
- Risk analysis
- Risk engineering

This data was used to inform the conceptual model developed for each specific site and the testing regime, chosen in accordance with European Standard pr ENV 12920 and applied to materials recovered. This data obtained during this Task informed the subsequent evaluation of S/S waste-form performance outlined in Task 5, below.

Sampling and Performance Testing (Task 3)

Sampling was of special importance and an agreed methodology covering extraction, storage and the transport of representative samples was formulated for each individual site. It should be noted that the reliance upon local contractors to extract samples meant that different drilling techniques were employed and this was accounted for in the approach adopted locally.

In the USA, the USEPA employed its own procedures for use on its own sites with the support of the University of New Hampshire. In France, sampling was carried out by INERTEC and in the UK sampling, was undertaken by the University of Greenwich, with the support of the University of Birmingham.

Once samples were extracted, they were tested in accordance with the original testing program employed (acceptance testing), as identified in Task 1. Additional testing methods including microstructural and thermal methods of analysis and the examination of phase chemistry were used to identify speciation of pollutants and their interaction with binding agents over time. These data were important to the identification of risk indicators. (Table C) gives the tests employed on S/S waste samples.

Laboratory Assessment of Long Term Behaviour (Task 4)

Materials collected from sites in Europe and the USA, were subject to a range of tests to assess their likely long-term behaviour. Using pr ENV 12920 to prepare the testing environments appropriate to the conditions of service, identified in Tasks 1 and 2, a range of geotechnical, hydrological and chemical testing conditions were used for the assessment of likely long-term behaviour.

Interpretation of Results and Modelling of Future Performance (Task 5)

Data obtained from Tasks 1 to 4 were placed on the database for use with numerical modelling packages, specifically LeachXS using the HATCHES database, and Visual Minteq using an expanded version of the MINTEQA2 database with inclusion of the thermodynamic constant values for the main hydration phases of cementitious systems. This work was carried out by the University of New Hampshire and the University of Rome “La Sapienza”, respectively. The chemical data obtained from leaching were used to predict the solubility controlling phases.

The database will be archived but be available for future use for the prediction of, for example, the long-term behaviour of waste forms for each of the disposal scenarios identified and examined during this work and to regulators of S/S and academic research organisations.

Reporting and Results Dissemination (Task 6)

A dedicated website was established to receive regular reports from the work and to receive the final project report.

A number of conference papers have been produced or are in preparation. Peer reviewed journal papers have been published: Antemir et al., 2010a; Antemir et al., 2010b. A dedicated workshop was held at WASCON 2006 in Belgrade (Antemir et al., 2006), and papers presented at STARNET 2005 (Antemir et al., 2005a), 25th International Cement and Concrete Science (Antemir et al., 2005b), Sardinia 2007 (Aubry et al., 2007), WasteEng 08 (Urso et al., 2008) and WASCON 2009 (Hills et al., 2009).

A report on the project will be published by CL:AIRE in the UK. Tentative discussions with the Cement Association of Canada on a report focussed towards North America have taken place.

A PhD thesis was submitted and approved, in July 2010.

4. SITE BY SITE STUDY: CONTAMINATED SOILS

4.1. Pepper Steel, Florida

The Pepper Steel site occupies 12 hectares and is located in Medley, Florida approximately 15 km northwest of Miami. Numerous industrial activities took place at the site from the mid-1960's, including battery and fibreglass manufacture, boat building, metal scrapping and construction with precast concrete.

The legacy of these industrial activities included soil and water contamination with metals and metalloids (lead, arsenic, cadmium, zinc, mercury, chromium, copper and antimony) and polychlorinated biphenyls (PCBs). Of these contaminants, lead, arsenic and PCBs were identified in concentrations that could pose a risk for human health and the environment. Certain areas of the site contained up to 50 mg/kg of PCBs, 1000 mg/kg of lead and 50 mg/kg of arsenic.

The risk posed by the presence of the contaminants in the soil was via migration into the groundwater, into the Biscayne Aquifer or the nearby Miami Canal and subsequently into the ocean. The Biscayne Aquifer is the sole source of drinking water for over 3 million people living in Southwest Florida.

In 1987 the remedial operation was initiated using cement-based solidification/stabilisation. The objectives of the remediation were:

- the treatment of leachable metals to prevent contamination the Biscayne Aquifer;
- removal of all PCBs contaminated soil above a level of 50 mg/kg.

The first objective was of primary concern to the PASSiFy project.

The site remedial operations started by the removal of all surface debris resulting from previous construction activities, followed by ex-situ S/S treatment. The contaminated soils were excavated and stockpiled outside the confines of the site. The soil was screened to separate debris (inorganic material as steel, concrete, etc.) from the contaminated soil, and transported and disposed at an off site landfill. The remaining contaminated-soil fraction was mixed with the binder system at a ratio of 20% reagent to soil by weight, was then backfilled in the excavation and capped with a 30 cm layer of crushed limestone (to match the geology on site and to prevent direct contact with the treated material). The binder used for treatment consisted of 40% fly ash and 60% cement by weight.

At the Pepper Steel site a drainage collar was installed to collect and infiltrate run-off, and inspection wells for post-remediation monitoring were constructed. The remediation was performed to a maximum depth of 3.6 m and was eventually completed in 1989.

The remediated site has received much interest for development, due to its convenient location to an industrial area and a nearby major highway. As reported by the USEPA, 2 hectares of the site has been sold and is in use as a truck staging area, whereas a further 4 hectares has been purchased for use as a concrete forming operation. The remaining 4 hectares also have a lease/purchase agreement for reuse (USEPA, 2007). In 2004, the USEPA conducted an evaluation to determine whether reuse of the site would be possible and to evaluate the efficacy of the remedial treatment employed. The USEPA approved reuse provided that the treated monolithic material was not disturbed. The USEPA has also conducted 5, 10, and 15-year post treatment reviews of the site all of which have confirmed continuing satisfactory performance.

4.1.1 Historical compliance results

The Pepper Steel site was one of the first site remedial actions undertaken by the USEPA and represents one of the first uses of solidification/stabilization (S/S) to remediate risks from toxic metals and PCBs. Records from this action have largely been lost and available information on the treatment standards and performance measures are sketchy. However the following is understood to generally represent the remedial action taken. In 1989, approximately 36,700 m^3 of soil contaminated with PCBs below 50 mg/kg, 9,500 m^3 of soil contaminated with lead, and 6,900 m^3 of soil contaminated with arsenic were excavated, screened to remove debris, mixed with 20% by weight reagent, and returned to the excavation to set up into a single monolithic structure (Figure 4.1). The reagent mix was reported to be 40% fly ash and 60% cement, by weight.

The precise treatment specifications, methods of measurement, and actual results on performance samples at the time of treatment are unclear. However the overall treatment objectives are documented along with certification that they were met.

The remedial action objectives were to remove soils, containing more than 50 µg/kg of PCBs along with debris, and send them to a secure off site landfill. The remaining soils containing PCBs, below 50 µg/kg along with lead and arsenic were to be treated with a cementing reagent and returned to the excavation so as to form a single low permeability monolith that would not leach toxic contaminants to the groundwater at levels above drinking water standards at that time. This was accomplished and based on subsequent 5, 10, and 15 year reviews, it can be concluded that the original treated material possessed properties of unconfined compressive strength above 0.69 MPa and a permeability less than $1x10^{-8}$ m/s. It is not known if a leaching specification was used, but it can be concluded that the treated waste did not leach contaminants above the drinking water standards that were in place at that time (50 µg/kg for both arsenic and lead). These drinking water standards have subsequently been lowered to 15 µg/l for lead and 10 µg/l for arsenic. Even with current lower standards the remedy is protective of the groundwater.

There is some evidence to suggest that at the time of treatment an unconfined compressive strength specification of 0.14 MPa may have been used and perhaps a permeability specification of $1x10^{-8}$ m/s.

4.1.2 Sampling / new physical and leaching results

A general sampling plan involving coring from three to four locations on each site was devised. Each sampling plan required that at least 1.2 m of material was recovered from each cored hole. The first 0.6 m was to be cored dry (without drilling fluid), but did not need to be intact. The purpose of this was to have material available for chemical leaching tests that was not “pre-leached” during the drilling, storage, and sample transport process. The remaining 0.6 m was to be recovered with intact core sections, suitable for strength and permeability testing. This section could be recovered using water as a cooling fluid during drilling. It was suggested that a 7.6 cm diamond core barrel be used for sampling, and was not available at each site from the contracted driller, and adjustments to total sample volume were made when a smaller core barrel was used (Figure 4.2).

The PS site was sampled in early December 2003. The initial drilling company, contracted by EPA was to use a 7.6 cm diameter core barrel, but the equipment brought to site was insufficient to sample the monolith. The EPA immediately contracted a second company to sample the site the same week and this time a smaller core barrel was used, resulting in cores approximately 5 cm in diameter (Figure 4.3). Material was recovered using both dry and wet coring.

In one area of the monolith, operators were unable to recover any intact material. The EPA representatives returned to the site at a later date to do some in situ strength and permeability tests, and were satisfied with the integrity of the monolith, despite the inability to extract intact material.

Figure 4.1: The covered monolith at Pepper Steel

The strength results for the PS site (the oldest site in the study) yielded the highest average strength of the five sites tested, but also showed one of the lowest values (Figure 4.4). The range of values was greatest at this site, from 0.1 MPa to over 4.5 MPa. All values, except the lowest, surpassed the design minimum value of 0.1 MPa.

Figure 4.2: Drilling at the Pepper Steel site

Figure 4.3: Recovered core at the Pepper Steel site

Out of concern over the lowest strength value recorded of 0.1 MPa, the USEPA representatives re-examined the PS monolith in the area where this sample was taken. In situ strength tests were performed by examining deflection at the top of the monolith when pressure was applied. The results of this testing, though not directly comparable, yielded results comparable to a UCS value of 4.1 MPa, suggesting that in some cases, sample retrieval may influence the results of the compliance testing and care should be exercised in evaluating such results.

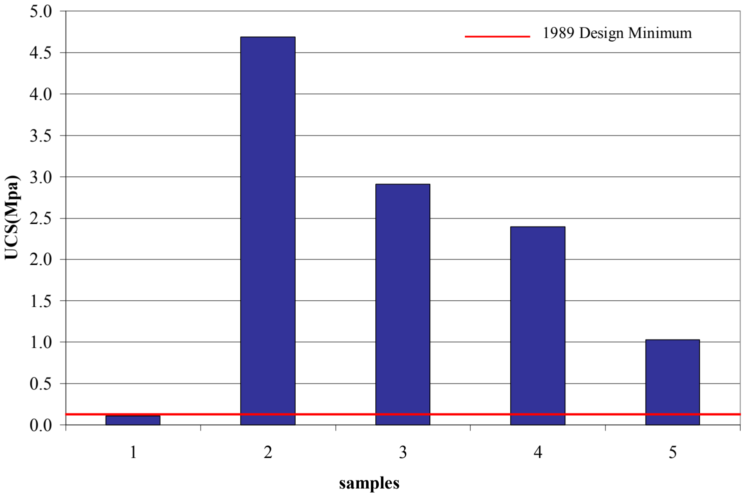

Figure 4.4: UCS Results for the 2003 sampling of the Pepper Steel site

In 2000, a ten -year review was conducted at this site. During that examination only one sample was retrieved in adequate condition for UCS testing. That sample had a strength value of 5.4 MPa; on par with the highest value found in the 2003 sampling effort.

The results for the Pepper Steel site showed three samples with permeability lower than the design specification and two samples failing to meet this performance criterion of 10^{-8} m/s. The 2003 data presented in Figure 4.5, can be compared to two sets of historical data. The 2000 permeability values were reported in the USEPA 10-Year Review of the Pepper Steel site (Black and Veatch, 2002). The 2000 samples were originally reported in units of square meters, but have been converted to m/s for the purpose of comparison with the most recent data. The 1989 samples were collected at the time of treatment and cured ex situ for two years.

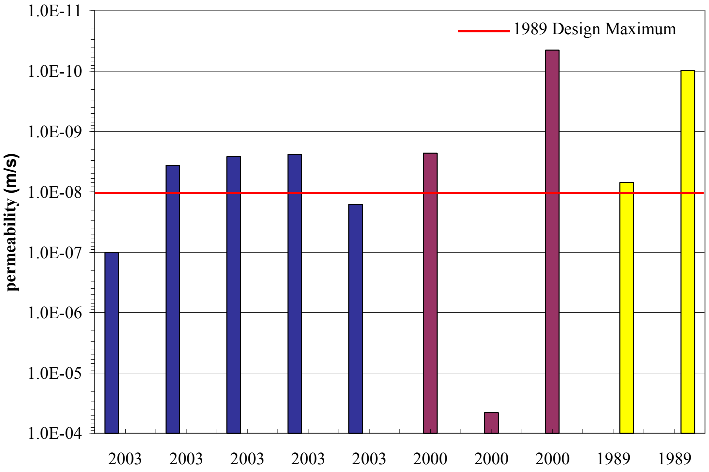

Figure 4.5: Permeability results for 1989, 2000, and 2003 sampling of the Pepper Steel

Both the 2003 and 2000 investigations resulted in samples with higher and lower values than the performance criteria originally set. The two 1989 samples showed lower permeability than the design maximum of 10^{-6}. Though limited in number, these sample-sets indicate that the older, in situ cured samples have higher permeability than the younger samples cured ex-situ and that some portions of the monolith do not meet the specification set forth at the time of treatment. Another explanation could be that coring induced micro cracks, or that over extended time, deleterious reactions in the monolith have increased the permeability.

The contaminants of concern tested for in the PS site material were arsenic and lead. Both were detectable in the cement matrix at total concentrations of 23µg/l for arsenic and 1728µg/l for lead. The average lead concentration for this 2003 sampling event was greater than those reported in 1993 and 2000. The average values were between 600 and 700µg/l, but the year 2000 range of values did overlap concentrations found in 2003.

Several leaching tests were performed for this site. The SPLP results are presented in the following Table 4.2 in order to compare to other sites, but there were no performance criteria set for SPLP leaching at the PS site. Often the EPA's Maximum Contaminant Level (MCL) for drinking water is used as a benchmark for comparing reasonable leaching levels and indeed, is set as the performance criteria for some of the sites in this study. However the MCL value is just as often viewed as a target to be achieved at a point of compliance down gradient that is protective of public health. In the later case, 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. For example, the acceptable level for lead was set at 232 ug/l at the Peak Oil Superfund site, based on predictive modelling results at the site boundary of 15 ug/l. The MCL for arsenic was 10µg/l and leaching results for this analyte fell below this mark. The MCL for lead was 15 µg/l and the results from the SPLP provided an average result of 29.8 µg/l.

Table 4.2: Results for the 2003 sampling of Pepper Steel

Sample	**Arsenic**		**Lead**	
	Total (mg/kg)	Concentration x 10^{-3} (mg/l)	Total (mg/kg)	Concentration x 10^{-3} (mg/l)
1	18	6	800	47
2	19	6	840	56
3	29	-	1300	24
4	25	8	3700	19
5	25	4	2000	-
average	23.2	6	1728	29.8
quant limit	0.2	3	2	3
performance criteria	-	-	-	-

Table 4.3: TCLP test results for Pepper Steel samples

Sample	**Arsenic concentration (mg/l)**	**Lead concentration (mg/l)**
TCLP1	< 0.1	0.2
TCLP2	< 0.1	< 0.1
TCLP3	< 0.1	< 0.1
TCLP4	< 0.1	0.2

Table 4.4: MEP test results for Pepper Steel samples

Stage	**Lead Concentration (mg/l)**			
	PS-01	PS-02	PS-03	PS-04
MEP1	< 0.1	< 0.1	0.4	< 0.1
MEP2	< 0.1	0.3	1.4	0.9
MEP3	< 0.1	< 0.1	0.2	0.3
MEP4	< 0.1	< 0.1	0.1	0.5
MEP5	< 0.1	< 0.1	0.1	< 0.1
MEP6	< 0.1	< 0.1	< 0.1	0.3
MEP7	< 0.1	0.1	0.1	0.3
MEP8	1	2.4	4.5	0.2
MEP9	< 0.1	< 0.1	0.2	0.2

The TCLP and MEP (Multiple Extraction Procedure) leaching tests were also performed samples retrieved from the Pepper Steel site (Tables 4.3 and 4.4). It should be noted that all arsenic results from the MEP were below the detection limit of 0.1 mg/l and thus, are not shown here. The results from these tests were similar to the results of the Five Year Review, performed in 2000, which did not raise any concerns for human or environmental health.

4.1.3 Transversal testing

4.1.3.1 Microstructure and mineralogy

The crystalline minerals in the treated soil were determined by X-ray diffraction (XRD). Both transmitted light and scanning electron microscopy (SEM) were used to study the microstructure of the S/S soils. The dominant peaks observed in the x-ray diffractogram obtained from PS were from quartz and calcite, but low intensity peaks from mullite, gypsum and ettringite were also identified (Figure 4.6).

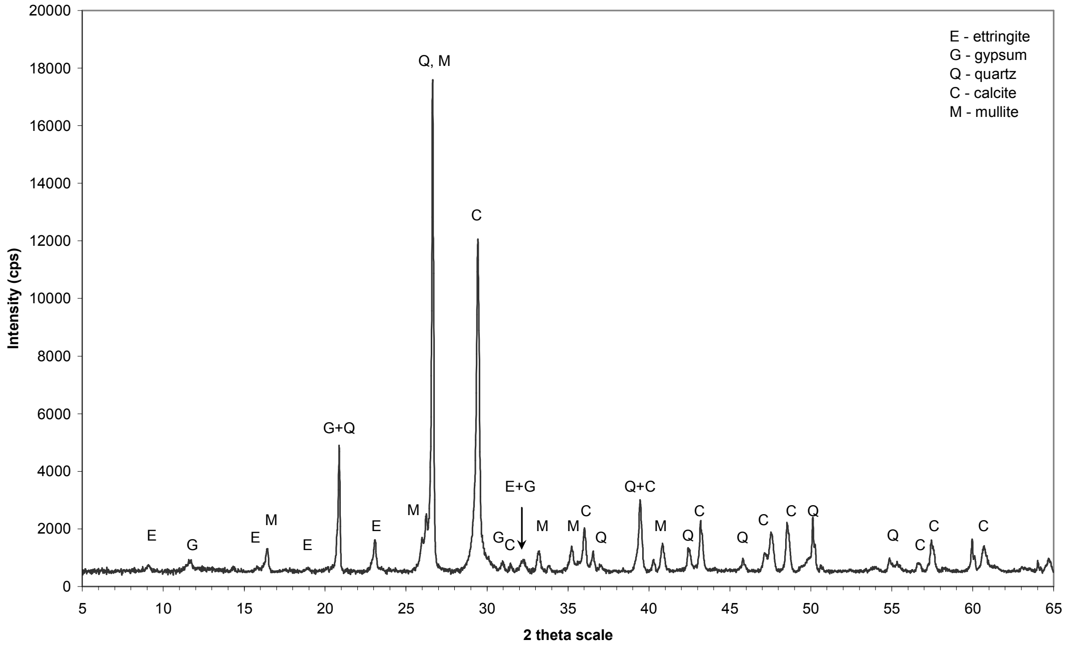

Figure 4.6: X-ray diffractogram of cement-stabilised soil retrieved from the Pepper Steel site

Quartz and calcite are naturally occurring minerals often found in soil, but they can also be found associated with cementitious binders. Calcite can form on exposure of cement-treated soil to atmospheric carbon dioxide. The soils around the Pepper Steel site are believed to be limestone rich reflecting the underlying geology and therefore, a high intensity peak for calcite may reflect this or at least be partially the result of carbonation of the cement-based binder.

Electron microscopic observations indicated that secondary carbonation of the matrix had indeed taken place in samples recovered between 0.5 m – 1.2 m depth. This carbonation was associated with distinct microcracks and the occurrence of voids (Figure 4.7). Less distinct, more diffuse areas that were carbonated were also identified.

Numerous small limestone fragments, several microns in size, were observed in the treated soil, and confirmed that the high intensity XRD peak was not solely from any secondary carbonation due to the reaction with CO_2 gas derived from the atmosphere.

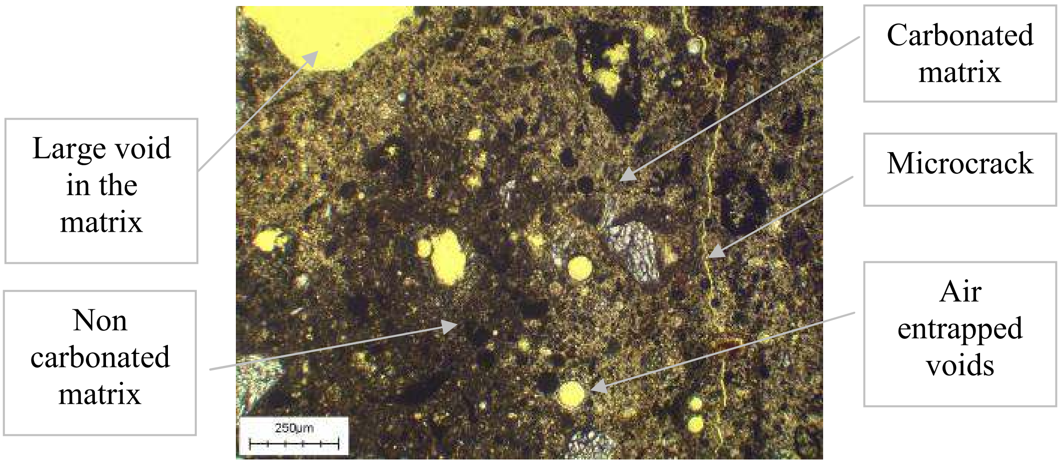

Figure 4.7: Photomicrograph of a microcrack and large void surrounded by a carbonated matrix

Mullite ($Al_6Si_2O_{13}$), a minor crystalline phase found in coal fly ashes, particularly in Class F fly ashes, was identified in the treated soil, indicating that there was a certain amount of un-reacted fly ash present.

Ettringite ($Ca_6Al_2(SO_4)_3(OH)_{16}{\cdot}26H_2O$), and to a lesser extent gypsum ($CaSO_4{\cdot}2H_2O$), are often associated with concrete degradation, but its presence does not necessarily mean that deterioration is, or will take place. The presence of ettringite in the samples retrieved at Pepper Steel was confined to entrapped-air voids, which provide space for crystallisation. Another sulfate bearing compound, thaumasite, was also readily identified intermixed with ettringite in some of the voids examined (Figure 4.8).

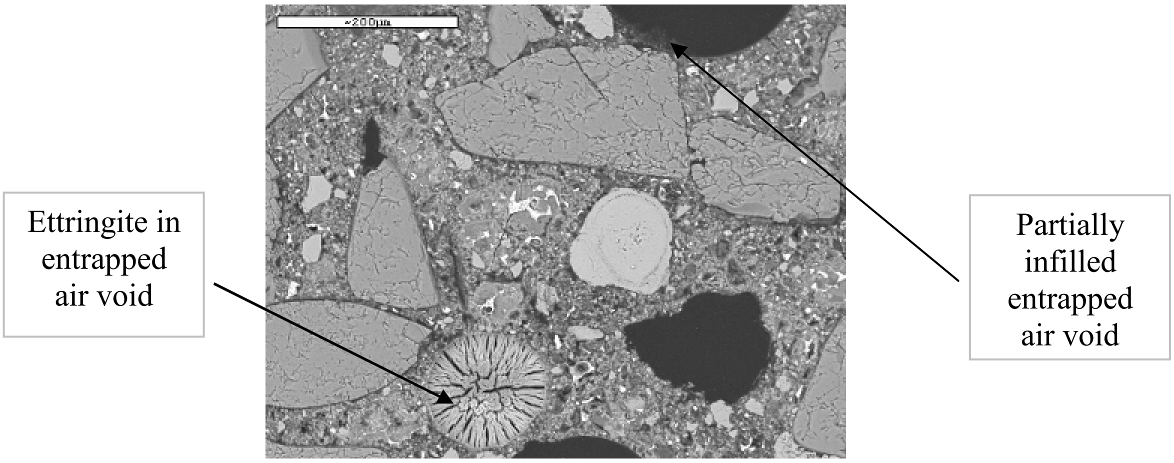

Figure 4.8: Backscattered image of ettringite growing in air void

The microstructure of the cement-treated soils obtained from the Pepper Steel site was generally of a dense fine-grained nature, containing a high level of hydrated cement, but also anhydrous cement grains and fly ash, often occurring as cenospheres. Some samples contained unreacted fly ash (Figure 4.9) that may have resulted from inefficient mixing of soil and binder, or the local lack of portlandite. Inclusions of unreacted fly ash in cement matrices may be vulnerable to, for example, freeze/thaw cycling (Klich, 1997).

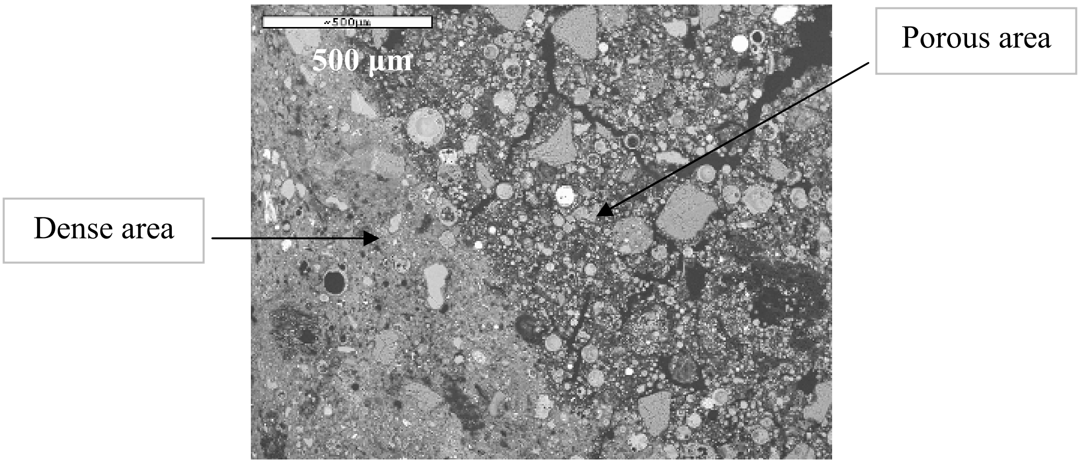

Figure 4.9: Zoning in the matrix at Pepper Steel, alternating dense areas with reacted fly ash and less dense with unreacted fly ash

One feature that is of potential importance in retrieved samples was the presence of microcracks with characteristic ‘map cracking’ morphology. Although, often associated alkali aggregate reactivity, in this instance it is likely that they are artifacts resulting from volume changes induced by desiccation during sample preparation.

4.1.3.2 Chemical characterisation

The results of the elemental analysis carried out on the material obtained from Pepper Steel sample are shown in Table 4.5.

Table 4.5: Total content analyses of the treated Pepper Steel soil (mg/kg)

	Concentration (mg/kg)		Concentration (mg/kg)
Insoluble residue (%)	8.15	Dry mass (%)	73.7
Cl	<100	Mo	<10
Al	68 867	Na	2 626
As	43	Ni	56
Ba	425	P_tot	702
Bi	0	Pb	1 754
Ca	111 554	S_tot	3 228
Cd	<10	Sb	44
Co	0	Se	<10
Cr	74	Si	56 957
Cu	486	Sn	15
Fe	20 388	Sr	900
Hg	<10	Te	0,00

K	6 776	Ti	2 392
Li	0	Tl	0
Mg	3 591	V	106
Mn	171	Zn	664

Contaminants of concern on this site were arsenic and lead. Other metals (Cr, Cu, Ni, Sb, Zn) were also quantified by total content analysis performed in 2006. Traces of cadmium and mercury were detected in historical studies but were not quantified in this study.

4.1.3.3 Leaching

a. Acid Neutralising Capacity

The material's acid-neutralizing capacity is approximately 3.5 mol H^+/kg of dry material. The material studied, contained calcium silicate hydrate (CSH) and carbonates, which both contribute to the buffering capacity.

Table 4.6: Results of the ANC tests (mg/l)

pH (t0+48h)	3.79	6.79	7.22	8.18	10.42	11.2	12.56	12.90
Cond (mS/cm)	16.50	15.60	8.11	5.05	1.02	0.64	8.01	16.30
Al	141.40	<0.05	<0.05	0.06	15.97	15.80	56.42	70.94
Ca	4116	5000	2020	1114	159	52	5	10
Fe	10.73	<0.05	0.02	<0.01	0.02	0.03	0.14	0.32
K	175	217	124	112	96	85	165	200
Mg	50	44	11	4	0	0	0	0
Na	59	31	43	36	25	23	1238	3023
Si	175	23	7	2	<1.0	2	22	29
As	<0.01	<0.05	<0.01	0.01	<0.01	<0.01	<0.05	0.08
Cu	2.53	0.40	0.34	0.40	0.52	0.69	1.35	1.75
Pb	7.46	<0.05	<0.01	<0.01	<0.01	<0.01	0.12	0.31
Zn	4.82	1.08	0.15	<0.05	<0.05	<0.05	<0.05	<0.05
Cl	7	7	6	5	<5	<5	6	6
TOC	60	88	88	77	63	70	89	116
IC	11	51	34	14	4	7	138	217
PO_4	617	<50	<50	<50	<50	181	<50	<50
SO_4	113	521	335	279	130	66	57	63

The metals As, Cu, Pb, Zn remain below or close to the detection limits of 0.05 mg/l, except under acid conditions <pH 4. Since the pH of the S/S soil is generally high (>8), the contaminants present at PS are effectively stabilised. The concentrations of the various solutions with pH are shown in Table 4.6.

An examination of the availability of contaminants shows that their solubility is, on the whole pH dependant. When the pH is acidic, Al, Ca, Fe, Si, PO_4, SO_4 are solubilised, whereas in alkaline conditions (over pH 12.5), Al, Na, Cl and total organic carbon (TOC) are solubilised.

b. Modelling

LeachXS results

Geochemical speciation modelling was conducted using the pH-dependence data in order to determine the major solubility-controlling phases. In general, the major ions were matched well using the speciation program LeachXS. Figure 4.10 shows an example of Si leaching and demonstrates reasonable representation of the pH-dependence data by the model.

Figure 4.11 shows the data and model agreement for Pb leaching from Pepper Steel pH-dependence experiments. Figure 4.12 shows the partititioning of Pb between the liquid and the solid phase(s) which explains the model shown in Figure 4.11. Figure 4.13 shows the significance of crystalline $Pb(OH)_2$ in controlling Pb leaching, and also shows the significance of dissolved organic carbon (DOC) in increasing the Pb leaching at pH values from approximately 8 to 11.

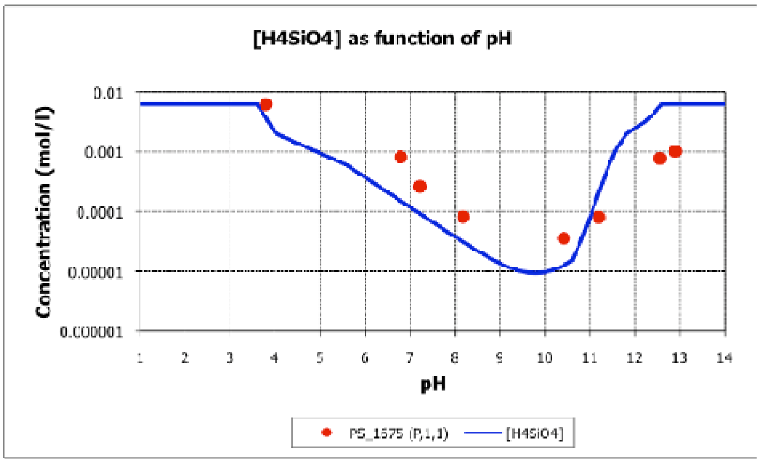

Figure 4.10: pH-dependent leaching of Si in Pepper Steel samples (data points) and model predictions (blue line).

Additional phases are significant in the neutral pH range, including $Ca_2Pb_2O(PO_4)_2$. The most significant result shown here is that the leaching behavior of Pb in the S/S material from Pepper Steel can be reasonably represented as the solubility of one or two solid phases, and secondly, that DOC, even at the relatively low levels here, can increase Pb leaching by an order of magnitude. This is quite significant to note for the practice of successful S/S for species that complex strongly with DOC.

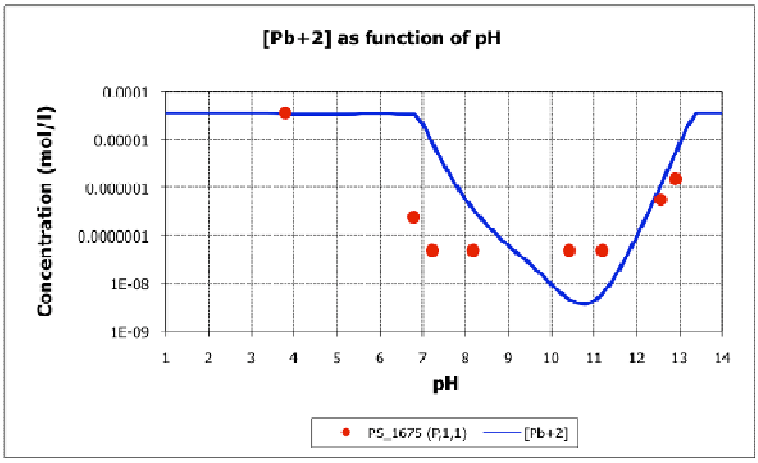

Figure 4.11: pH-dependent leaching of Pb

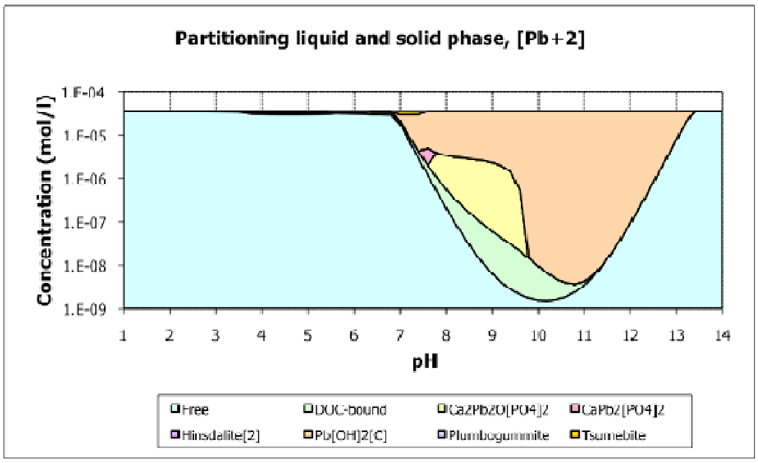

Figure 4.12: Solid-liquid partitioning of Pb

Visual Minteq results

The modelling results obtained using Visual Minteq are reported in Figure 4.13 for the main major elements and for Pb, the main contaminant of concern. In Figure 4.13, the elemental concentrations in the leachate as a function of pH, are compared with the predicted solubility curves of selected solid phases that may have solubility control for the element of concern.

Among the major elements, Al appeared to be controlled by $Al(OH)_3$ at alkaline pH values (≥ 10), and by microcline ($KAlSi_3O_8$, a tectosilicate of the alkali feldspar group), in the intermediate pH range (6–8). In the same pH range microcline was also found to be a good candidate for solubility control of Si, while at higher pH's either microcline or leucite ($KAlSi_2O_6$, another feldspathoid) may control Si leaching from the solidified material. Although quartz was one of the crystalline minerals identified by XRD, no evidence for solubility control by this phase was obtained from modeling the leaching solutions, and may bedue to the presence of phases with different solubility or in non-crystalline forms in the material.

Calcium leaching was found to be controlled either by hydrated calcium carbonate ($CaCO_3{\cdot}H_2O$) or by dolomite ($CaMg(CO_3)_2$) below pH 10 (with dolomite appearing as a good candidate controlling the release of Mg), and by wollastonite ($CaSiO_3$) above this threshold. The presence of carbonates as solubility-controlling minerals is ettringite. As a consequence these phases, although present in the S/S soils, could not be recognized as influencing the release of Ca and SO_4 from the solidified matrix.

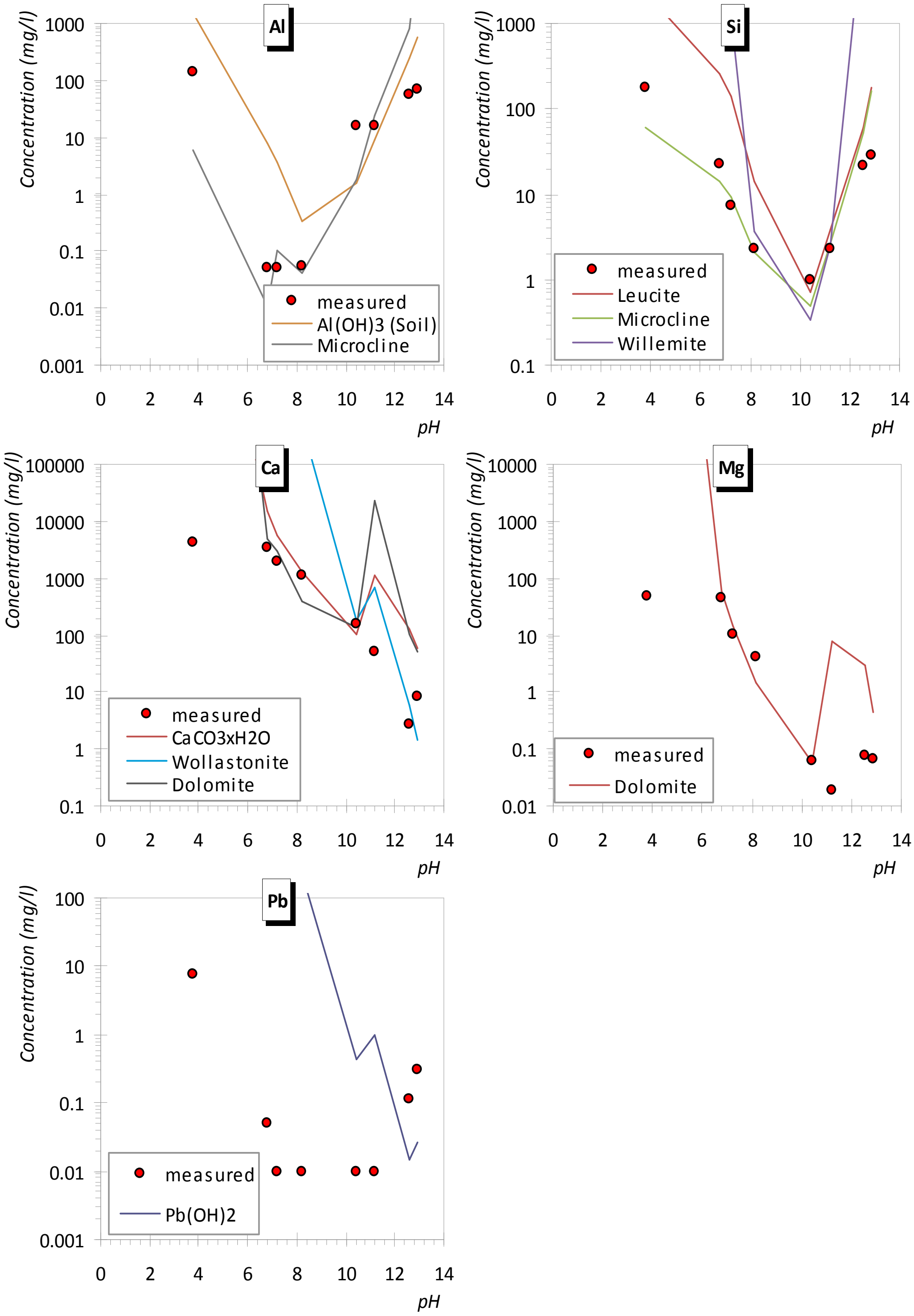

Figure 4.13: pH-dependent leaching of Al, Si, Ca, Mg and Pb in Pepper Steel samples and model predictions

Among the major elements, Al appeared to be controlled by $Al(OH)_3$ at alkaline pH values (≥ 10), and by microcline ($KAlSi_3O_8$, a tectosilicate of the alkali feldspar group) in the intermediate pH range (6–8). In the same pH range microcline was also found to be a good candidate for solubility control of Si, while at higher pHs either microcline or leucite ($KAlSi_2O_6$, a tectosilicate of the alkali feldspathoid group) may control Si leaching from the solidified material. Although quartz was one of the crystalline minerals identified by XRD analyses, no evidence for solubility control by this phase was gained from geochemical modeling of the leaching solutions, likely due to the presence of phases with different solubility or in non-crystalline forms in the material.

Ca leaching was found to be controlled either by hydrated calcium carbonate ($CaCO_3 \cdot H_2O$) or by dolomite ($CaMg(CO_3)_2$) below pH 10 (with dolomite appearing as a good candidate for control of Mg release as well), and by wollastonite ($CaSiO_3$) above this threshold. The presence of carbonates as solubility-controlling minerals is supported by XRD and SEM observations (see above). The leachates were always undersaturated with respect to calcium sulfate phases including gypsum and ettringite, with saturation indexes (SI) in the ranges (-0.2;-5.4) for gypsum and (-1.7;-40.5) for ettringite. As a consequence such phases, although identified through mineralogical observations, could not be recognized as potential candidates dictating the release of Ca and SO_4 from the solidified matrix.

As for Pb leaching, none of the mineral phases included in the extended MINTEQA2 database was found to be a good candidate for solubility control. Only at pH values > 12 did predicted Pb concentrations in the eluate (assuming $Pb(OH)_2$ as the controlling phase) describe the measured levels; for lower pH values, Pb leaching was always much lower than the theoretical solubility of Pb hydroxide. This finding may suggest that Pb was efficiently retained in the solidified matrix as a result of immobilization mechanisms in the hydrated binder matrix.

4.1.4 Summary

The Pepper Steel monolith has been in-place for over 15 years and remains a solid concrete-like monolith with a high compressive strength (~5MPa) and low permeability (~10^{-8} m/s).

The 5, 10, and 15 year reviews have all concluded that the monolith is functioning as designed and the regular sampling of wells sunk at the edges of the monolith have not indicated significant leaching of any of the contaminants.

Performance samples collected for this project do not indicate any significant deterioration of treated soil properties. Some variability between samples is normal due to sampling impacting upon materials properties as well as the spatial variations in soil properties existing from the time of remediation.

The geochemical modelling has provided some understanding of the Pb leaching values.

The data obtained from the Pepper Steel site shows that there is no long-term leaching or structural issues arising, and that the waste form is performing satisfactorily.

4.2 American Creosote, Tennessee

The American Creosote site is a 24-hectare former wood preservation facility located in Jackson, Tennessee, USA, and was one of the many sites across the US operated by the American Creosote Company.

For over forty years, until 1973, the plant discharged untreated process water, causing routine pollution of the Forked Deer River, located at the south boundary of the site. The contamination containing creosote and pentachlorophenol (PCP) was found in soil, surface water, sludge and shallow subsurface water (Figure 4.14). In addition, metals and metalloids including lead and arsenic were identified above the regulatory limits.

The risks associated with contamination were a threat to human health and following the site operator becoming insolvent the USEPA conducted the site assessment and subsequent remedial operation.

Remedial work took place between the autumn of 1999 and the Spring of 2000 (USEPA, 2004). Some 81,000 tons of contaminated soil was excavated and treated by ex situ S/S in a pug mill, using a formulation of 5% Portland cement, 4.5% fly ash and 1.3% powdered activated carbon by weight to the untreated soil. The treated soils were placed back in the excavation, compacted, covered with a geosynthetic clay liner (GCL), and capped with 0.6 m of clean fill and 0.12 m of topsoil (Figs 4.15, 4.16). The last stage of the remedial operation was seeding with grass, to improve drainage and the installation of protective fencing around the site, to restrict unauthorised access.

The action levels (required for treatment) were set for risk-based industrial re-use standards as: arsenic 225 mg/kg; benzo(a)pyrene, 41.5 mg/kg; dibenzo(a,h)anthracene, 55 mg/kg; pentachlorophenol, 3,000 mg/kg and dioxin, 0.00225 mg/kg. These values were calculated to achieve the cancer risk protection level for future workers on site or trespassers (Table 4.7).

Figure 4.14: American Creosote before remediation

Figure 4.15: Treated Soil Placement at American Creosote Site

Figure 4.16: Treatment Plant at American Creosote Site

The effectiveness of the remediation is currently reviewed every five years and potential contaminant leaching is monitored quarterly using perimeter wells. Previous monitoring indicated contamination with wood treatment compounds of the underlying aquifer and it is generally assumed this predated the remedial operation. The concentrations of contaminants showed a variable evolution with time, but the trend was steadily decreasing, and is predicted to continue as the source is now contained. A 5-year review conducted in 2004 concluded that the monolith was functioning effectively (USEPA, 2004).

The site has since been purchased by a local company and is now used for light industrial operations and equipment storage (Figure 4.17).

4.2.1 Historical compliance results

Between the Autumn of 1999, and the Spring of 2000, 81,000 tons of soil contaminated principally with creosote, PCP, and dioxins was excavated, treated in a automated pug mill mixer. The binder consisted of 5% Portland cement, 4.5% fly ash, and 1.3% activated carbon, all weight percents to the untreated soil. Treated soil was replaced in the excavation, compacted and cured into a monolith, and then capped with a GCL cover and soil. During the treatment operations, over 100 performance samples were collected from the freshly treated soil, packed into cylindrical moulds, that were then cured in a humid atmosphere prior to testing to assure compliance with the performance standards.

All samples tested met the performance requirements cited in the following table. As an overall average, the unconfined compressive strength exceeded 1.4 MPa, the permeability was in the 1x10^{-9} m/s, and contaminants leached at less than half the allowed amounts.

Table 4.7: American Creosote Site Performance Requirements

	Average	Allowance	Method
UCS (MPa)	> 0.7	> 0.6	ASTM D 1633
Permeability (m/s)	< 1x10^{-8}	< 1x10^{-7}	ASTM D 5084
Leaching			SW 846(MTD 1312) SPLP
Arsenic (µg/L)	< 50	< 75	
PAHs (µg/L)	< 10	< 15	
Dibenzo(a,h)anthracene	< 4.4	< 6.6	
PCP (µg/L)	< 200	< 300	
Dioxins (pg/L)	< 30	-	

Figure 4.17: Reuse of the American Creosote Site

4.2.2 Sampling / new physical and leaching results

The American Creosote (AC) site was sampled in mid-December 2003. Site sampling was undertaken by the EPA in association with staff from the University of New Hampshire (UNH). Cores were initially extracted using a 3-inch (75mm) diamond core barrel. Material was recovered using dry and wet drilling methods, but minimal intact material was retrieved even when using water to cool the coring process. Only one intact sample was available for each of the strength and permeability tests. Early in the sampling, the core barrel seized up due to excessive heat and could not be retrieved. Thereafter, samples were obtained using a solid stem soil auger, without water, but this material was retrieved in a broken, ground condition, due to the action of the auger.

The sampling of the AC site was conducted using a trailer mounted portable rotary coring apparatus capable driving core barrels or augers (Figs 4.18, 4.19). As mentioned, the results yielded little intact sample material due to the loss of the diamond core barrel early and completion of the by alternative means. The single intact sample obtained for UCS testing was required to have a strength above 0.69 MPa (the 1999 UCS design goal) and the result recorded of 2.2 MPa comfortably exceeded this value.

Only one permeability analysis was obtained for the AC site. The value obtained of, $6.2x10^{-7}$ m/s, gave a higher permeability than the performance criteria, set at an average permeability of 10^{-8} m/s, and also failed to meet the absolute maximum permeability set at 10^{-7} m/s. The microscopic analysis discussed below was used to evaluate whether sampling of the monolith may have impacted sample integrity and caused the unacceptably high permeability values.

Of the five S/S sites in this study, the AC site contained the most contaminants: arsenic, PCP, PAH, and dioxin. Performance criteria for all contaminants were set for leachability results of the SPLP test; these criteria are shown along with the test results in the Tables 4.8 and 4.9 below. The PAH and dioxin performance criteria was based on toxicity equivalencies (TEQ); the BaP (benzo-a-pyrene) equivalency for PAH and the total TEQ values for dioxin in the SPLP extracts.

Figure 4.18: Sampling at the American Creosote Site

Figure 4.19: Pressurized air system for collecting dry samples and mitigating dust generation

Table 4.8: SPLP leaching results 2003 Sampling of the AC

Sample	Arsenic	
	Total (mg/kg)	Concentration x 10^{-3} (mg/l)
1	5.2	BDL
2	5.2	BDL
3	6.0	BDL
4	5.4	20
5	6.2	BDL
average	5.6	20
quant limit	0.2	20
performance criteria	-	<50

The SPLP results for all four contaminants were below the established performance criteria. The total concentrations for PCP were all below the detection limit even when leaching tests did produce quantifiable concentrations. Overall, the results indicate satisfactory retention of contaminants in the cement matrix, based on the original performance criteria of SPLP testing.

4.2.3 Transversal testing

4.2.3.1 Microstructure and mineralogy

The mineralogy of cement-treated soils taken from the American Creosote site is dominated by quartz, and reflects the presence of this mineral in the treated soil.

Lower intensity reflections corresponding to kaolinite, feldspar, calcite, dolomite and ettringite were also present, as can be seen in Figure 4.20.

Table 4.9: SPLP leaching results from the 2003 sampling of American Creosote

Sample	PAH		Dioxin		PCP	
	Total (mg/kg)	Conc x 10^{-3} (mg/l)	Total x 10^{-6} (mg/kg)	Conc x 10^{-9} (mg/l)	Total (mg/kg)	Conc x 10^{-3} (mg/l)
1	653.2	319.7	6.5	6.4	BDL	230
2	631	139.3	5.1	6.3	BDL	90
3	180.7	BDL	6.4	6	BDL	BDL
4	119.8	BDL	-	6.4	BDL	BDL
5	89	BDL	n.a	n.a	BDL	BDL
average	334.7*	229.5*	6.0[#]	6.3[#]	BDL	160
quant limit	0.5	0.8			10	20
performance criteria	-	<10**		<30	-	<200

average total PAH; ** average BaP equivalent; [#] average TEQ equivalent; n.a not analysed; BDL below detection limit

As indicated by the diffractogram in Figure 4.20, minerals such as portlandite were absent, however ettringite was present. Fragments of dolomite and limestone were observed during the microstructural examination and this is reflected in the Figure 4.21.

The generalised microstructure of samples retrieved from American Creosote site, were heterogeneous and relatively coarse grained. The waste form contained zones of apparent higher porosity, containing large voids up to 600 μm in diameter. Although voids larger than 1 mm do not normally influence the transport properties of cement-based materials they may have a negative impact on the soundness of the microstructure.

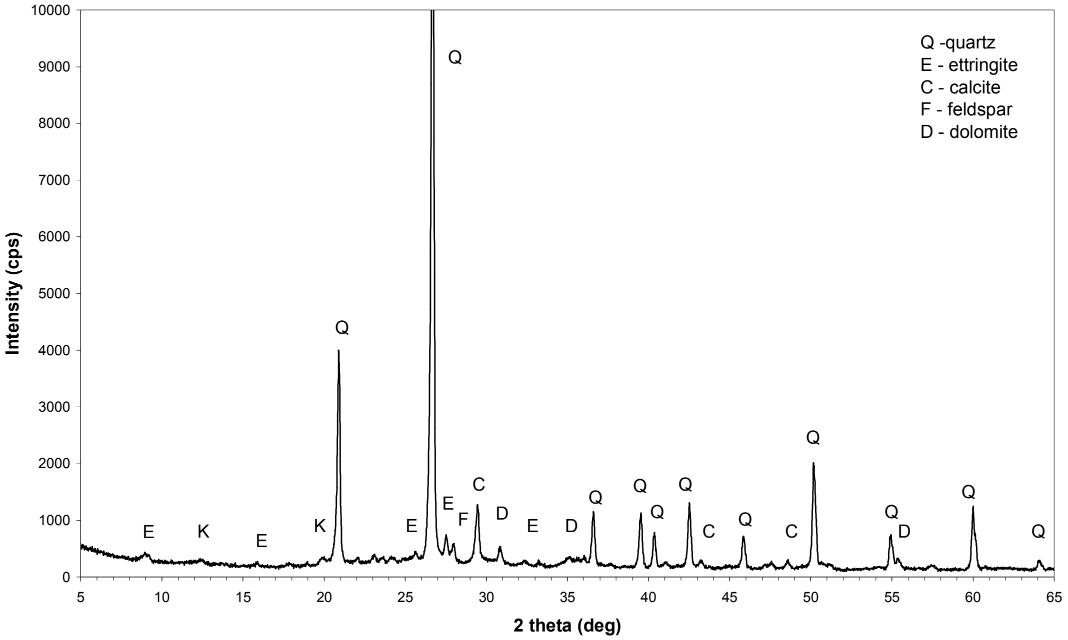

Figure 4.20: X-ray diffractogram from cement-stabilised soil retrieved from the American Creosote site

Open microcracks, which may have been caused during sampling, were present and relatively numerous, although in some instances, ettringite, identified by the low intensity reflections in Figure 4.21, was found to be formed in some of the microcracks, in isolated, or small needle clumps.

A large proportion of the quartz grains examined appeared to be strained in nature. There was no indication of reaction with the matrix, or resulting from the drilling operation used in the collection of samples. One possibility was that the undue stresses were generated during sample preparation by grinding, but the wider disruptions to the sample matrices that would have resulted were absent.

Relics of fly ash and fragments of coal, probably originating in the pozzolanic binder or in the activated carbon were numerous and scattered throughout the matrix of the cement-solidified samples.

Although it is unlikely that portlandite was present in samples due to the pozzolanic binder system employed, this cannot be completely ruled out. An examination by thermal analyses (TG) showed an event between 400 - 480ºC, which may have corresponded to the dehydroxylation of portlandite (Dweck et al., 2000; Lawrence et al., 2006), but more likely the loss of water from the structure of kaolinite (Wang et al., 2004) (Figure 4.22), which was identified as being present by both XRD and by microscopy, in the samples examined.

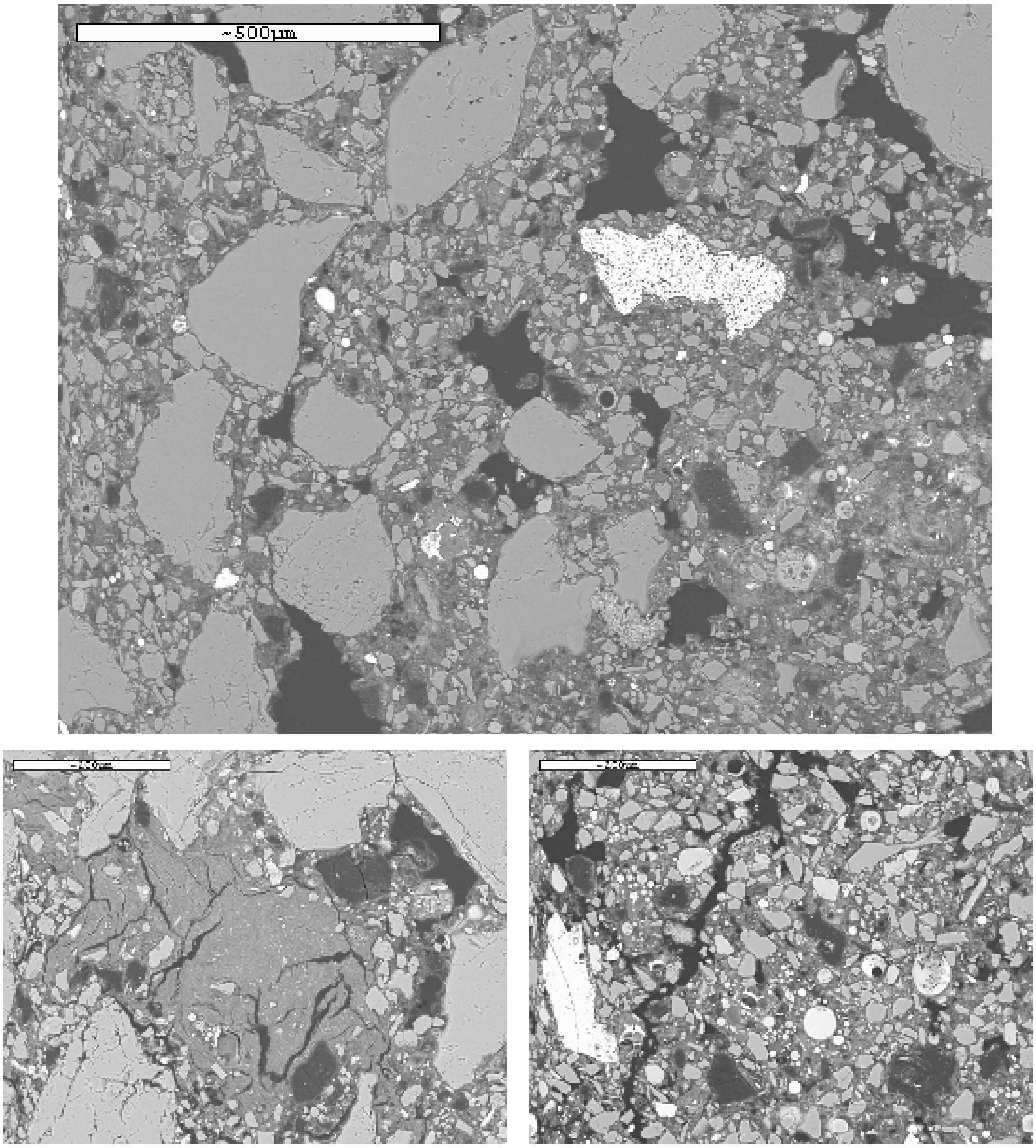

Figure 4.21: Backscattered electron image of a) granular nature of the soils recovered from American Creosote site; b) shrinkage cracks in clay particle; c) microcrack caused by sample preparation

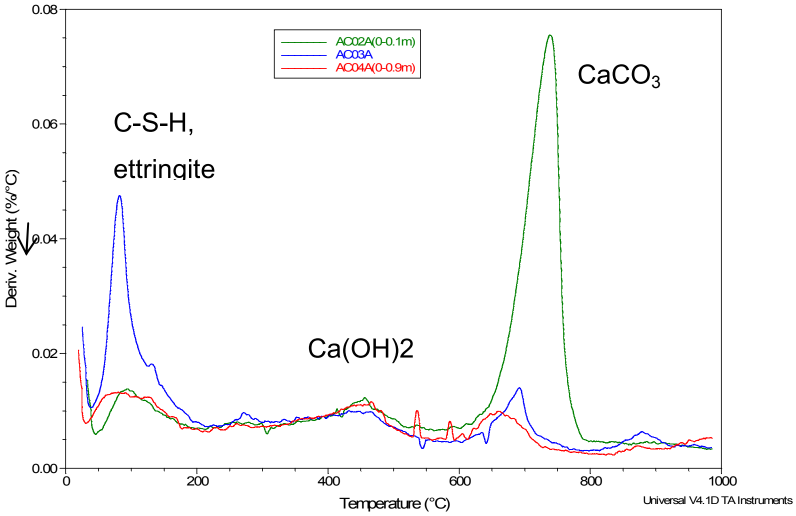

Figure 4.22: Thermogram of the S/S soils from American Creosote, USA

4.2.3.2 Chemical characterisation

The results of the elemental analysis carried out on retrieved material are shown in Table 4.10.

Table 4.10: Total content analysis of treated soil from American Creosote (mg/kg)

	Concentration (mg/kg)		**Concentration (mg/kg)**
Insoluble residue (%)	47	Dry mass (%)	nd
Cl	<100	Mn	379
Al	37244	Mo	<10
As	12	Na	3 300
Ba	262	Ni	39
Bi	0	P_tot	313
Ca	48467	Pb	23
Cd	<10	S_tot	2 090
Co	0	Sb	<10
Cr	33	Se	<10
Cu	125	Si	49 744
Fe	16 007	Sn	<10
Hg	<10	Sr	227
K	8 497	Ti	1 598
Li	0	V	63
Mg	3 452	Zn	162

The results show that some heavy metals are detected: Cr, Cu, Ni and Zn. However, the total quantities of these elements are low. They were not contaminants of concern for the remediation. Furthermore, for information, such a soil would be considered in France as an inert waste in relation to metal contents, according to professional guidelines. However, it should be noted that these results must be judged with caution, because the insoluble fraction after the acid digestion represented 47 %.

4.2.3.3 Leaching

a. Acid Neutralisation Capacity

The material’s acid-neutralizing capacity is about 1.2 mol H^+/kg of dry material. The exact value was not determined during the tests.

The concentrations of the various elements depending on the pH, obtained during the ANC test, are shown in Table 4.11.

As far as the availability of the pollutants is concerned, the results show that overall the leaching of contaminants of concern, were low. The quantities of Ca, K, Mg and SO4 released increase as the pH decreases, contrary to those of Al, Na and IC. Metals are not detected in the equilibrium solution because they re-precipitate immediately. The Fe, Cl, PO_4 and PAH are practically absent in the solutions at different pH values obtained during the ANC tests.

Table 4.11: Results of the ANC tests

pH (t0+48h)	**5.88**	**7.34**	**8.49**	**9.17**	**9.92**	**10.27**	**10.56**	**11.01**	**11.29**	**12.55**
Cond.(mS/cm)	10.10	7.37	6.28	4.60	2.95	2.21	1.45	0.58	0.48	7.96
Al [mg/l]	<0.05	<0.01	<0.01	<0.01	<0.01	0.15	0.29	1.10	2.40	22.76
Ca [mg/l]	2254	1717	1488	1090	675	461	244	70	27	5
Fe [mg/l]	<0.05	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.05
K [mg/l]	95	77	73	99	68	65	61	51	46	94
Mg [mg/l]	106.9	58.19	40.74	13.99	1.55	0.42	0.14	0.03	0.02	<0.05
Na [mg/l]	27	27	27	27	26	26	26	23	23	1062
Si [mg/l]	24.30	11.62	6.78	4.74	4.71	4.62	5.00	6.10	9.31	49.96
Cl [mg/l]	12	<5	<5	41	6	<5	<5	<5	<5	14
TOC [mg/l]	15	21	22	20	18	15	12	9	10	10
IC	2	13	10	9	6	6	3	4	7	93
PAH [µg/l]	nd	<7	<9	<8	<9	<9	<8	<9	<7	<7
SO4 [mg/l]	366	467	349	314	224	189	131	<5	<5	71
PO4 [mg/l]	<10	<50	<50	<50	<50	<50	<50	193.5	156.4	<10

Nd: not determined

b. Modelling

Visual Minteq results

The resuts of leachate modeling results are reported in Figure 4.24 for the main elements of concern. In Figure 4.24, the element concentrations measured in the leachate as a function of pH are compared with the predicted solubility curves of the potential solubility controlling phases.

The modelling calculations indicated a variety of potential candidate minerals. In the alkaline pH range (≥ 10), the solubility-controlling solids for Al included gibbsite ($Al(OH)_3$), CO_3-hydrotalcite ($Mg_4Al_2(OH)_{12}(CO_3)\cdot 2H_2O$, an anionic clay mineral commonly found as a secondary mineral in serpentinite rocks), and a number of aluminosilicates, namely two zeolite phases (chabazite, $CaAl_2Si_4O_{12}\cdot 6H_2O$, and Ca zeolite P, $CaAl_2Si_{2.6}O_{12.4}H_{6.4}$), kaolinite ($Al_2Si_2O_5(OH)_4$, a clay mineral of the phyllosilicate group also identified by XRD analyses), as well as microcline and leucite (which were also identified in Pepper Steel soils).

At alkaline pH's, all the phases had similar solubilities and no particular mineral was selected. However, as the as the theoretical solubility curves for Ca zeolite P, chabazite and microcline showed a good match with the measured Si, these may be the most likely candidate's. In addition, Ca zeolite P also appeared to describe the observed Ca leaching quite closely; however, it should be noted that hydrated calcium carbonate ($CaCO_3 \cdot H_2O$) was also found to be a good candidate to control Ca leaching. This finding may be supported by microstructural examination, which revealed the presence of a number of carbonate minerals. The leaching of Mg, was shown to be controlled by CO_3-hydrotalcite, although forsterite (Mg_2SiO_4, a nesosilicate of the olivine group) displayed a good fit with the experimental leaching data.

No evidence for solubility control by other observed phases including quartz and ettringite, was gained from geochemical modelling of the leachates. In particular, although the eluates were found to be relatively close to equilibrium with quartz, with SI values between -1.7 and 0.95, the shape of the predicted solubility curve for this phase did not fit that of the experimental concentrations. On the other hand, the leaching solutions were observed to be strongly undersaturated with respect to ettringite (SI values between -3.4 and -25.6).

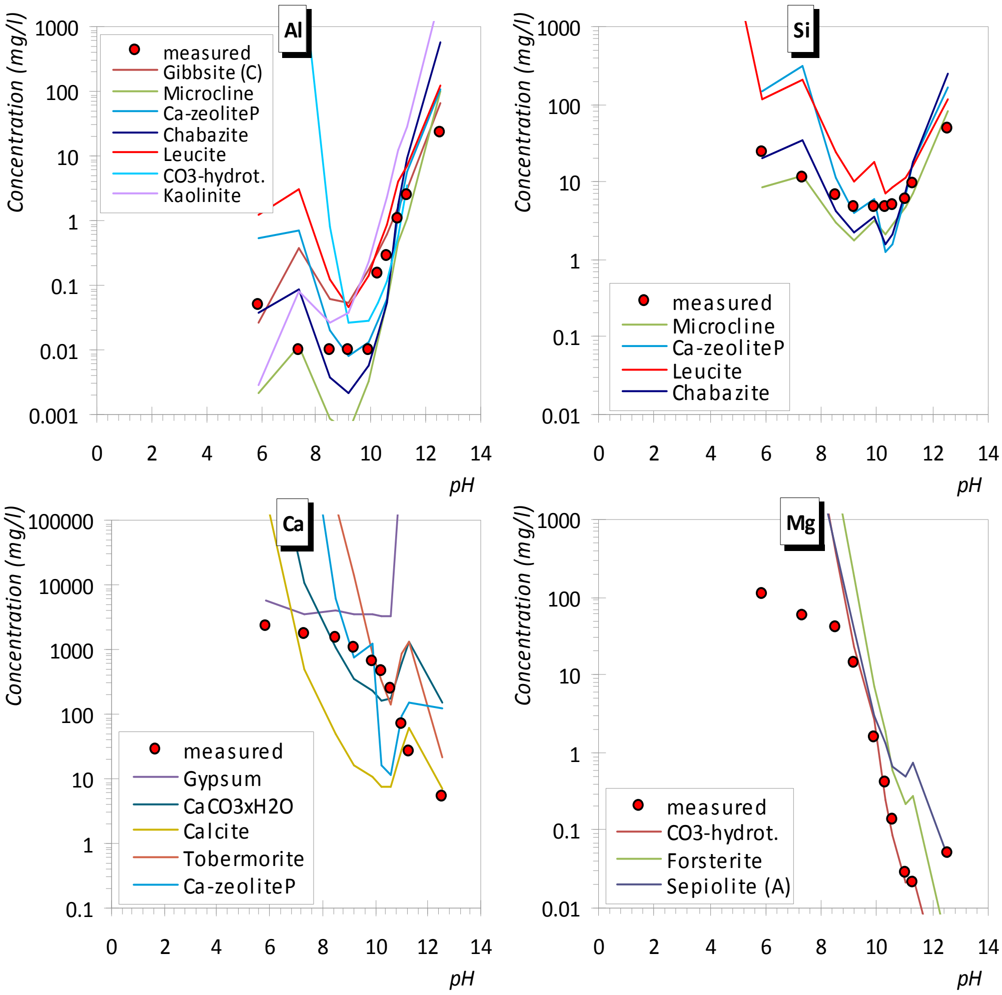

Figure 4.24: pH-dependent leaching of Al, Si, Ca and Mg in American Creosote samples and model predictions.

4.2.4 Summary

Samples collected from the American Creosote site about 5 years after treatment indicate that the unconfined compressive strength was over 2.1 MPa, well above the treatment target of 0.69 MPa. All leaching results using the SPLP, were well within the original targets limits. However, the permeability test indicated values higher, more permeable, than the original targets even though all samples at the time of treatment met the target of $1x10^{-8}$ m/s. It is believed that the increased permeability is the result of sample disturbance during the time of sampling. Sampling was conducted using a rotary coring device and diamond core barrel. However, at the time of coring, considerable heat was observed and along with some fracturing of samples. The results of leaching of samples showed that there were some mineral phases that were responsible for the solubility control of species, however, the release of contaminants was well within limits and as such, no long-term issues were identified for this site.

4.3 Astra Pyrotechnics, Kent

The Astra Pyrotechnics site is located in Dartford, Kent, UK and covers an area of approximately 8.5 hectares. The site was used for the manufacturer of low-grade military explosives and fireworks over a period of 50 years, and this was the main cause of contamination. Currently, the site is designated as a Site of Special Scientific Interest (SSSI), despite high levels of contamination, such as by copper (96,000 mg/kg) and zinc (81,000 mg/kg). Lead and nickel were also found in concentrations of up to 700 mg/kg (Blue Circle, 2000).

One of the hotspots located at the east of the site, measuring 10 m x 20 m, was chosen for a pilot scale S/S trial in the autumn of the year 2000. The soils were excavated to a depth of 0.6 m, stockpiled outside the site and shredded prior to the treatment with cement. Four fully HDPE lined cells were constructed with an inspection chamber for collection of leachates.

The soil was quartered and separately mixed with the binders in a cement mixer. Portland cement (PC) and finely ground Sulfate Resisting Portland Cement (SRPC) at a ratio of 20 wt% to soil were used. Cell 1 was left untreated, Cell 2 was mixed with 20 wt% PC, Cell 3 was mixed with 20 wt% SRPC and cell 4 was mixed with 20 wt% SRPC in carbon dioxide atmosphere. The treated soils were backfilled without compaction and left uncovered, to promote weathering. As a result no target values for strength or permeability were established, at the time of the treatment.

4.3.1 Historical compliance results

The two leaching tests were carried out the DIN 38414-S4 (DIN NORMEN, 1983) and TCLP 1311 (USEPA, 2003). Leachates were required to comply with the UK Drinking Water Inspectorate (DWI) limits, which are 5 mg/l for copper, 5 mg/l zinc and 0.05 mg/l for lead (DWI, 2000). Although DIN is appropriate for assessing immediate potential threat, the long-term release or the bio-availability of contaminants is not rigorously evaluated. As a consequence, TCLP was employed.

The results obtained are given in Table 4.12. The regulatory limits for metal leaching in each test are shown in Table 4.13.

Table 4.12: Metal leaching from cement-treated soils at the time of soil treatment (from Blue Circle, 2000)

Metals of concern	DIN 38414-S4			TCLP 1311		
	untreated	OPC	SRPC	untreated	OPC	SRPC
Zinc	0.18	0.02	0.03	14.48	n.d.	n.d.
Lead	0.02	n.d.	n.d.	0.03	n.d.	n.d.
Copper	0.05	0.92	0.94	0.24	0.59	0.57

Values in mg/l; n.d. not detected

Table 4.13: Regulatory limits for metal leaching

	DIN 38414-S4			TCLP 1311		
	Zinc	Lead	Copper	Zinc	Lead	Copper
Regulatory limit	5[1]	0.05[1]	5[1]	5[3]	5[2]	1[3]

Values in mg/l; [1] = EC (1991); [2] = according to RCRA Primary Drinking Water Quality ; [3] = according to RCRA National Secondary Drinking Water Quality (40CFR143.1)

The results showed that the metals were released from the remediated soil at levels below the regulatory limits for both the tests employed. However, the leaching of copper was increased by the treatment with cement, compared with the untreated soil.

4.3.2 Sampling / new physical and leaching results

The sampling of cement-treated soils was carried out in November 2004. A number of 100 mm cores were obtained by dry coring technique. Due to the shallowness of the treated material and to minimise the risk of piercing the cell liner, a hand driven core cutter was used. Granular material was also collected from a 0.5 m x 1 m x 0.6 m deep trial pit excavated by hand (Figs 4.25, 4.26).

Figure 4.25: Trial pit at the Astra Pyrotechnics site, PC treated cell

Figure 4.26: Hand extraction of a core sample at Astra Pyrotechnics site

Granular soil material obtained from the top and the bottom of each cell, were acid digested according to USEPA 3050B (USEPA, 1980a). The results obtained are indicated in Table 4.14.

Table 4.14: Metal content of the Astra Pyrotechnics soil

Metals of concern	Depth	Total metal concentration (mg/kg)		
		Untreated	PC	SRPC
Zinc	Top	1457	444	725
	Bottom	1383	388	600
Lead	Top	428	133	126
	Bottom	279	447	39
Copper	Top	644	59	103
	Bottom	295	47	107

Table 4.15: Metal leaching for selected cement-treated soils at the Astra Pyrotechnics site

Samples	Depth	DIN 38414-S4			TCLP 1311		
		Untreated	PC	SRPC	Untreated	PC	SRPC
Final pH	T	7	9.5	11.5	5	9.3	10.9
	B	7	11.6	12.4	5	9.9	10.9
Zinc	T	0.71-1.40	0-0.04	0.01	0.71-0.13	0.03	n.d
	B	1.10-1.30	n.d	0.01-0.02	0.87-0.88	0.03	n.d
Lead	T	0.02-0.06	n.d	n.d	0.04-0.05	n.d	n.d
	B	n.d	n.d	n.d	0.04-0.05	n.d	n.d
Copper	T	0.32-0.43	0.31-0.32	0.67-0.70	0.51-0.60	n.d	n.d
	B	0.40-0.41	0.96-1.02	0.54-0.57	n.d	0.85-0.99	n.d

Values in mg/l; n.d – not detected

Soil samples obtained from upper and lower profile of each cell were subjected to the same leaching tests as those performed after the remediation. The results obtained from the two tests were similar. The treated cells leached zinc and lead in lower quantities than the untreated soil. However, copper leaching was increased by the addition of PC, which was in accordance with the results of the leaching tests carried out at the time of the treatment. Nevertheless, the leaching results obtained four years after treatment by S/S met the regulatory limits for all metals of concern.

4.3.3 Transversal testing

4.3.3.1 Microstructure and mineralogy

The treated soils were examined and compared with untreated soil. The dominant minerals were clays, feldspar, quartz and muscovite. Portlandite, ettringite and calcite were also present, originating from the cements used. The diffractograms obtained from the each soil are presented in Figure 4.27.

The microstructure of the untreated soil was dominated by clay with quartz grains up to 500 µm in size (Figure 4.28a). The samples prepared for optical and electron microscopy displayed cracking and shrinkage-related artefacts as a result of desiccation during sample preparation. Minor mineral phases including monazite, zircon, feldspar and hematite were observed, as well as fragments of plant root and brick.

The contaminated soil contained finely distributed metal particles of approximately 1 µm, but also metals intimately intermixed with the clayey matrix, including copper, zinc, titanium and iron from the manufacturing or aerial testing of fireworks, and identifiable by x-ray area microanalysis.

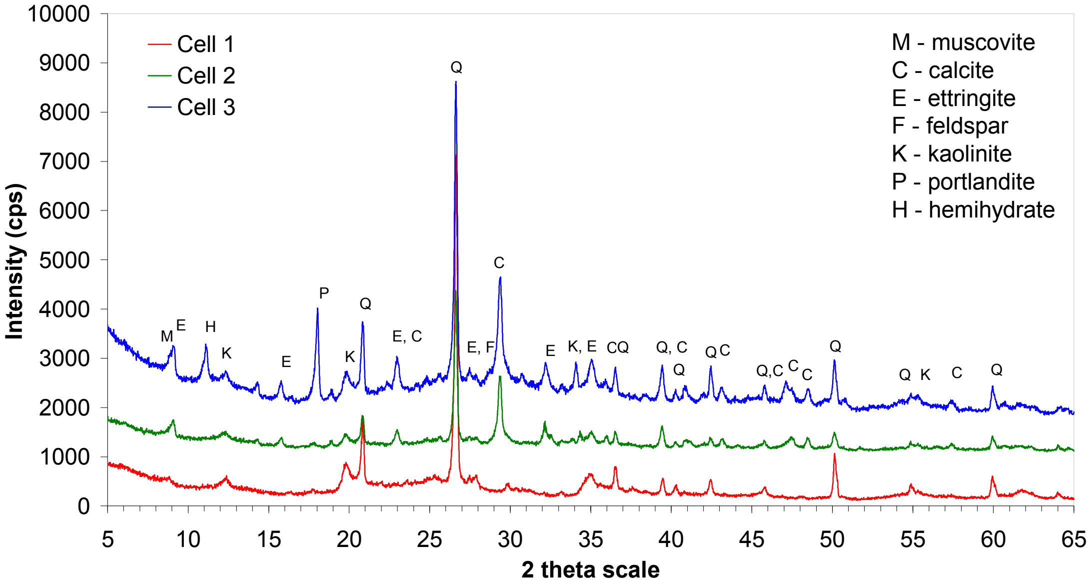

Figure 4.27: X-ray diffractogram of soils recovered from Astra Pyrotechnics

The microstructure of the PC-treated soil (cell 2) was very porous and was composed of distinct clayey agglomerations intermixed with unhydrated or poorly hydrated cement grains, some greater than 100 µm in size (Figure 4.28b).

The microstructure of the SRPC-treated soil (cell 3) was less porous with a higher degree of carbonation (Figure 4.28c). Both cement-treated samples were microcracked, most likely resulting from the lack of soil compaction and the sampling technique employed.

In the SRPC-treated soil, ettringite occurred as needles of between 200-250 µm in length in larger voids. A finer grained, microcrystalline form of ettringite was also identified at high magnifications. Large parts of the soil matrix in the SRPC-treated sample, were carbonated, and had a lower apparent observable porosity. Portlandite was identified under polarised transmitted light.

The metals of concern being copper, lead and zinc were present in the soil at concentrations well above the regulatory thresholds. The speciation of these metals in the cement-treated product could not be elucidated by EDAX.

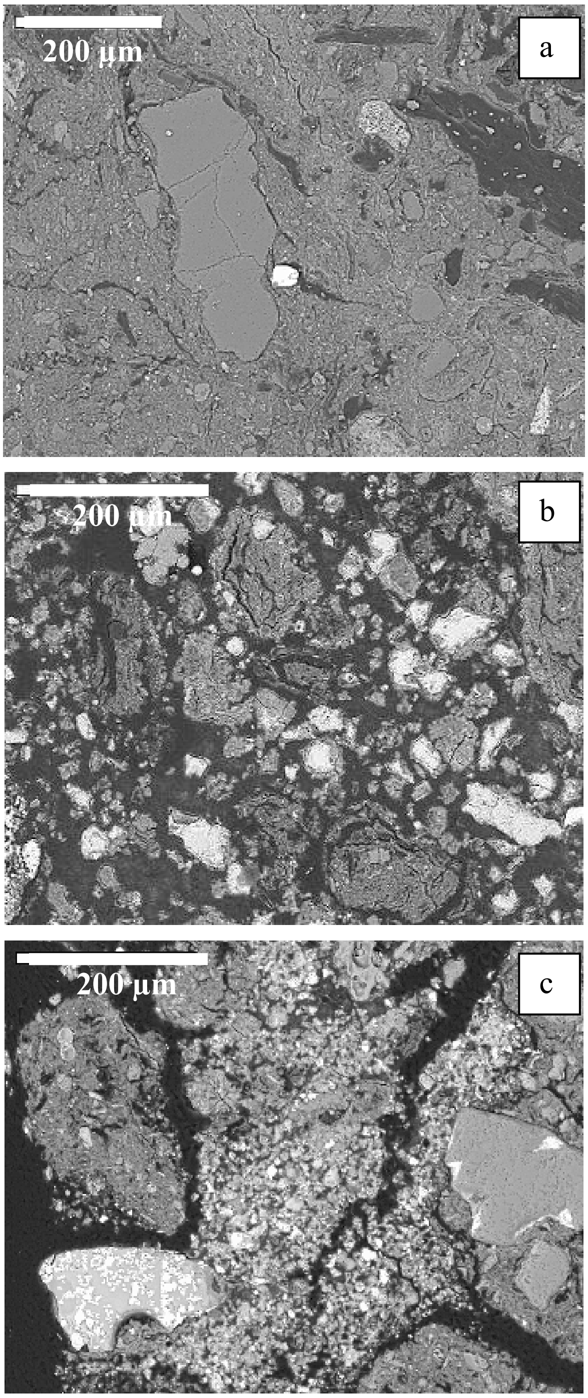

Figure 4.28: Backscattered electron micrograph of a) untreated soil; b) PC-treated soil; c) SRPC-treated Astra soil

4.3.3.2 Chemical characterisation

The results of the elemental analysis carried out on the ASTRA Pyrotechnics Cell 1 and Cell 2 samples are shown in Table 4.16.

Table 4.16: Total content analyses of the soils from the Astra Pyrotechnics site (mg/kg)

	Cell 1	Cell 2	Cell 3		Cell 1	Cell 2	Cell 3
Insoluble residue (%)	3.8	20.6	15.5	Dry mass (%)	84.6	78.7	78.8
Cl	1 400	<100	< 50	Mn	70	329	nq
Al	103 000	59 522	50,010	Mo	<19	<5	nq
As	30	18	nq	Na	3 050	2 516	1,797
Ba	600	351	nq	Ni	60	56	54
Bi	nd	nd	nq	P_tot	700	768	576
Ca	8 965	85 117	153,095	Pb	140	154	116
Cd	<19	<5	nq	S_tot	1 380	2 783	4,584
Co	<5	<5	nq	Sb	<19	<5	nq
Cr	100	85	65	Se	<19	<5	nq
Cu	420	222	260	Si	114 290	115 183	34,138
Fe	42 950	48 830	40,200	Sn	<19	13	nq
Hg	<19	<5	nq	Ti	<80	0	nq
K	20 210	14 893	10,735	V	190	0	nq
Li	nd	nd	nq	Zn	1 590	747	1,016
Mg	7 730	9 459	7,746	Loss on ignition (%)	nq	nq	nq

nq not quantified; nd not detected

4.3.3.3 Leaching

a. Equilibrium test

The equilibrium tests were carried out using several L/S ratios (1.9; 8.6; 16.9 and 33.5) on the sample taken from the PC treated soil. First the sample was crushed to <1 mm and placed in contact with demineralised water for a period of 7 days. The results are shown in Figure 4.29 and 4.30.

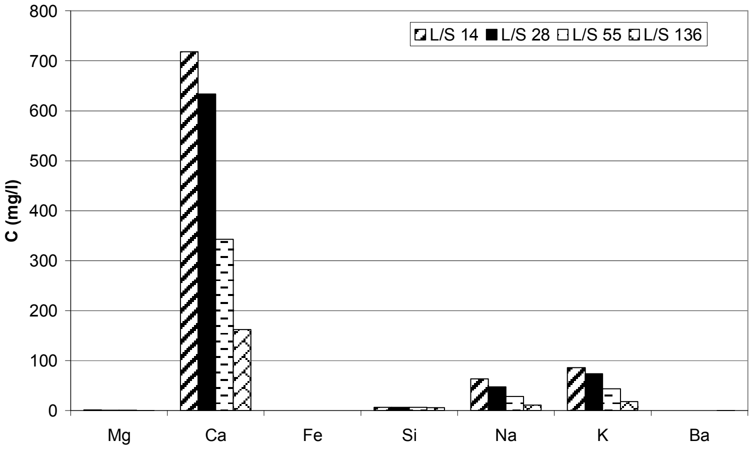

Figure 4.29: Equilibrium test – cations

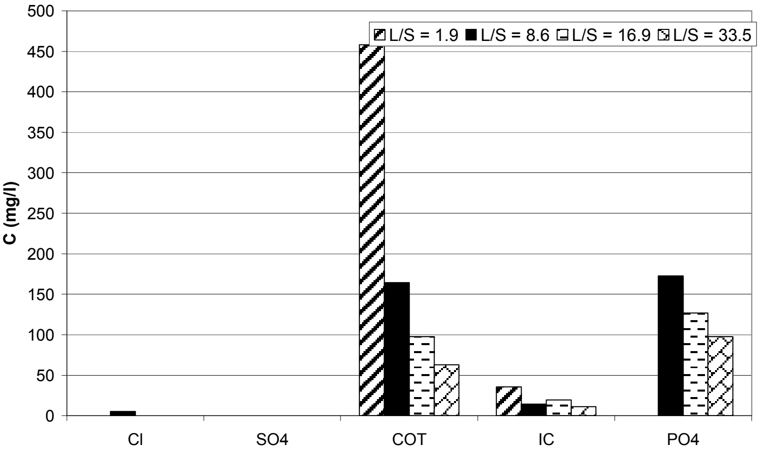

Figure 4.30: Equilibrium test – anions

The pH values of the supernatant solutions varied between 9.5 for the L/S ratio 1.9 and 11.0 at L/S ratio 33.5.

The main metals released were calcium, sodium and potassium. Among the anions leached were phosphate and carbonate. Chloride and sulfate were not present, but the quantities of organic carbon measured were not insignificant. The other elements, aluminium and silica, are released in low quantities. The heavy metals (Cr, Cu, Ni, Pb and Zn) remained practically undetected in the equilibrium solutions. These results indicate that the metallic pollutants have indeed been stabilised and remain immobile.

b. Acid Neutralisation Capacity

The acid neutralisation capacity of the three treated Astra soils are given in Table 4.17.

Table 4.17: Acid neutralisation capacity of the Astra soil

Sample	**$ANC_{4.0}$ (mol H^+/kg)**
Cell 1	0.1
Cell 2	2.6
Cell 3	6.2

The results clearly show the effect of the cement stabilisation on buffering capacity, which was very low for the untreated soil (Cell 1) compared to Cells 2 and 3.

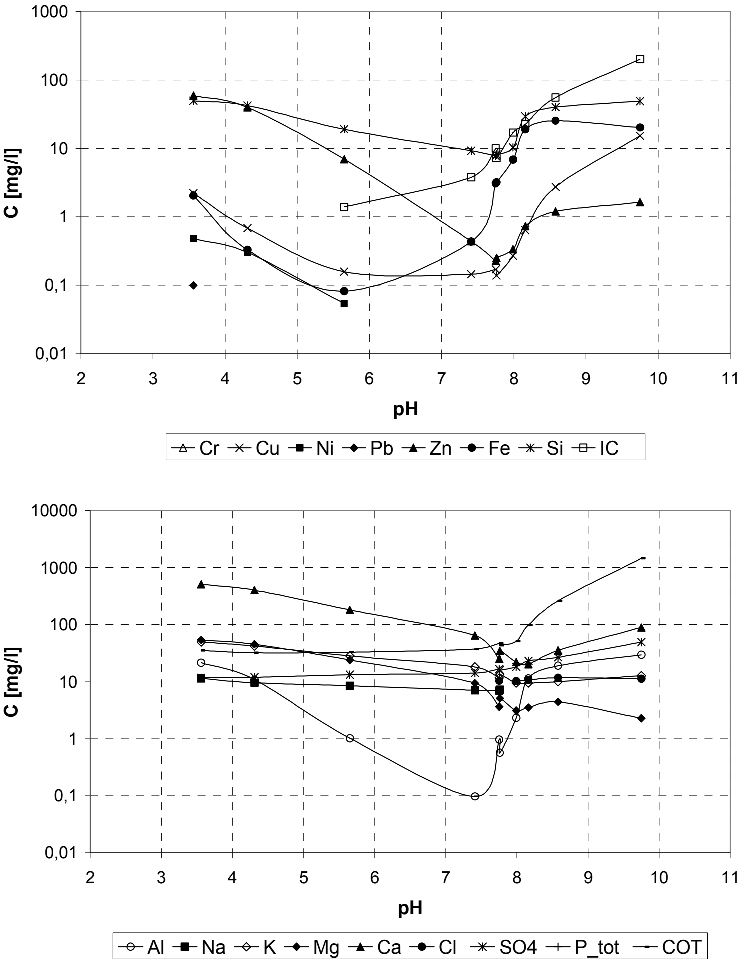

Figure 4.31: ANC test results - Cell 1

The concentrations of the various elements were pH dependent as shown in results of the ANC test (Figure 4.31). The ‘natural’ pH of Cell 3 was 12.5, and 11.5 for Cell 2.

The results obtained from the untreated soil were very different from those obtained for Cells 2 and 3, where the release of most species increased as pH is decreased, In Cell 1 a minimum was obtained between pH 7 and 8.

Copper, zinc and lead were not released from treated soils, except under acidic conditions. In the non-treated soil, the behaviour of lead was similar, but zinc and copper were amphoteric corresponding to copper and zinc hydroxy-oxide and/or carbonates.

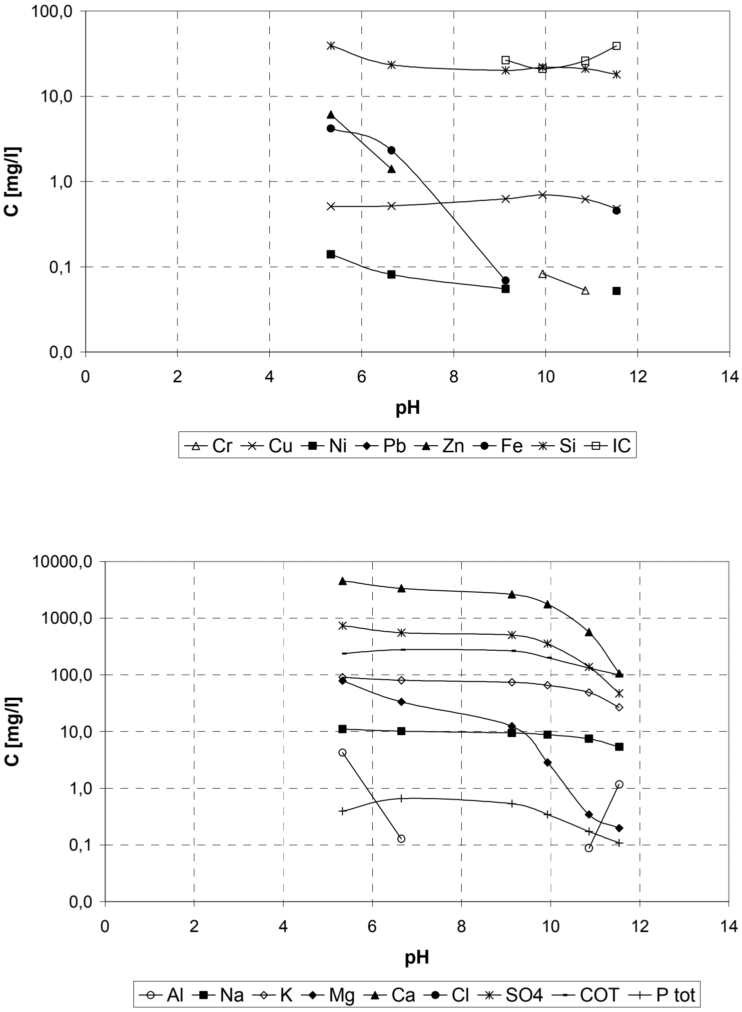

Figure 4.32: ANC test results – Cell 2

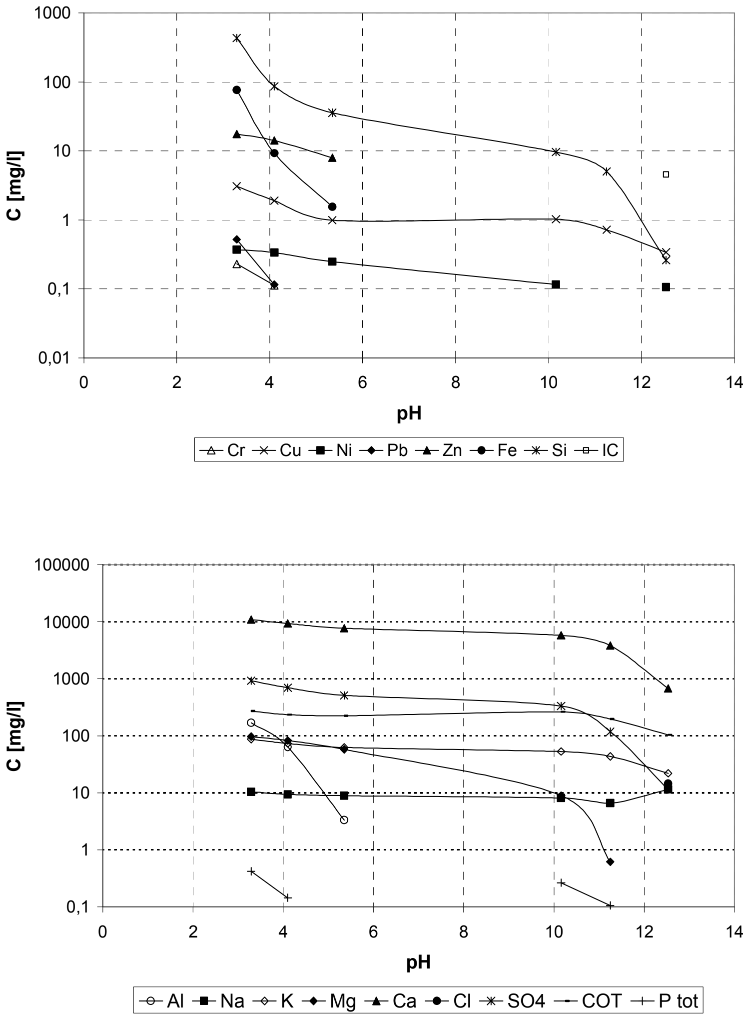

Figure 4.33: ANC test - Cell 3

c. Modelling

LeachXS results

Geochemical speciation modelling was conducted for the Astra Cell 2 , and results for a major ion (Al) and a trace element (Zn) are shown here (Figs 4.34-4.37). It is clear for Al that three different solid phases are important for its leaching in the pH range 9 through 12 and it can be expected that these phases will be important in the long-term leaching process as the buffering capacity of the S/S material is depleted. The pH-dependent behaviour of Zn was well described by the geochemical modelling and Figure 37 shows the significance of Willemite on the leaching profile observed. The significance of DOC in increasing the observed solubility of Zn was apparent (up to approximately two orders of magnitude) in the pH range of 8 to 11.

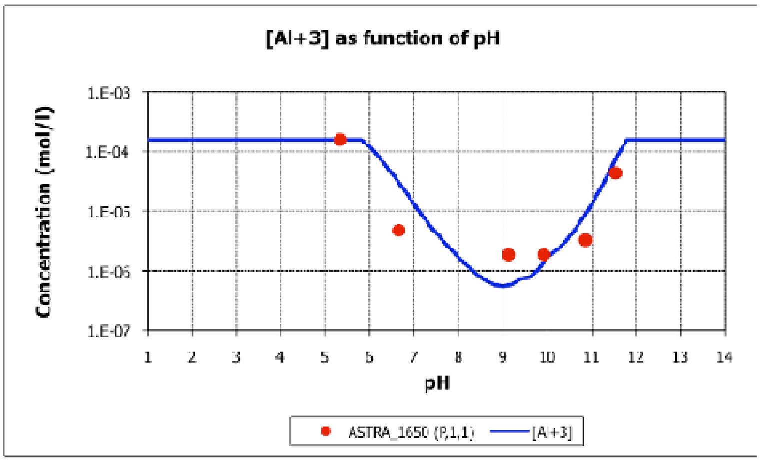

Figure 4.34: pH-dependent leaching of Aluminum in Astra site sample

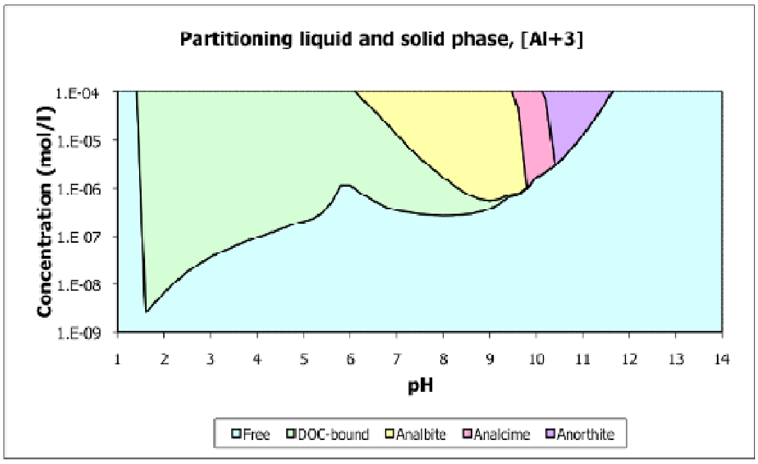

Figure 4.35: Solid-liquid partitioning of Aluminum

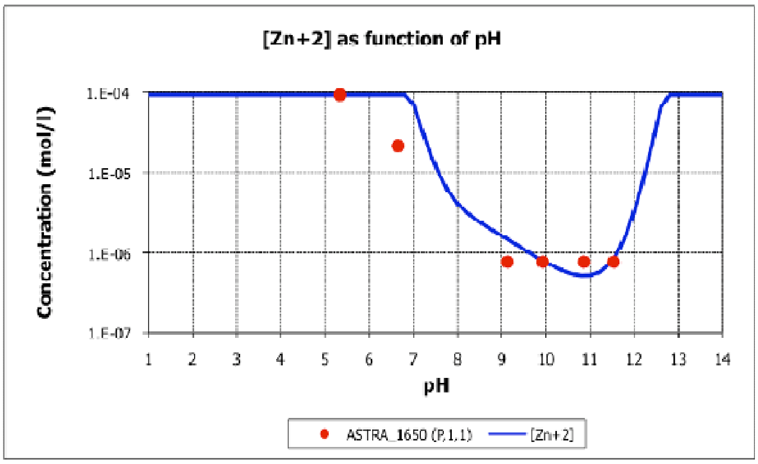

Figure 4.36: pH-dependent leaching of Zn

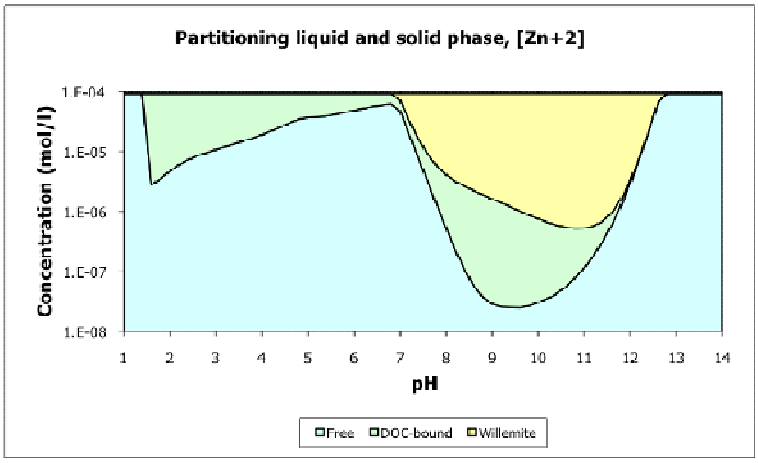

Figure 4.37: Solid-liquid partitioning of Zn

Visual Minteq results

The modeling results obtained for the ASTRA site using Visual Minteq are reported in Figs 4.38 - 4.40 for cells 1, 2 and 3, respectively. In such figures the measured concentrations of major elements and sulfate in the leachate as a function of pH are compared with the predicted solubility curves of solid phases selected as potential candidates for solubility control for the element of concern.

It was observed that in general the leaching of major cations and sulfate from the materials sampled at the three cells was controlled by different minerals.

For Cell 1, it was difficult to get reliable information on the solubility-controlling phases for both major elements/species and heavy metal contaminants. In general, the model predictions showed a reasonably good fitting of the experimental data in a limited pH range (~7–8.5 units), with the most probable leaching-controlling phases being amorphous $Al(OH)_3$ for Al, leucite and amorphous silica for Si, carbonate forms (including calcite or vaterite) for Ca, as well as barite for Ba and SO_4. In other pH regions, modeling predictions were very poor, likely indicating that the solubility of major constituents was dictated by complex solid phases that were not included in the thermodynamic database used.

For the three heavy metals of concerns Cu, Pb and Zn, the leaching curves (as a function of pH), were not described by any mineral included in the expanded Visual Minteq thermodynamic database. This may be an indication of the fact that metal contaminants were present in the mineral structure of more complex phases, which are difficult to describe as pure solids. Such a hypothesis may also be supported by the findings from microstructural observations, which were not able to clarify the speciation of metal contaminants in the untreated soil.

The Astra Pyrothechnics soil treated using PC (Cell 2) displayed solubility control of Al in a wide pH range by either anorthite, a calcium aluminosilicate mineral of the feldspar group having the chemical formula $CaAl_2Si_2O_8$, or wairakite, a tectosilicate of the zeolites group having the chemical $CaAl_2Si_4O_{12}{\cdot}2H_2O$. On the basis of the microstructural observations discussed above, both minerals appear to be good candidates for solubility control of Al. In the case of the sample treated using SRPC (Cell 3), Al leaching appeared to be dominated by a number of (hydr)oxides ($Al(OH)_{3soil}$, gibbsite [$Al(OH)_3$] and boehmite [AlOOH]) at low pH values, and possibly by gehlenite hydrate (also known as strätlingite, an AFm phase having the composition $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 8H_2O$). In 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. As a result, it may also be probable that other less soluble phases may be controlling the actual leaching of Al; however, without detailed data on the real (trace) levels of Al in solution at pHs > 10, no final conclusion can be drawn on this issue.

As for Ca and Si, the leaching from ASTRA Cell 2 at pH > 8 may be controlled either by hydrates from the C-S-H solid solution (including C-S-H at Ca/Si ratios of 0.8 and tobermorite, a hydration phase of the same solid solution series with a Ca/Si ratio of 0.83), or by ettringite phases (with Fe-ettringite giving the best fit with the measured concentrations). In the acidic pH range, the release of both Ca and sulfate appeared to be controlled by the solubility of gypsum.

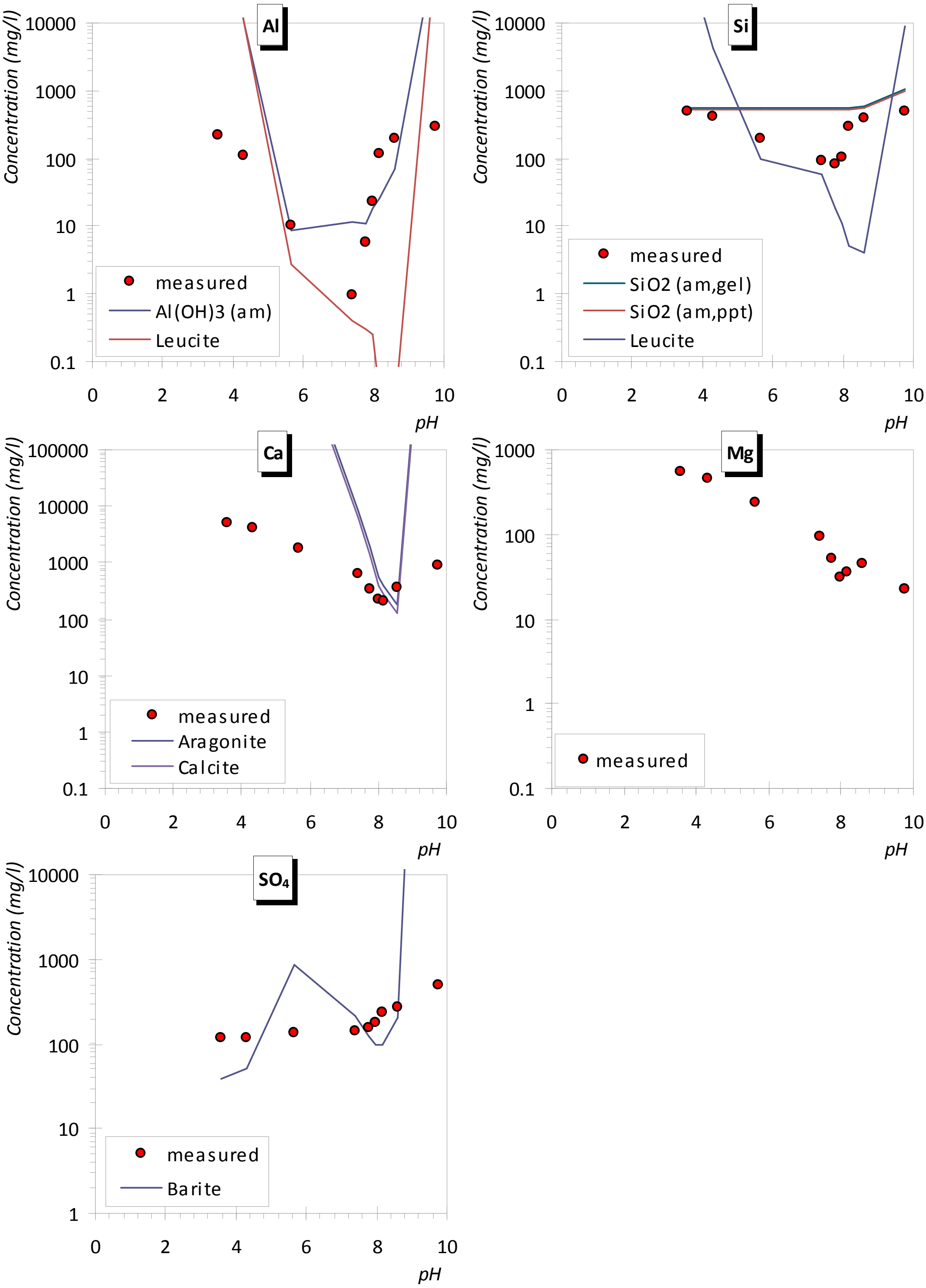

Figure 4.38: pH-dependent leaching of Al, Si, Ca, Mg and SO_4 in Astra samples (Cell 1) and model predictions.

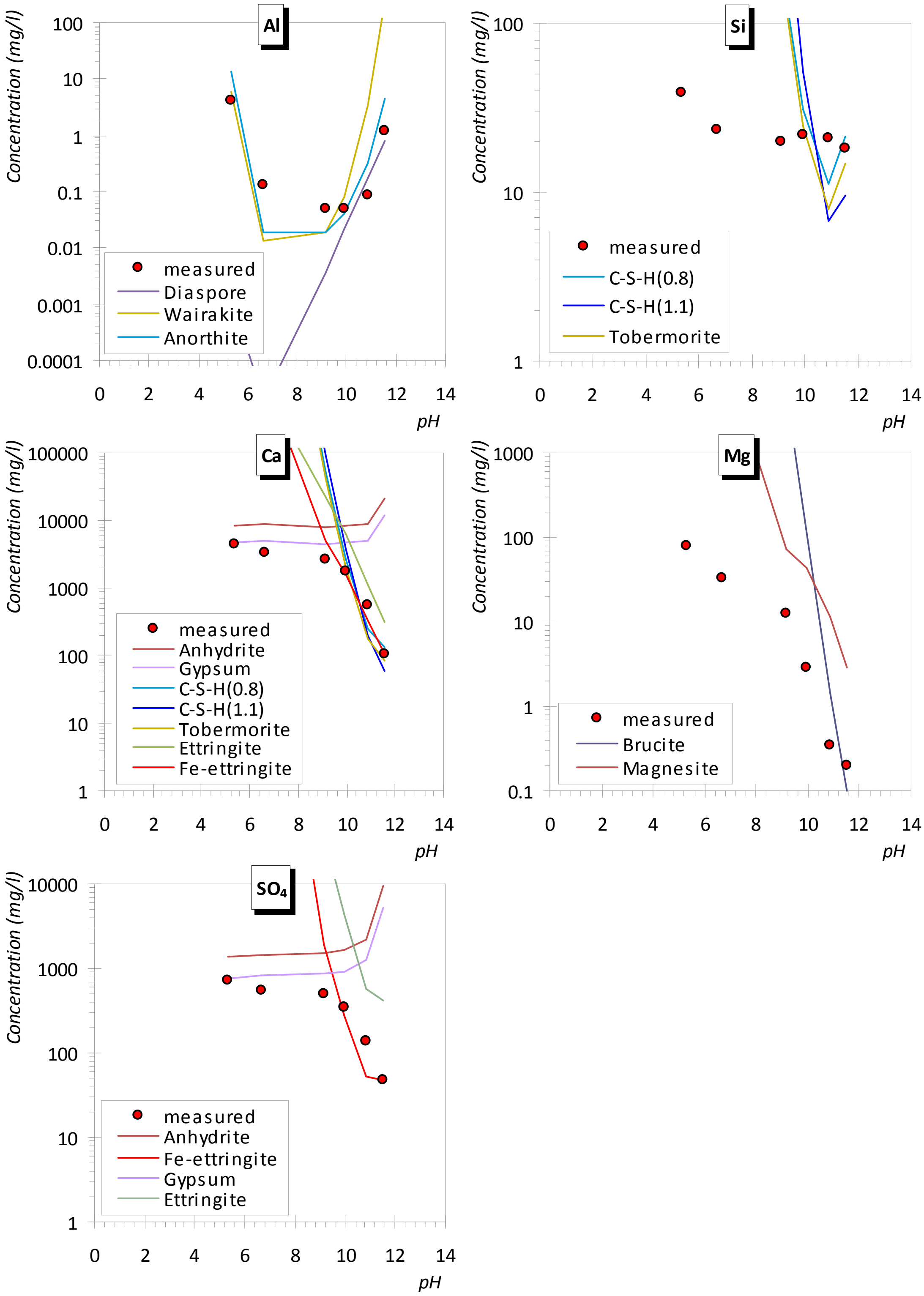

Figure 4.39: pH-dependent leaching of Al, Si, Ca, Mg and SO_4 in Astra samples (Cell 2) and model predictions.

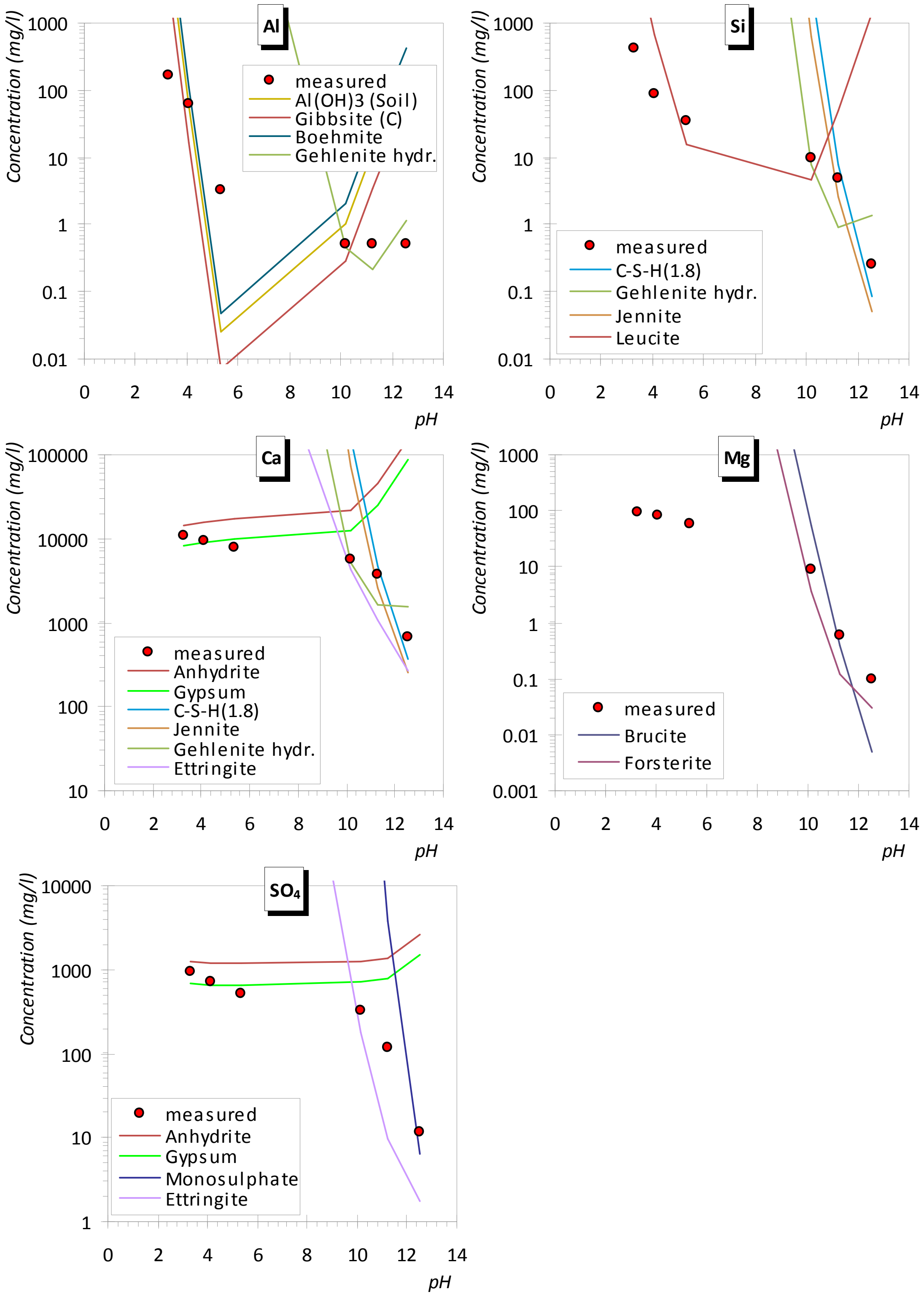

Figure 4.40: pH-dependent leaching of Al, Si, Ca, Mg and SO_4 in Astra samples (Cell 3) and model predictions

For the ASTRA Cell 3 sample the release of Ca and Si in the alkaline pH range appeared to be related to solubility control by Ca-rich C-S-H phases, including jennite (Ca/Si = 1.7) and C-S-H at a Ca/Si ratio of 1.8. The differences in the solubility-controlling phases for PC- and SRPC-treated ASTRA soil can be explained considering the different composition of the binder used in the s/s treatment. The leaching solutions were found to be slightly oversaturated in ettringite. At acidic pH values the leaching of Ca and Si was found to be dictated by gypsum and leucite, respectively.

Although carbonated forms were detected through microstructural analyses in the ASTRA Cell 3 sample (see above for details), no carbonate phase was found to explain the leaching behavior of major elements in the treated material.

In both ASTRA Cell 2 and Cell 3 samples Pb and Zn were found to be leached at appreciably lower levels (and even more considering that most of the measured leachate concentrations were below the analytical detection limit) than predicted on the basis of the solubility of the respective oxide, hydroxide and silicate mineral forms included in the MINTEQA2 thermodynamic database. As noted previously, this may be an indication of incorporation of these metals in the mineral structure of the hydration phases formed.

4.3.4 Summary

The levels of contaminants in the Astra soil were relatively high, but they remained immobilised in the treated soil to a high degree. This made modelling the leaching data difficult and the investigation of the mechanism of immobilisation was impracticable. This was surprising as the Astra site was established in such a way as to promote weathering, to facilitate the study of the release of contaminants.

The Astra soil was granular in nature and as such, strength and permeability were not evaluated. The soils were heavily carbonated and evidence was obtained to show this extended to a lesser degree to 1m in the 5 years following treatment. The soils also contained a relativel high amount of anhydrous cement, showing that the binder can remain potentially active over extended time. Despite a high degree of exposure, carbonation and incomplete hydration of the binder, the leachates produced from the treated soil met DIN drinking water standards.

The microstructure of the soil was dominated by carbonate-phases, infilling porosity. Ettringite and bassanite were present throughout the full depth of the treated soil profile, despite a significant reduction in pH near the top surface of the waste form.

4.4 South 8th Street, Arkansas

The South 8th Street (S8) Site is a Superfund Site situated on the flood plain of the Mississippi River in West Memphis, Arkansas. Following use as a gravel quarry, the site was used for the disposal of acid oily sludge and municipal waste (Figure 4.41). An area of approximately 6.5 hectares was specifically reserved for the sludge from an oil recycling operation, operating between 1960 and 1970. The contamination caused by the sludge, which had a pH of 1 or less, involved petroleum hydrocarbons, sulfuric acid and high amounts of lead.

The contaminants of concern were both the lead (22,000 mg/kg), and the acid and acid gases. The groundwater table is located at about 1.5 m below the ground in the vicinity of the sludge pit, which itself was about 5.5 m deep, was vulnerable to contamination by the Pb and the low pH of the sludge. This aquifer does not supply drinking water, but does connect with nearby ponds and the Mississippi River. As such, the risks to human health were from possible contact exposure to the highly acidic sludge or inhalation of toxic gases (sulphur dioxide and hydrogen sulphide) given off by the sludge.

Evaluation of in-situ and ex-situ treatment options for the oily sludge waste confirmed that the former was more appropriate, as it reduced the release of acid gases. The target criteria established for the treated material were permeability of 1 x 10^{-8} m/s, leachability of metals within the groundwater maximum contaminant levels established under the Federal Safe Drinking Water Act (i.e. 15 ppb for lead), a pH within the range of 7-11.5 (as this kept the solubility of Pb minimised) and an unconfined compressive strength of 0.34 MPa.

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. 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 and to raise the pH around 4.5 from around zero, to prevent release of acid gases through excessive heating from subsequent reagents.

The second stage treatment involved a mixture of ordinary Portland Cement and Fly ash, applied in a proportion of 20/10 percentage by weight to untreated 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.

This site is privately owned and is currently undergoing redevelopment as an industrial site on the Mississippi River.

Figure 4.41: South 8th Street (acid oily pit) before remediation

4.4.1 Historical compliance results

Remediation of the S8 site was completed in August 2000 and involved the treatment of 14,814 cubic meters of oily sludge waste and 15,576 cubic meters of ancillary soils (Figure 4.42). This report however deals only with the oily sludge waste. The remedial action targets that were used to select which materials required treatment are listed in the following Table 4.17. Table 4.18 gives the performance targets.

Performance samples were collected during treatment at a frequency of about every 380m^3. Samples were collected by lowering a piston tube into the freshly treated column. The withdrawn sample was placed in a bucket and used to make samples. Right cylinder moulds were then packed with this material and cured in a humid environment. All samples met the performance criteria save for a couple of samples that leached lead slightly above the criteria. Rather than force excavation and re-treatment, the USEPA allowed the responsible party to add a geosynthetic clay liner to the originally specified soil cap, as this provided at least as great a measure of protection as re-treating a handful of columns.

Table 4.17: South 8th Street Remedial Action Targets

Contaminant	Remedial Goal
Total PAHs as measured by benzo(a)pyrene equivalents	3 mg/kg
PCBs (total)	10 mg/kg
Lead	500 mg/kg

Table 4.18: South 8th Street treatment performance criteria

Test	Method	Design Criteria
Toxicity	SW 846 1312	SPLP Performance Criteria
pH	SW 846 9045	7.0 < pH < 11.5
UCS	ASTM D2166	0.34 MPa @ 28 days Average of all samples 0.27 MPa @ 28 days Minimum of any sample 0.17 MPa @ 3 days Average of all samples
Permeability	SW 846 9100	1 x 10^{-8} m/s @ 28 days Average of all samples 1 x 10^{-7} m/s @ 28 days Maximum of any sample
Wet/Dry Durability*	ASTM D4843	<30% loss of mass after 12 cycles
Volumetric Expansion	On-Site Measurements	<65% volumetric expansion

* During the first month of the stabilization in the ancillary soil area, the requirement for wet/dry durability testing was eliminated from the quality control testing since it was determined not to be relevant for the site conditions

In 2004, the USEPA conducted a 5 year review of the remediation and concluded that it was meeting its stated objectives.

Figure 4.42: Crane and Auger Assembly at South 8th Street

4.4.2 Sampling / new physical and leaching results

The S8 site was sampled in February 2004. No significant problems were experienced during this sampling, except for extraction of the cores from the Rotosonic drilling apparatus. Despite this, the amount of intact/granular materials recovered was comparable to the traditional auger/core barrel method.

The S8 site had the lowest average strength at 0.1 MPa, of all the sites examined in this study. All four UCS samples showed strength values significantly less than the value set as the design minimum at the time of treatment, and this may be the result of the use of the sonic component of the drilling, which may have fractured the samples. Nevertheless, the original design specifications for the S8 site were set to allow for some samples to fall below the established targets for physical and chemical properties. The rationale behind this allowance was that due to the heterogeneity of the contaminated material at the site, some treatment batches may fall below a specified minimum while others may far exceed. So an average design target was set, with a specified number of failures allowed, as well as an absolute minimum below which the batch must be examined.

As indicated in Figure 4.43 for UCS-S8, the average strength of the QA/QC samples exceeded the design average. The QA/QC samples consisted of 48 samples tested after 7-28 days of ex situ curing. The strength values ranged from 0.1 to 1.1 MPa, with an average value of 0.5 MPa.

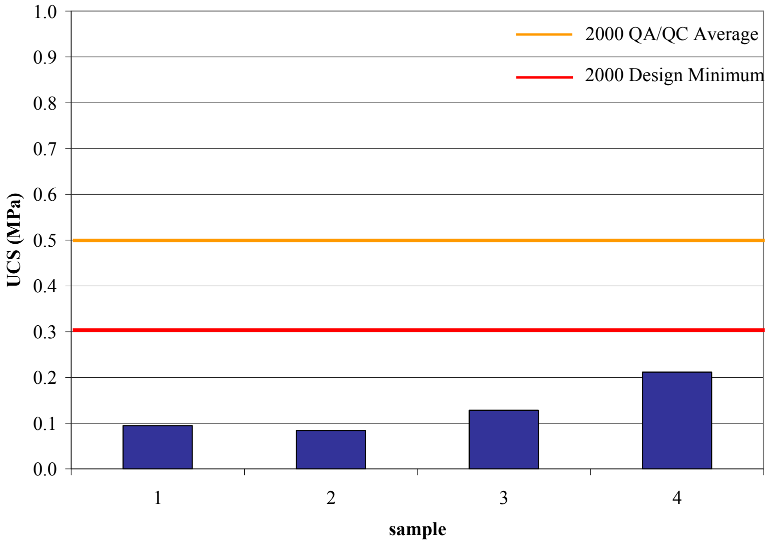

Figure 4.43: UCS Results for 2004 Sampling of the S8 Site

The difference between the ex-situ cured QA/QC samples and the four in-situ samples collected in 2003 for this study represent a significant discrepancy. The reasons for this difference could be the difference in ex-situ versus in situ curing condition, a degeneration of the S/S waste form over time, and/or the extraction procedure used in sampling resulting in weakening. An assessment of the microstructure of the samples indicated microcracking to a degree that there was significant evidence of sampling stresses.

The average permeability of the S8 site was on the order of 10^{-7} m/s. This was greater than the performance criteria set at 10^{-8} m/s maximum permeability. The QA/QC samples, tested after 28-days of ex-situ curing, showed permeability less than 10^{-8} m/s. The permeability measured on the S8 samples extracted would have been adversely influenced by the microcracking associated with sampling stresses, as described above.

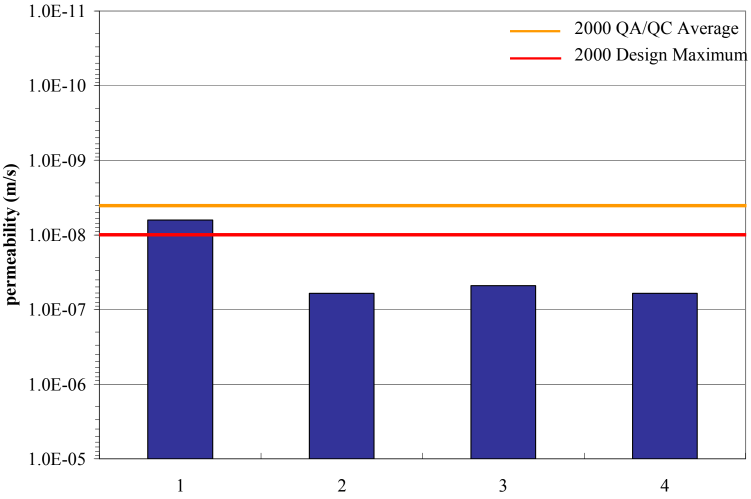

Figure 4.45: Permeability results for the 2004 Sampling of the S8 Site

In the five-year review of this site, the USEPA included the strength and permeability data generated as part of this study and concluded that despite the low strength values, the permeability of the site was still sufficient to be protective of human health.

Table 4.19: Lead results for the 2004 sampling of S8

Sample	**Conc x 10^{-3} (mg/l)**
1	28
2	6
3	99
4	66
5	8
average	41.4
quant limit	3
performance criteria	< MCL (15 μg/L)

The SPLP results for the S8 site showed three out of five samples to leach lead at levels above the drinking water action level performance criteria of 15 μg/L (Table 4.19). SPLP leaching was used in this study to compare between S/S sites with the same contaminants. SPLP use by regulatory agencies allows for measurement under specified test conditions, but does not necessarily represent contaminant behaviour in the S/S monolith. In June 2003, the EPA issued a report stating the groundwater concentrations of contaminants had met remedial goals and the site treatment was effective in cleaning up the groundwater contamination.

4.4.3 Transversal testing

4.4.3.1 Microstructure and mineralogy

The mineralogy of the S8 cement-treated sludge was very similar to that seen at Pepper Steel, except that high intensity peaks of ettringite and gypsum were observed. At the S8 site, the remedial operation required the treatment of the acidic tars prior to the addition of cement (Figure 4.43). As a consequence, the acid rich residues were neutralised with calcium carbonate, a relatively weak alkali. The gypsum observed by XRD could therefore, have been formed during the pre-treatment, with potential for augmentation by secondary reactions involving free sulfate.

Ettringite was not detected in all the samples analysed indicating its presence was localised. Calcite (a major crystalline phases identified by XRD) was present in the limestone used for neutralizing the acid tar and may also have resulted from natural carbonation of the resultant cement-stabilised medium. Other phases observed were quartz and feldspars.

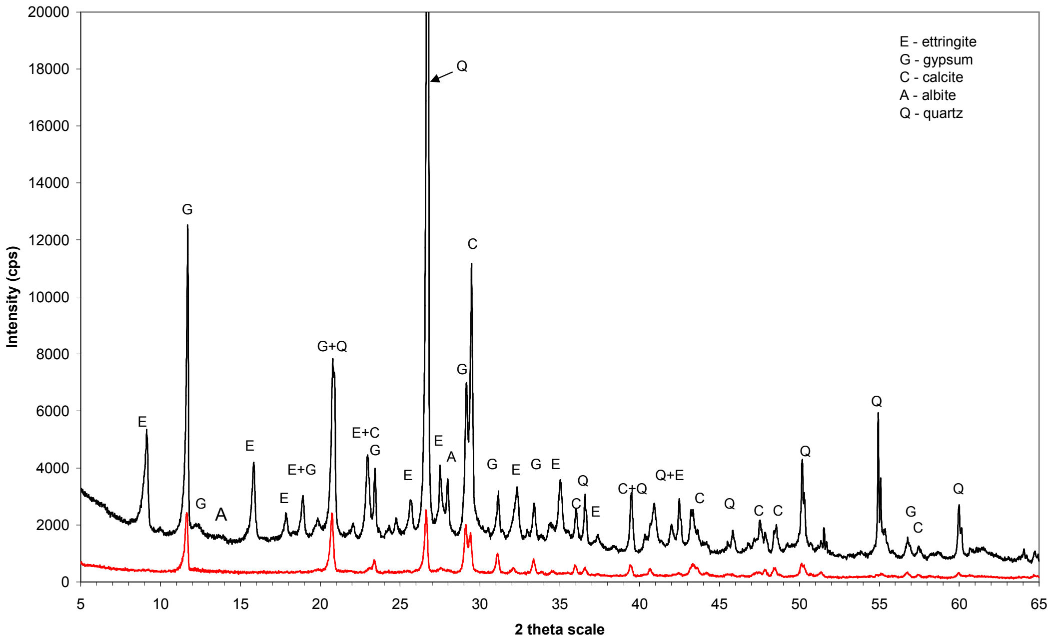

Figure 4.43: X-ray diffractogram from the treated soil from South Eight Street

Ettringite was observed in the matrix and may have been in the plastic state in the presence of excess sulphate, including the gypsum formed by the pre-treatment. Both ettringite and gypsum were observed infilling voids in the matrix and in microcracks which, they appeared to progressively infill. Ettringite was found to be present in the gap between quartz particles and the matrix suggesting its formation at an early age, or subsequent to dimensional changes that may have taken place within the matrix of the cement-solidified product.

Although microcracks were commonly observed in the cores extracted at the South Eight Street site, and believed to be caused by the method of extraction. The recovered samples were poorly indurated and had a high density of clearly visible cracks. Nevertheless, a small number of microcracks were partially infilled by precipitated material Figure 4.44 showing that these were formed prior to the sampling and extraction.

The hardened matrix contained relics of partially hydrated cement and fly ash, fragments of limestone, rock, feldspar and opaque material of a tarry nature, as confirmed by SEM Figure 4.44. The sample was desiccated by the specimen preparation procedures leading to separation of organic-rich inclusions from the matrix. This gave the sample the appearance that it had a larger void content than it actually had.

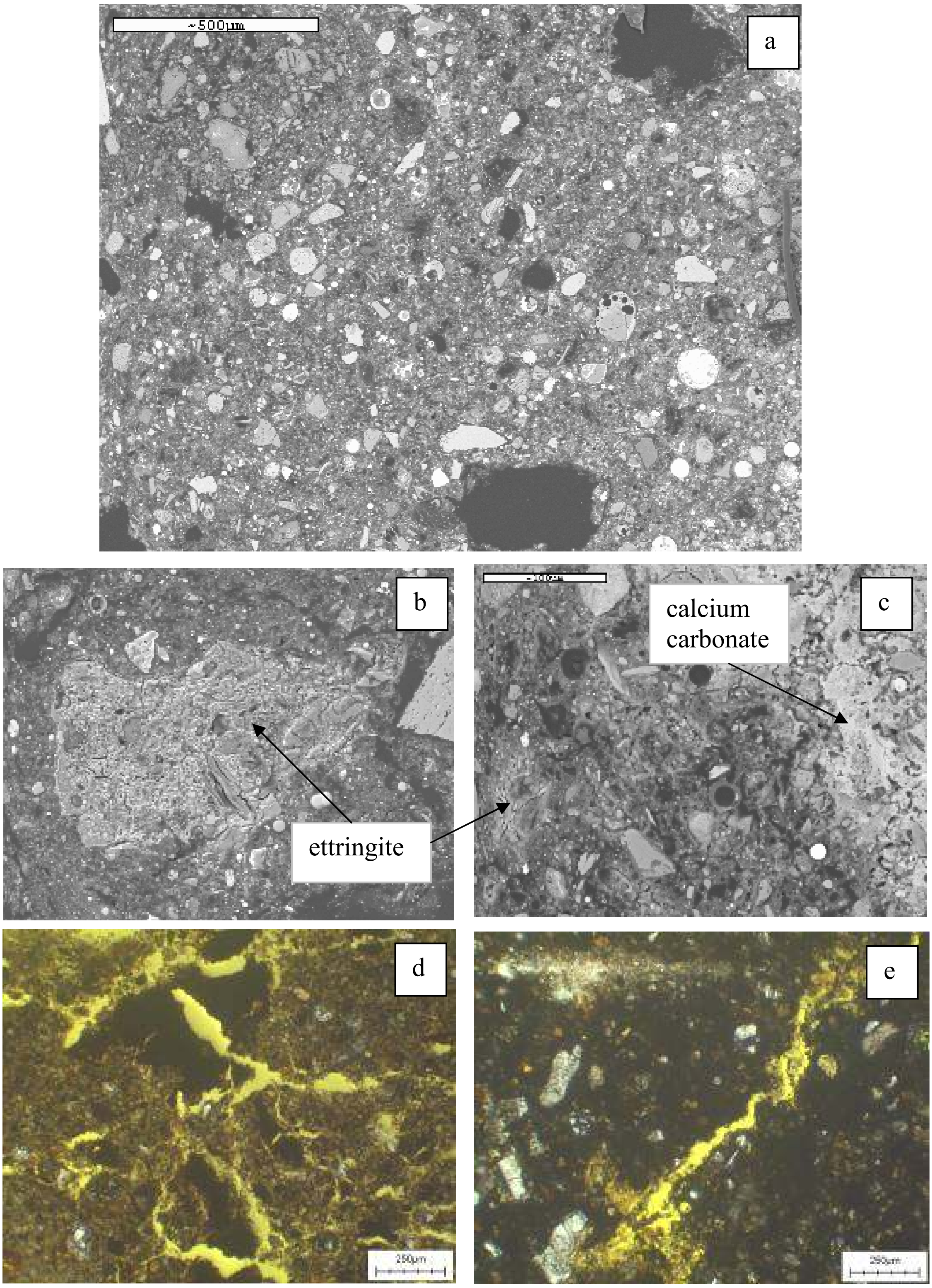

Figure 4.44: Treated soil from S8 a) BSE micrograph showing the dense microstructure with porsity; b) ettringite growth in the matrix; c) partially carbonated matrix with adjacent ettringite; d), e) transmitted light micrograph showing organic material within the stabilised matrix (note that shrinkage cracking resulting from sample preparation)

4.4.3.2 Chemical characterisation

The results of the elemental analysis carried out on the S8 samples are shown in Table 4.20.

Table 4.20: Total content analyses of the soils from S8 site

	concentration (mg/kg)		concentration (mg/kg)
Insoluble residue(%)	8.2-24.6	**Dry mass (%)**	60.9-64.8
Cl	N.D - 333	**Mn**	239 - 246
Al	27 517- 32 643	**Mo**	6.5 – 6.8
As	<5 – 5.34	**Na**	2 895 - 3694
Ba	357-964	**Ni**	34 - 37
Bi	N.D	**P_tot**	1 192 - 1378
Ca	107 782 - 126603	**Pb**	10 349 - 13253
Cd	<5	**S_tot**	23 454 - 27642
Co	<5-5.9	**Sb**	<5
Cr	55.91 - 60	**Se**	<5
Cu	61-62	**Si**	67 823 - 87583
Fe	18 368 - 22639	**Sn**	10 -11
Hg	<5	**Sr**	N.D
K	6 529 - 8580	**Ti**	N.D - 1 063
Li	N.D	**V**	N.D - 50
Mg	7 853 - 9189	**Zn**	847 - 895

The results obtained corresponded well with the historical data available as metals were observed in the samples studied, including Pb, Cu, Ni, Mo and Zn.

4.4.3.2 Leaching

a._Equilibrium test

The equilibrium tests for the S8 material were carried out for L/S ratios of 3, 14, 28, 55, 136. First the sample was ground to 1 mm and then placed in contact with demineralised water for a period of 7 days. The results are shown in Figs 4.45 and 4.46.

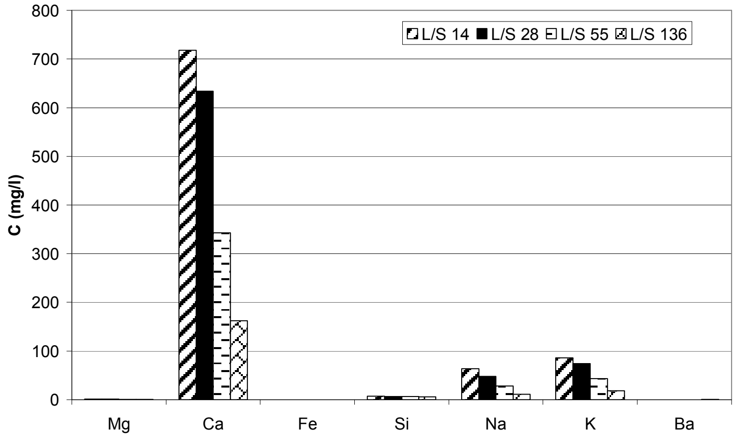

Figure 4.45: Equilibrium tests – cations

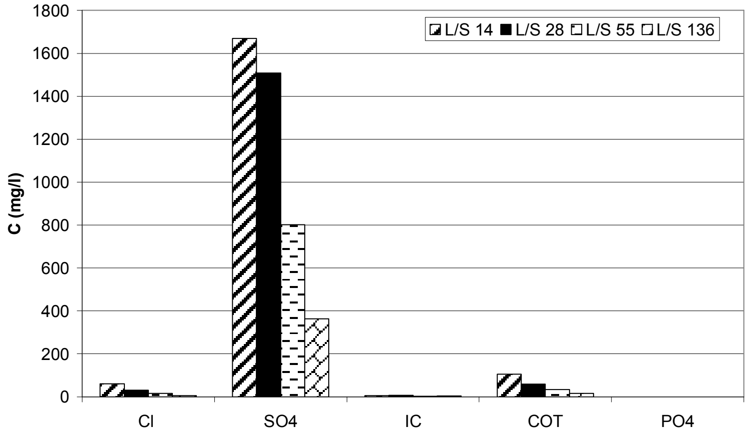

Figure 4.46: Equilibrium tests – anions

A reliable analysis of the equilibrium solution produced at an L/S ratio = 3 could not be readily obtained due to the small quantity. The pH values of the supernatant solutions varied between 9.64 for an L/S ratio = 14 and 10.41 for an L/S ratio = 136.

The main elements in solution observed were calcium and sulfate in equi-molar proportions suggesting that this was due to the dissolution of $CaSO_4$, a mineral described earlier as present in abundance.

The other elements - sodium, potassium and chlorides, were leached in markedly lower quantities, whereas Zn and Pb were not detected in the equilibrium solutions.

PAHs were not measured in the equilibrium solutions because their presence in the tests previously carried out was below the detection threshold.

b. Acid Neutralisation Capacity

The treated S8 material's acid-neutralising capacity was approximately 3 mol H^+/kg of dry material. The concentrations of the various elements depending on the pH, obtained during the ANC tests, are shown in Table 4.21.

Table 4.21: Results of the ANC tests (mg/l)

pH (t0+48h)	3.77	6.57	6.91	8.12	8.68	9.2	9.78	10.82	11.85
Cond.(mS/cm)	22.9	9.04	13.7	5.58	4.29	3.01	2.4	3.69	5.85
Al	158.40	0.07	<0.05	0.03	0.09	0.14	0.06	0.10	0.68
Ca	4972	2362	1233	1492	1194	832	692	473	95
Fe	14.49	0.04	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01
K	138	95	100	104	108	112	90	106	132
Mg	3692.40	46.80	104.00	12.33	4.00	1.49	0.51	0.07	0.02
Na	60	66	59	82	90	95	73	565	1518
Si	121.90	21.00	20.09	6.62	3.40	2.39	3.88	15.64	9.72
Pb	33.29	0.13	0.37	0.02	0.02	0.01	<0.01	<0.01	<0.01
Zn	20.24	1.18	1.93	0.03	0.03	0.03	<0.01	<0.01	<0.01
Ba	0.16	0.39	0.22	0.15	0.16	0.13	0.09	0.08	<0.01
Cl	82.26	80.04	79.44	71.66	81.16	81.47	78.86	77.98	82.47
TOC	96	106	120	98	113	112	103	120	130
IC	<10	<10	<10	<10	<10	26.43	0.021	3.413	8.446
PAH (µg/l)	Nd	Nd	Nd	<10	<10	<10	<10	Nd	Nd
PO4	<50	<50	<50	<50	<50	<50	<50	<50	<50
SO4	1049	1184	1049	1455	1432	1480	1581	2019	2406

Nd: not determined

As far as pollutant availability is concerned, the results show that: the quantities of Ca, Mg and Si released increase as the pH decreases whereas, the leaching of K, TOC and SO_4 was independent of the pH. Aluminium, Fe, Pb, Zn and PO_4 were largely absent in the solutions across the different pH values obtained during the ANC tests, except at an acid pH less than 4, where destruction of the material fabric commences.

c. Percolation test

The percolation test was carried out using demineralised water with an increasing flow rate, in accordance with CEN/TS 14405 (2004). The column used was 10 cm in diameter and 30 cm high, and the applied flow rate applied was constant and equal to 48 ml/h when the percolation column was empty.

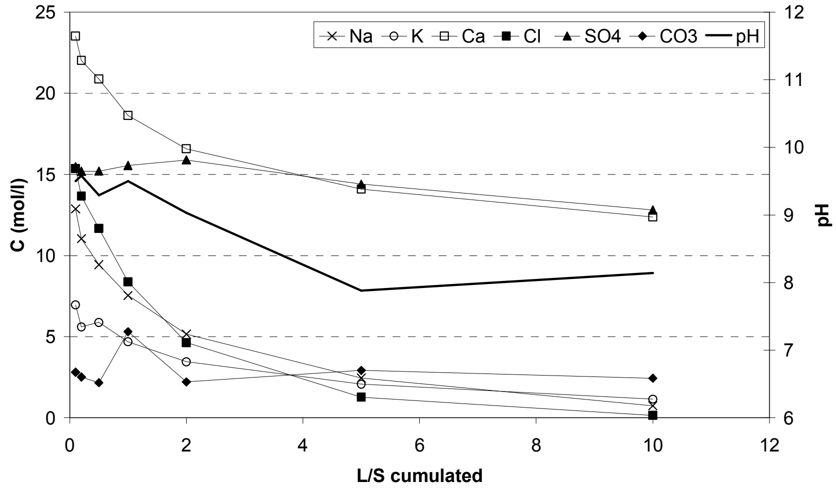

Figure 4.47: Percolation test, follow-up the concentration of Na, K, Ca, Cl, SO_4, CO_3 according to the ratio cumulated L/S

The behaviour of the Ca and the SO_4 (Figure 4.47) confirmed that from L/S = 2, their leaching was controlled by the dissolution of the $CaSO_4$. For lower L/S ratios, the leaching of calcium was most likely controlled by the dissolution of the organic matter.

The increase in the concentrations of Na and Cl were similar suggesting that this resulted from NaCl. The quantity of TOC released decreases over time, to close to 0 at the end of the experiment (Figure 4.48).

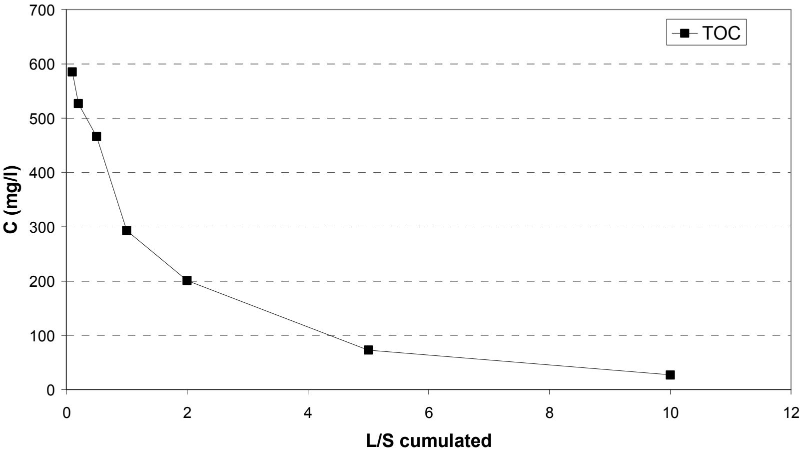

Figure 4.48: Percolation test, follow-up the concentration of TOC according to the ratio cumulated L/S

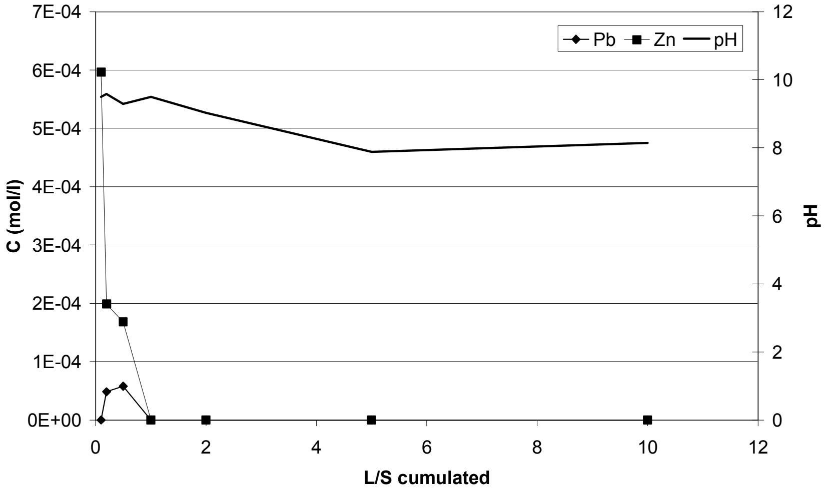

Figure 4.49: Percolation test, follow-up the concentration of Pb, Zn according to the ratio L/S cumulated

Heavy metals were detected in very low concentrations in the first three solutions, whereas, the concentrations of PAH's were below the detection threshold (9-10 µg/l) (Figure 4.49). These results show that the S8 material is indeed effectively stabilized and that the pollutants initially present in significant quantities remain practically immobile.

d. Modelling

LeachXS results

The geochemical modelling results for the S8 sample show agreement with the findings from modelling the pH-dependent leaching of other S/S waste forms presented earlier in this report. Figs 4.50 to 4.51 show the agreement between modelled and measured Pb data and the major controlling solid phase, respectively. As shown earlier, it appears that $Pb(OH)_2$ is the major controlling solid phase, and again the significance of DOC is seen in increasing the Pb solubility at the slightly alkaline pH values between 8 and 11.

Zinc speciation also followed what has been observed at the other sites investigated, that is, Willemite provides fairly close agreement between measured data and model trends (Figs 4.52, 4.53). In this case, it appears calcium zincate may be significant at the higher pH values, above approximately 12. And as with Pb, the significance of DOC complexation is apparent.

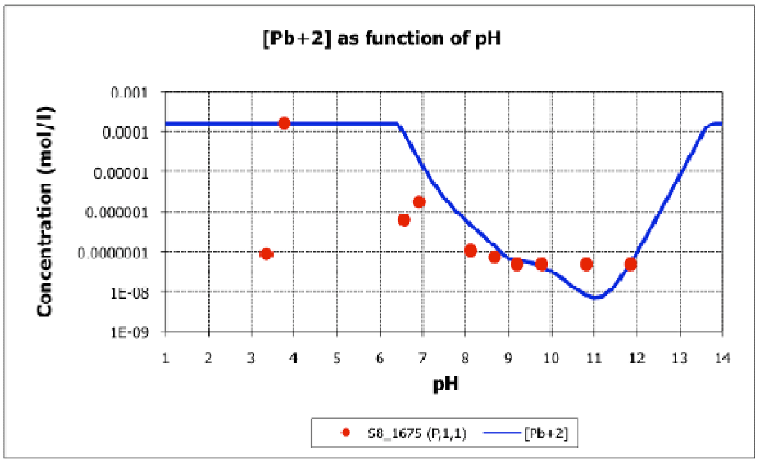

Figure 4.50: pH-dependent leaching behavior of S8 sample and model agreement

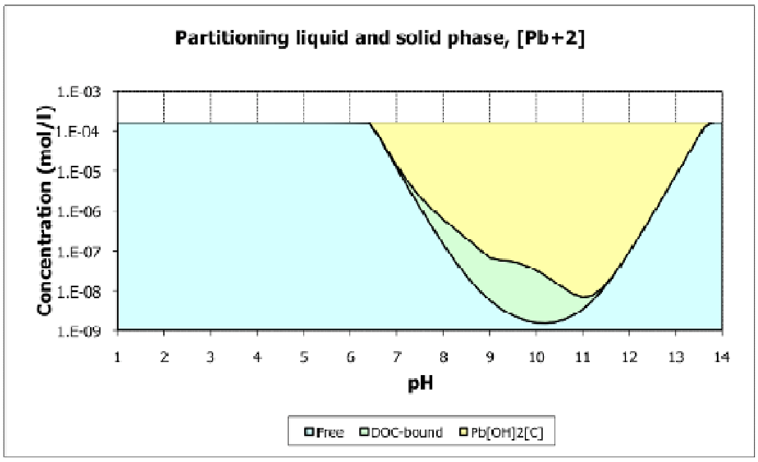

Figure 4.51: pH-dependent phase partitioning model of Pb in S8 sample

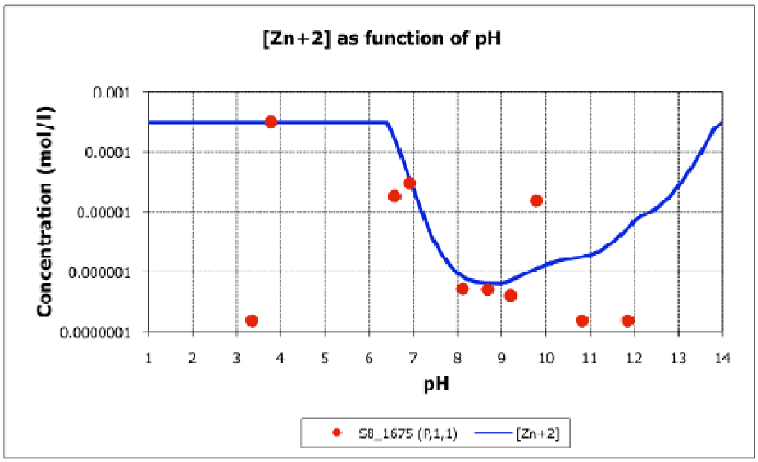

Figure 4.52: pH-dependent leaching behavior of Zn in S8 sample and model agreement

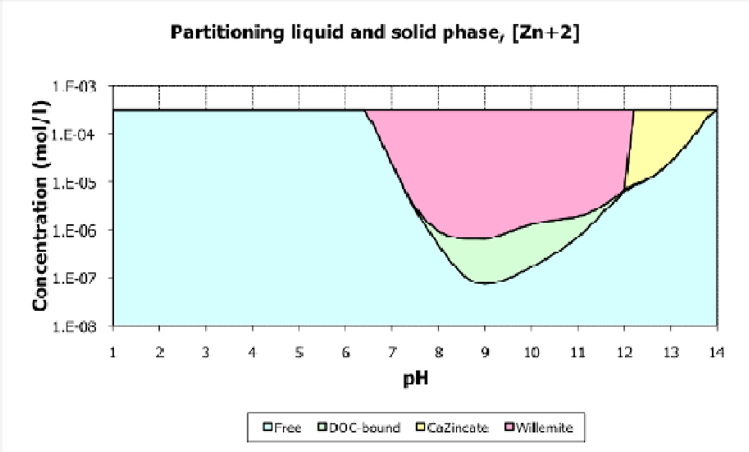

Figure 4.53: pH-dependent phase partitioning model of Zn in S8 sample

Visual Minteq results

The modeling results obtained for the South Eight site using Visual Minteq are depicted in Figure 4.54, which compares the measured concentrations of major elements, sulfate and Zn in the leachate as a function of pH with the predicted solubility curves of solid phases selected as potential candidates for solubility control.

According to the modeling calculations, the leaching of Al and Si appeared to be controlled either by microcline or Ca-based zeolite P in a wide pH range; although zeolite P displayed a better fitting of the experimental leaching data at moderately alkaline pH values. The presence of microcline is supported by the results from microstructural characterization (XRD and SEM analyses),

The release of Ca was largely explained by the solubility of gypsum (which also closely matched with the data of sulfate leaching) for pH values up to ~11; at higher pHs both C-S-H with a Ca/Si ratio of 1.1 and ettringite were good candidates for solubility control of Ca.

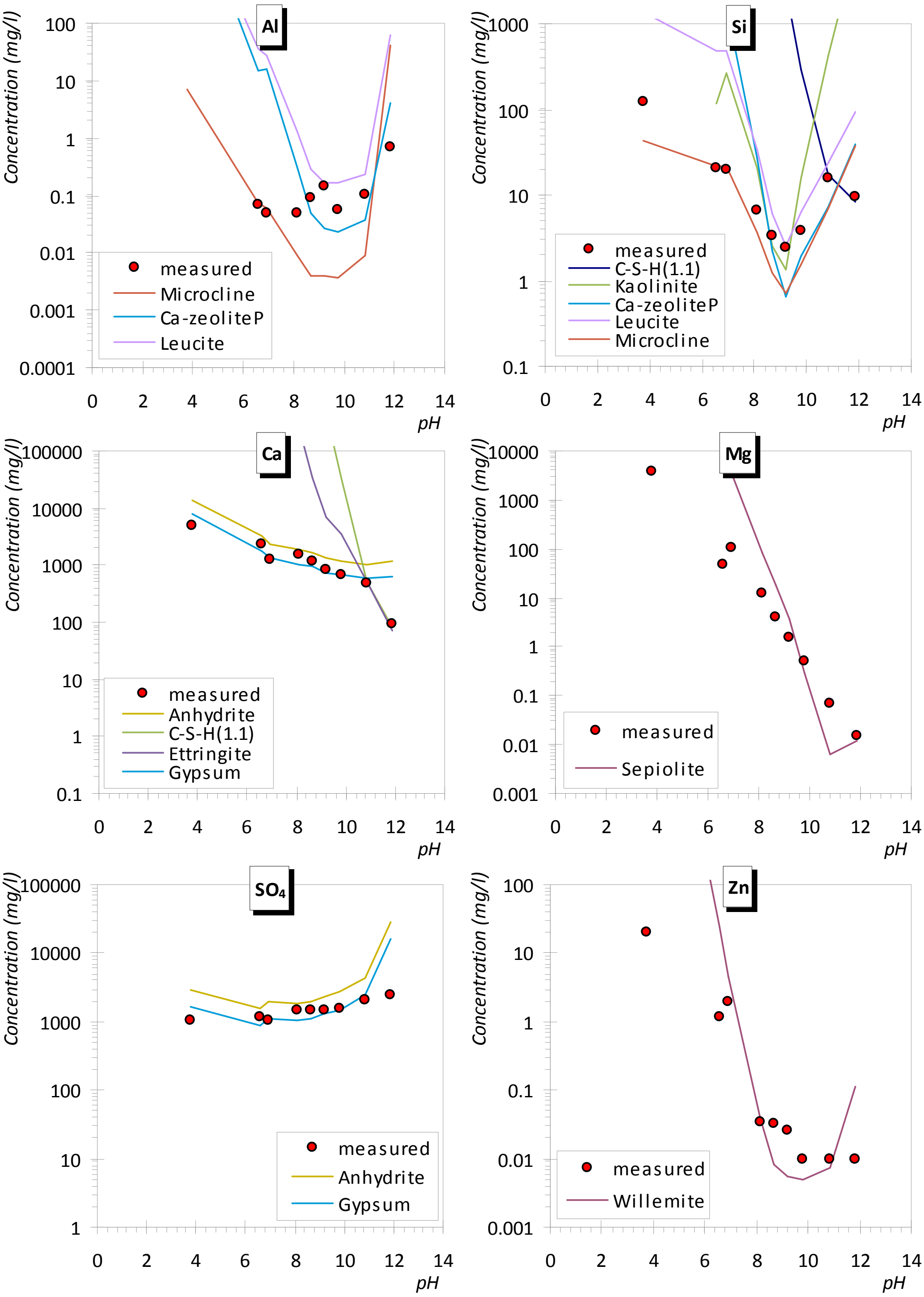

Figure 4.54: pH-dependent leaching of Al, Si, Ca, Mg, SO_4 and Zn in S8 samples and model predictions

The leaching behaviour of Mg was found to be dictated by sepiolite ($Mg_4Si_6O_{15}(OH)_2 \cdot 6(H_2O)$, a phyllosilicate mineral).

No conclusion could be derived on possible solubility control by carbonate minerals, which were nevertheless detected through microstructural investigation, due to the scarcity of data on inorganic carbon concentrations in the eluates.

Among the investigated heavy metals, Zn leaching appeared to be in good agreement with solubility data for willemite (Zn_2SiO_4), while in the case of Pb the leaching solutions appeared to be strongly undersaturated in $Pb(OH)_2$.

4.4.4 Summary

Samples from the South 8th Street site were collected using a rotosonic drilling rig. Since this equipment uses sound waves along with water to core, it is possible to introduce some fractures or otherwise compromise the samples collected. This may account for the lower unconfined strength test results on these samples compared to samples at time of treatment (average of 0.1 MPa vs 0.5 MPa respectively).

Permeability results from these samples ranged between $1x10^{-7}$ to $1x10^{-8}$ m/s, slightly more permeable than at the time of treatment. The cause may well be the same as field observation during sample collection noted that the coring method tended to fracture the samples.

SPLP leaching on samples from the South 8th Street site indicated lead levels that ranged from 8 to 99 µg/L, above the original criteria of 15µg/L average. However monitoring wells next to the monolith have not reported lead levels above the 15µg/L criterion (data not included in this report).

The South 8th Street site was different from the other sites in that large quantities of ground limestone were employed to neutralise the acidic sludge (sulphuric acid) and this resulted in the massive precipitation of gypsum. The gypsum was then encapsulated by the binder system. Although the presence of gypsum is important in the leaching of eluants, other mineral phases were identified, by modelling, including sepiolite and willemite.

The data indicates that there are no long-term leaching issues associated with the South 8th Street site.

4.5 Halton, Cheshire

The Halton site, also known as the Hutchinson Street Site, covered an area of 2.5 ha. Located in north-west England, the site was intensely contaminated by industrial activities from the 1880s. These included 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 to be up to 4 m thick. Other contaminants including arsenic, lead, zinc, cadmium, copper, nickel and chromium were also present. The pH of the contaminated soil varied from 2.6 to 12.2, with the acid pH conditions being prevalent within the first 1 – 2 m depth (Curtis and Holt, 2004). The contamination of controlled waters by heavy metals was the main risk identified at the site.

Because of the considerable amount of contaminated soil that needed treating (87,000 m^3) it was decided to create an impermeable cap effectively sealing off the site from water ingress. A binder containing 6% w/w Portland Cement and 0.5%

w/w proprietary additive (Powercem 2, PowerBetter Environmental Processes Ltd) was used to treat the contaminated soil. Shallow in-situ mixing, involving the top 35 cm was completed using a rotovating type-plant. Once hardened, 20 cm of reclaimed railway ballast, followed by Terram geotextile and 10 cm of sand and topsoil were placed upon the treated monolith. The remediated site was then laid to grass to prevent erosion and limit surface infiltration.

4.5.1 Historical compliance results

This site did not have specified performance criteria for permeability and strength. The results published in 2002 by the Contractor indicated that a significant improvement in the permeability and strength of the soil was achieved (Powerbetter Environmental Processes, 2002).

Twenty-eight days after the treatment the permeability decreased from 10^{-5}-10^{-6} m/s (the untreated soil) to 0.22×10^{-8} m/s, and after six months to 0.5×10^{-8} m/s. Laboratory-based CBR tests showed a strength increase in excess of 180 % and 200 % after a 7 and 28 day curing, respectively. In situ CBR tests were also performed and the values obtained exceeded 50 % up to 7 days after treatment (Curtis and Holt, 2004; Powerbetter Environmental Processes, 2002).

4.5.2 Sampling /new physical and leaching results

Sampling was carried out in November 2005 and material was recovered using a 150 mm diamond core barrel and water to avoid overheating (Figure 4.45). Before coring, grass, top-soil, gravel and geotextile were removed to a depth of 30- 40 cm below ground level to expose the top of the monolith (Figure 4.46).

Intact cores of 30 cm length were obtained from a number of locations around the site (Figure 4.47).

Figure 4.55: Equipment used for core extraction

Figure 4.56: Layering on site, above the stabilised monolith

Figure 4.57: Core sample extracted from Halton

4.5.3 Transversal testing

4.5.3.1 Microstructure and mineralogy

Upon examination, it was found that the treated soils contained crystalline phases, originating from the soil and from the cement-binder system. Calcite, gypsum and ettringite were encountered in all the specimens analysed.

The soil at the site was originally alluvium with varying amounts of calcium carbonate, some of which resulted from soap manufacture. The highest intensity peak in the treated soil was calcite, possibly augmented by natural carbonation of the monolith. The cement-stabilised soil was capped with layers of permeable material, but upon sampling, standing water was observed in places on the surface of the treated material. The low permeability (Curtis and Holt, 2004), would suggest that the bottom of the monolith (30 cm deep) would not be affected by carbonation, because carbonation rates will not normally exceed 2 mm, even after many years of exposure in such low permeability materials (St. John et al., 1998). By way of contrast, the granular exposed waste form at the Astra site showed signs of carbonation to its full 60 cm depth, indicating ingress at a rate of 10 cm/year.

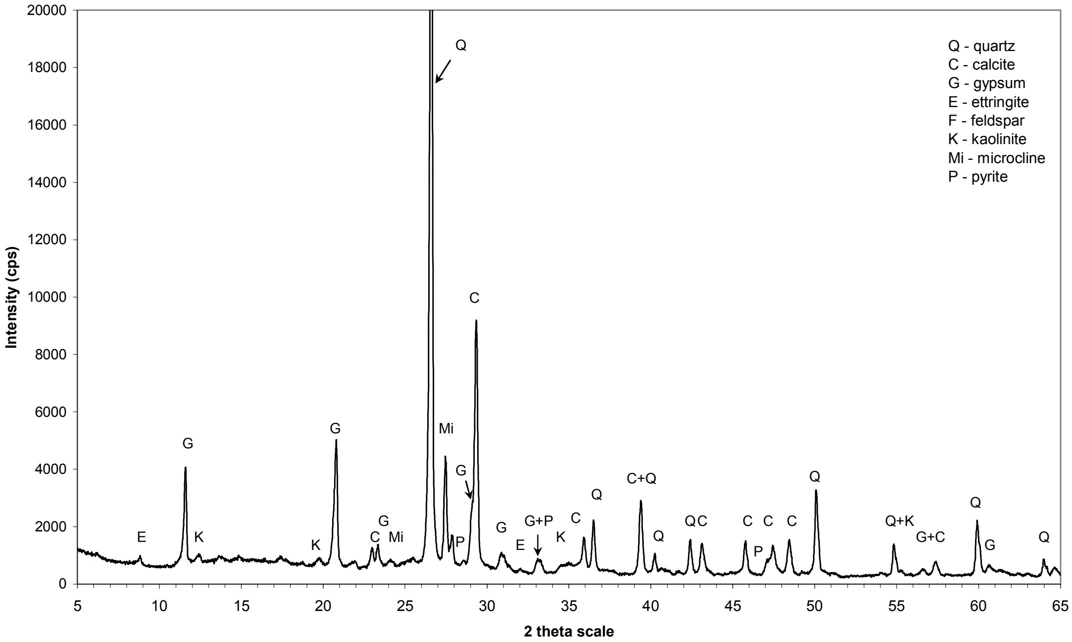

Figure 4.58: X-ray diffractogram of cement-stabilised soils from Halton

Ettringite and gypsum were identified by XRD with the latter being present in significant quantities (Figure 4.58). The contaminated soil had a high sulfate and aluminium content. Pyrite was identified by XRD and by x-ray microanalysis and its oxidation may have generated sulfate for subsequent gypsum and ettringite formation.

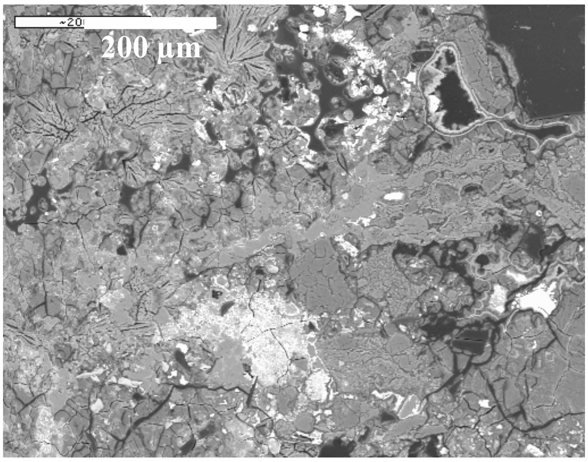

Figure 4.49: Backscattered electron image of an altered area of the matrix containing ettringite

Ettringite was seen growing adjacent to crystalline pyrite with grain sizes ranging between 2-5 µm. Larger voids were often filled with ettringite (Figure 4.49). The matrix was highly carbonated, with euhedral calcium carbonate identified in voids as perfect rhombohedral crystals. Infrequently, aragonite was present in needle-like clusters, whereas elsewhere, globular agglomerations of calcium carbonate may have indicated the presence of vaterite. It is interesting to note that the co-existance of the three polymorphs of calcium carbonate has been recently reported to form in naturally carbonated samples (Hidalgo et al., 2008).

The presence of calcium carbonate in microcracks and voids may reflect the importance of potential pathways for the ingress of ions into the solidified matrix.

A variety of metal contaminants were observed. Fine particles containing metal, metal oxides (including Zn, Cu and Cr) were identified in C-S-H gel. Other, larger particles of copper sulfide, iron oxide, iron sulfide, iron sulfate, chromium oxide, barium sulfate, and others containing copper, zinc, iron, chromium were also unevenly distributed throughout the matrix of the waste form.

4.5.3.2 Chemical characterisation

The results of the total element analyses are shown in Table 4.22.

Table 4.22: Total content analyses of the treated Halton soil

	concentration (mg/kg)		**concentration (mg/kg)**
Insoluble residue (%)	24.9-42.4	**Dry mass (%)**	65.92-84.7
Cl	<100 – 256	**Mo**	<5-10.17
Al	30421-34 211	**Na**	2495-3 188
As	488-524	**Ni**	125-450
Ba	729-833	**P_tot**	480-498
Ca	51366-69 896	**Pb**	677-797
Cd	Nd-15.15	**S_tot**	15323-29 406
Cr	248-369	**Sb**	Nd-46
Cu	442-3 353	**Se**	Nd - <10
Fe	59794-76 136	**Si**	57 018-68681
Hg	<10	**Sn**	Nd-36
K	7522-13 656	**Ti**	1 128-1273
Mg	3598-3 886	**V**	Nd-79
Mn	247-314	**Zn**	505-1 476

The elemental analysis confirmed a high level of sample heterogeneity, with the main contaminants being: As, Cr, Cu, Ni, Zn.

4.5.3.3 Leaching

a. Acid Neutralisation Capacity

The acid-neutralization capacity of the treated material was approximately 3 meq/g of dry material.

The concentrations of the various elements depending on the pH, obtained during the ANC tests, are shown in Table 4.23.

Table 4.23: pH dependent leaching from treated Halton soil (mg/l)

pH (t0+48h)	1.67	2.31	4.76	9.19	10.07	11.21
Conductivity (ms/cm)	27.1	18.3	12.87	6.74	3.05	0.769
Cr	12.46	3.79	<0.1	<0.1	0.13	<0.1
Cu	29	10	0.15	<0.1	<0.1	<0.1
Ni	0.85	0.56	0.11	<0.1	<0.1	<0.1
Pb	9	3	<0.1	<0.1	<0.1	<0.1
Zn	47	25	4.17	<0.1	<0.1	<0.1
Al	316	123	0.23	<0.1	<0.1	0.38
Na	21	18	15	12	10	9
K	96	85	62	45	39	26
Mg	128	95	43	12.46	0.97	0.70
Ca	5304	4699	3096	1911	812	152
Fe	411	115	0.83	<0.1	<0.1	<0.1
Si	507	317	56	12	10	11
Cl	<10	<10	<10	<10	<10	11
SO4	1 515	1 346	1 332	1 098	645	274
TOC	16	7	5	9	7	6
IC	<1	<1	6.35	5.73	2.81	3.28
P tot	Nd	Nd	<0.1	<0.1	<0.1	<0.1
PO4	<1	<1	<1	<1	<1	<1

The pH dependent leaching results showed that most of the elements were solubilised in acid conditions. At the natural pH of the treated soil, pH 11.21, leaching levels were low.

b. Modelling

Visual Minteq results

The modeling results obtained for the Halton site using Visual Minteq are reported in Figure 4.50, where the measured concentrations of major elements and sulfate in the leachate as a function of pH are compared with the predicted solubility curves of solid phases selected as potential candidates for solubility control.

Among the solid phases selected as possible candidates for solubility control of the elements of concern, gibbsite and halloysite ($Al_2Si_2O_5(OH)_4$, a phyllosilicate mineral of the kaolinite group) showed the best fit with the measured leachate concentrations in the pH range ~4.5-11. Solubility control by halloysite may also be supported by both microstructural observations, which indicated the presence of kaolinite (see above), and by the fact that the theoretical solubility curve for this phase was also found to match the leaching of Si, although within a more limited pH range. At high pH values, Si may be controlled by low Ca/Si ratio C-S-H (likely Ca/Si = 0.8). The same phase also showed a good fit with Ca leaching at high pH values, possibly together with carbonate phases (dolomite or, more likely, hydrated calcium carbonate, which were detected during microstructural observations), which appeared to describe the release of Ca down to pH ~8.

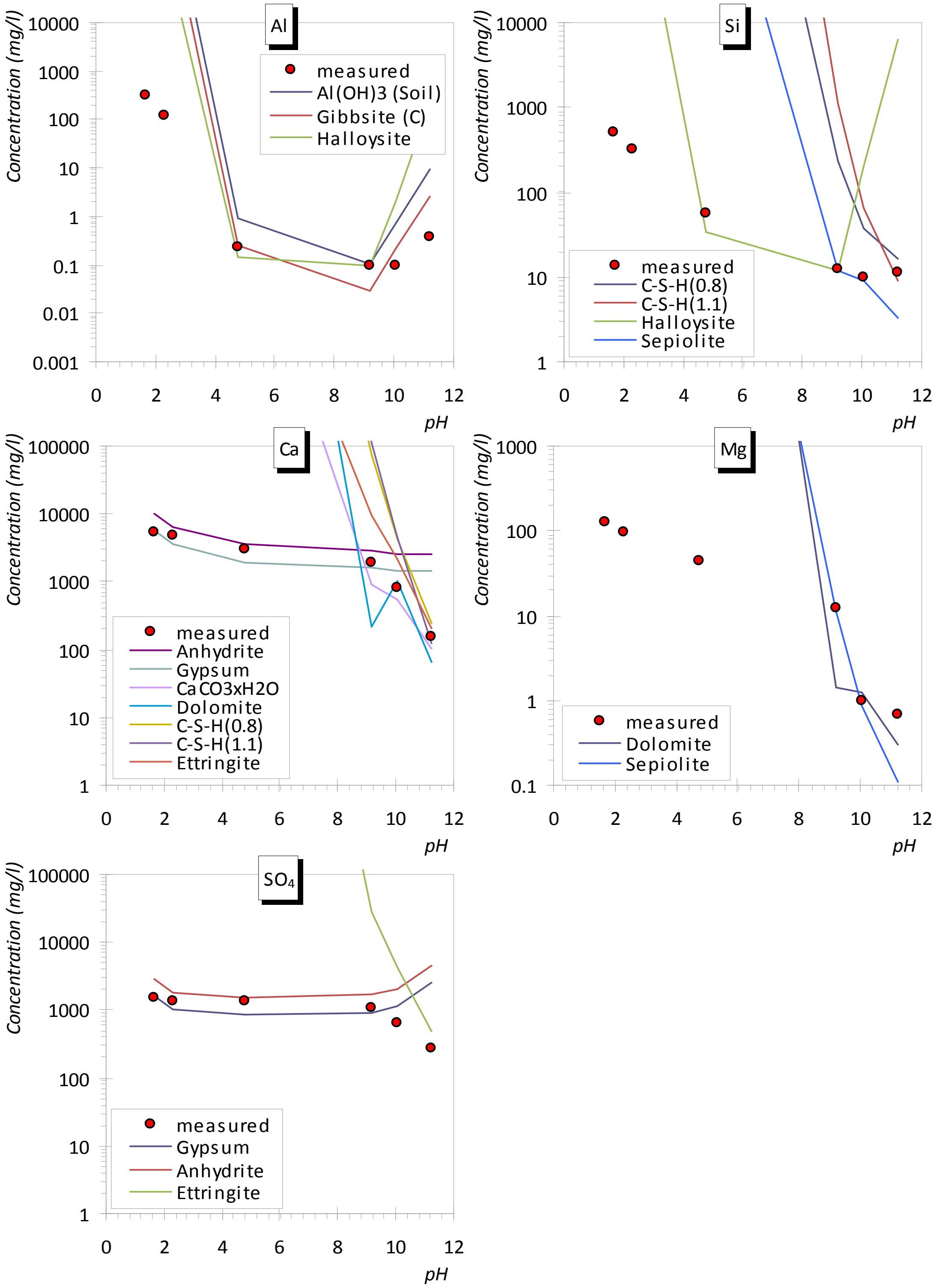

Figure 4.50: pH-dependent leaching of Al, Si, Ca, Mg and SO_4 in Halton samples and model predictions.

In the acidic pH range, both Ca and sulfate were controlled by gypsum, which was also observed through mineralogical analyses. Possibly, ettringite may be responsible for sulfate leaching from the treated material at high pH values (> 10).

As for Mg, the best fit with the experimental leaching data was displayed by dolomite, indicating carbonation as an important process governing the release of major elements.

As far as modeling of heavy metal leaching was concerned, it was not possible to derive any indication about the potential solubility-controlling minerals, since metal concentrations were below the analytical detection limit in a wide pH range. While on one hand this does not allow to infer about the geochemical mechanisms governing contaminant mobility from the S/S Halton soil, on the other hand it is an indication of the efficient immobilization of metals within the solidified matrix.

4.5.4 Summary

The Halton site was remediated by S/S to a depth of 30cm to create a thin monolithic layer, covering the entire site.

The nature of the soil dictated that the S/S material was very heterogeneous in nature, containing sulfate bearing materials and a range of metallic contaminants. The samples retrieved appeared weathered, and altered by carbonation. Ettringite was abundant in voids and cracks in the solidified soil.

The leaching of the treated material showed that the metals of concern were strongly retained within the waste form and, according to the contractor, met the unspecified targets set for the treatment.

4.6 Quarry Dump

The Quarry dump site, Georgia, comprising 4 ha, operated as a quarry in the 1800's, between 1890-1926 the site was used as a cooling pond/reservoir related to steam generation. Prior to 1965, "inert materials" were periodically disposed of in the cooling pond. Construction debris such as excavated soil, rock, and cobblestone were also disposed. Later, the site was also used to store and repair PCB-containing transformers.

The primary contaminant of concern were: TPH, PCB and PAH's. In 1992 the site underwent treatment by in-situ S/S using a 25% (Type I) Portland Cement binder.

4.6.1 Historical compliance results

No historical performance data was available for Quarry Dump

4.6.2 Sampling / new physical and leaching results

The Quarry Dump was sampled in November 2004 by the private company, which had treated the site. Samples of approximately 2 inches in diameter were recovered by wet coring.

Two samples were tested for UCS, and strengths of 1.4 and 1.2 MPa were recorded. The original design strength was 0.4 MPa, which was surpassed by both samples in this study. It should be noted that the cores were recovered from the same location on the site, therefore the data may not be representative of the entire monolith.

All three permeability samples from Quarry Dump site failed to meet the performance criteria of a maximum permeability of 10^{-7} m/s, though all were within one order of magnitude from this mark. No QA/QC data was available to show previous permeability results from site samples.

TPH was the only contaminant of concern. Four samples were tested, two of which had total concentrations greater than the detection limit. The SPLP results were below detection limit for all four samples (Table 4.24).

Table 4.24: TPH Results for the 2005 Sampling of Quarry Dump

Sample	Total Conc (mg/kg)	Conc x 10^{-3} (mg/l)
1	300	BDL
2	2100	BDL
3	BDL	BDL
4	BDL	BDL
average	1200	BDL
detection limit	300	300
performance criteria	-	-

The samples were packed in ice during shipping to the laboratory. However, some ice melted causing saturation of some of the intact samples. This water was collected and tested for TPH to determine if leaching had occurred, and TPH was found to be 1800 ug/l. This surprising result contradicted the SPLP leaching results obtained from samples 1 and 2, where TPH was not detected in the leachates. A literature search on the leachability of TPH from cement matrices was unable to shed any light on these issues.

4.6.3 Transversal testing

4.6.3.1 Microstructure and mineralogy

The major crystalline phases identified by XRD in the treated material originated in the soil, together with those resulting from the cement binder (Figure 4.51). Calcite was identified by SEM in trace amounts and was attributed to atmospheric carbonation (Figure 4.52). The sulfate-bearing phases, ettringite and gypsum were present as well developed crystals, found in voids and microcracks.

Some microcracks were partially or completely infilled with ettringite. Open microcracks were also present, most likely being due to the strain developed during sample extraction (Figure 4.52).

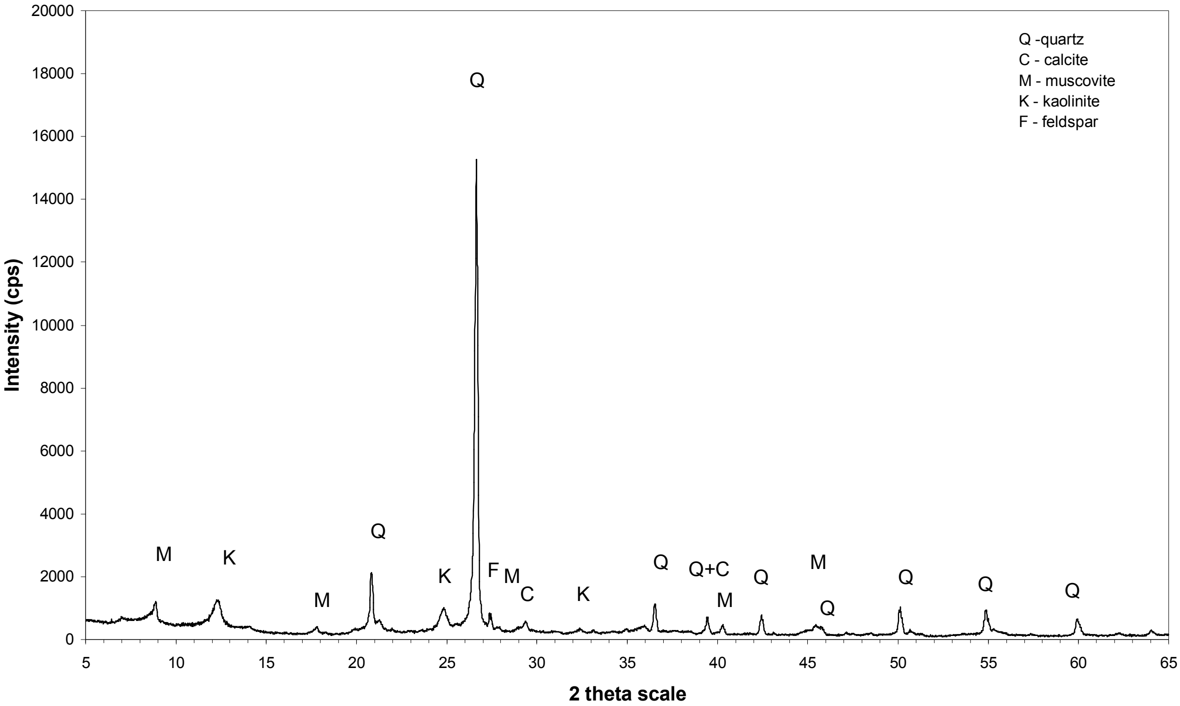

Figure 4.51: X-ray diffractogram of the treated QD soil

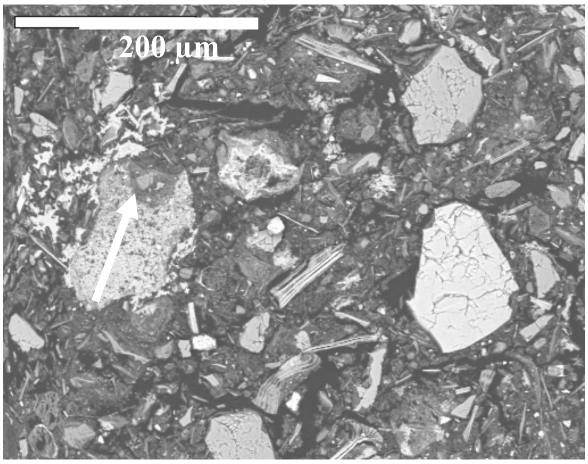

Figure 4.51: Typical microstructure of PC-treated soils from QD, showing calcium carbonate infilling voids

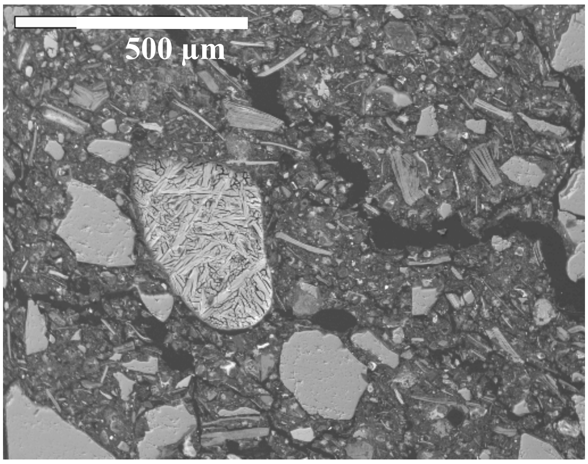

Figure 4.52: Backscattered electron micrograph of a) ettringite infilling a void and; b) open microcrack from sample extraction/handling

4.6.3.2 Chemical characterisation

The results of the elemental analysis are shown in Table 4.25.

Table 4.25: Total content analyses of the soil from Quarry Dump (mg/kg)

	concentration (mg/kg)		concentration (mg/kg)
Insoluble residue (%)	30.7-54.8	Dry mass (%)	73.6-84
Cl	130-295	Mn	147-335
Al	29523-41 367	Mo	<5
As	<5	Na	2 697-3 255
Ba	326-417	Ni	8-23
Bi	<5	P_tot	150-308
Ca	7 317-55276	Pb	13-115
Cd	<5	S_tot	1647-2206
Co	<5-10	Sb	<5
Cr	22-34	Se	<5
Cu	10-126	Si	61370-73696
Fe	12 019-23 423	Sn	<10-13
Hg	<10	Ti	1 853-2 833
K	8502-9784	V	29-60
Li	<10	Zn	51-168
Mg	2093-3538	Loss on ignition (%)	3.9-10.6

4.6.4 Summary

Only a limited amount of data was available from the remediation of the Quarry Dump site. The materials retrieved appeared to have high porosity and were moderately carbonated, with carbonate minerals, particularly infilling mirocracks. Ettringite was observed in the materials retrieved. The samples examined exhibited a greater strength than the original design criteria and leaching of TPH by SPLP was below instrument detection limits.

4.7 Columbus MGP

The former 1.6 ha Columbus MGP site, is located on the bank of the Chattahoochee river, Georgia. The privately owned site was used for various actvities from the 1850s to 1931. the main contaminants were PAH, BTEX and cyanide, including 300 mg/kg of VOC, 2,400 mg/kg of PAH, and about 5,500 mg/kg of oil and grease.

The remediation involving in-situ S/S with PC was conducted using a hollow stem auger in 1992 in an area adjacent to the river. The slurry binder contained ordinary Portland cement and water to 1:1.5 ratio at 25 percent by weight. In total, 70,000 cubic meters were treated in situ using 1,800 overlapping columns.

Treatability studies were performed for determining the appropriate mix design for the rest of the site and the criteria evaluated were UCS, permeability and leachability for PAHs. Based on the results of the study, 10 percent ordinary Portland cement binder met best the established remedial goals.

Approximately 65,000 cubic meters of soil, from areas away from the River were excavated and segregated into "affected" and "non-affected", with the former soils being returned to the site and stabilized to a maximum depth of 4.5 m, followed by compaction, and slopping to assure the drainage. The entire area treated was covered with a 60 mm HDPE liner. The "non-affected" soils, previously excavated were used as backfill over the liner and compacted. The remainder was used in other application off site (e.g. daily cover for a landfill)

Following remediation the site was donated to the city for use as part of a riverside redevelopment and it is currently used as intended (Figure 4.53).

4.7.1 Historical compliance results

The Columbus MGP, Georgia, manufactured gas plant site was remediated in 1992, by the Georgia Power Company and other private parties using in situ S/S applied through use of a large hollow stem auger. Ten years later, In 2003, the Electric Power Research Institute (EPRI), in cooperation with other private parties, conducted a 10 year evaluation of the continued effectiveness of this remedial operation. Cored samples were obtained and tested for geotechnical properties, solid phase geochemistry, contaminant analysis, leach testing, and groundwater modelling.

The EPRI evaluation concluded that “the structural integrity and geochemical nature of the solidified mass continues to exceed the original performance standards established prior to implementation of S/S and that data reveal no evidence that long term future integrity of the site would be less stable than current site conditions (EPRI, 2003).

4.7.2 Sampling / new physical and leaching results

The Columbus MGP site was sampled in November 2004, as a follow on sampling to the EPRI sampling cited above, and were furnished as a courtesy by Richard Esposito, Southern Companies. An attempt to recover material dry, without water to cool the drill, was made, but a cable on the drill rig broke during the process (Figure

4.54). A second attempt was not made due to inclement weather and time limitations. One dry sample was recovered from the first attempt. All other sampling material was collected using water during the coring process (Figure 4.55). Cores of approximately 5 cm in diameter were successfully recovered.

Figure 4.53: View from the treated area at the Columbus MGP

Figure 4.54: Drilling rig at the Columbus MGP

Figure 4.55: Core barrel collection at the Columbus MGP

The Columbus MGP consisted of two different S/S mixes. The majority of the site was mixed to a cement content of 10%, but a higher cement content of 25% was used at the outer edge of the site adjacent to the river. Strength results from the 2004 sampling are present in Figure 4.56 and indicate the percent cement in the materials tested. Ironically, the single 25% cement sample was considerably lower in strength than the three 10% cement samples.

The same site was sampled in 2002 as part of a separate study. These results showed the 25% cement mix to have a higher average strength than the 10% cement mix samples, but the ranges of the two mixes overlapped (see Figure 4.57).

It should also be noted that the unconfined compressive strengths in the 2002 sampling were notably higher, regardless of cement content, than the 2004 samples. Both of the 2002 and 2004 samples, were collected by the same drilling company and is it believed that the sampling was done in the same manner. The 2002 review concluded that the structural integrity and geochemical nature of the solidified mass continues to exceed the original performance standards established prior to implementation of S/S and that data reveal no evidence that long term future integrity of the site would be less stable than current site conditions (EPRI, 2003).

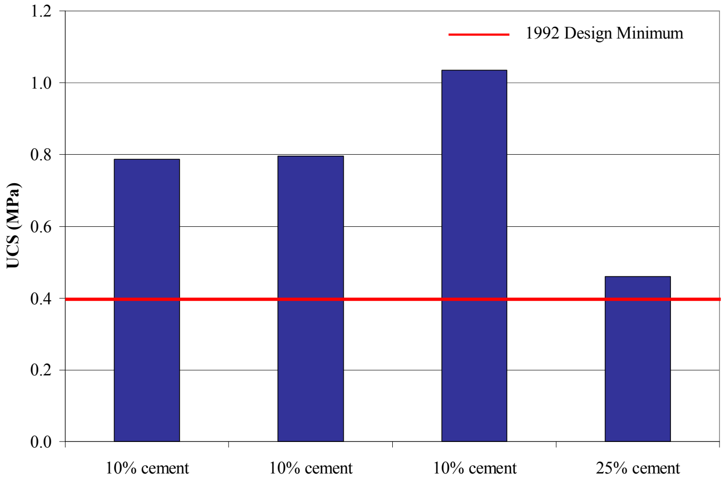

Figure 4.56: UCS Results for the 2004 Sampling of the Columbus MGP

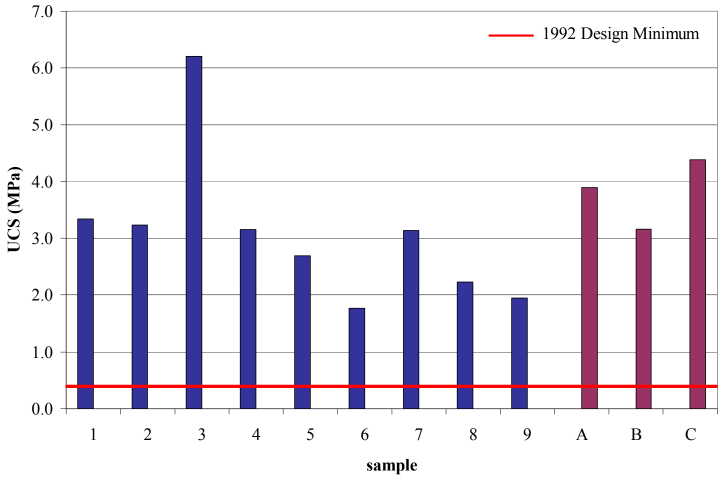

Figure 4.57: USC Results for the 2002 Sampling of the Columbus MGP (sample 1-9 contain 10% cement; samples A-C contain 25% cement)

The 2002 strength values were collected using ASTM C39, while the 2004 UCS values were collected using method ASTM D1633. The 2004 UCS results averaged over 0.69 MPa, as compared to a design minimum of 0.41 MPa, and were similar to those of the 1992 QA/QC samples, which were tested after 28 days of ex situ curing. There is no reason to believe that the difference in strength measurement method (C39 or D1633) would result in the systematic bias shown in the data. The average results from 1992, 2002, and 2004 for the 10% cement S/S material are presented in Figure 4.58.

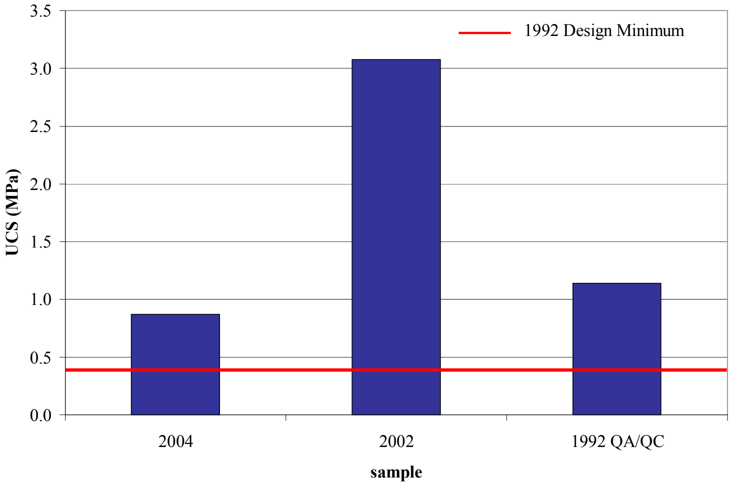

Figure 4.58: UCS Results for the 1992, 2002, and 2004 sampling of the Columbus MGP site

Permeability (ASTM D5084) of the four samples indicated values very close to, but just greater than, the design permeability of $1\text{x}10^{-7}$ m/s (Figure 4.59). However the values were close to the design specification; the observed difference may have been caused by micro fractures induced by the coring operation.

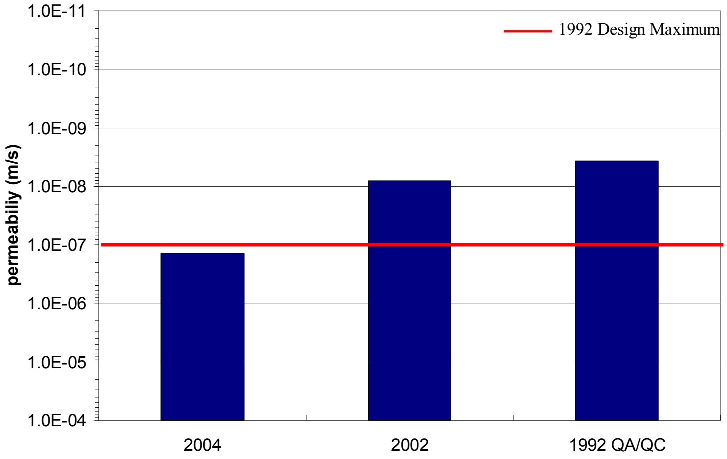

Figure 4.59: Permeability Results for the 1992, 2002, and 2004 sampling of the Columbus MGP site

All the permeability samples for the 2004 sampling demonstrated permeabilities slightly greater than the design maximum of 10^{-7} m/s. There was no difference in permeability or strength between the 25% cement mix region and the 10% cement mix region for either the 2004 or 2002 sampling events (Figs 4.60, 4.61).

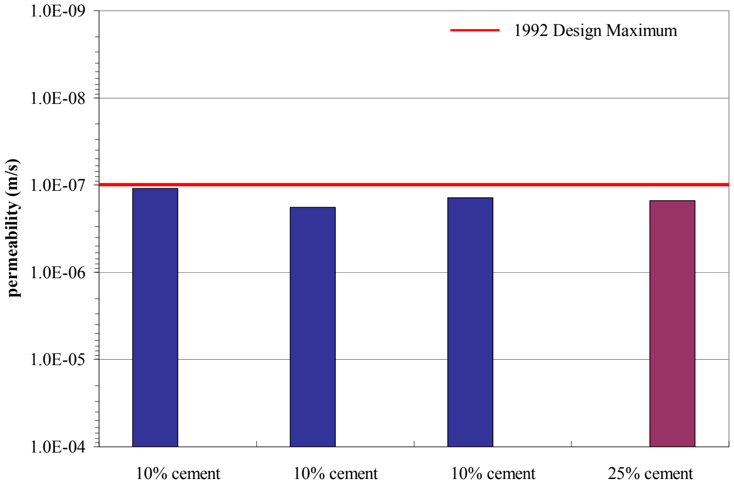

Figure 4.60: Permeability Results for the 2004 sampling of the Columbus MGP site

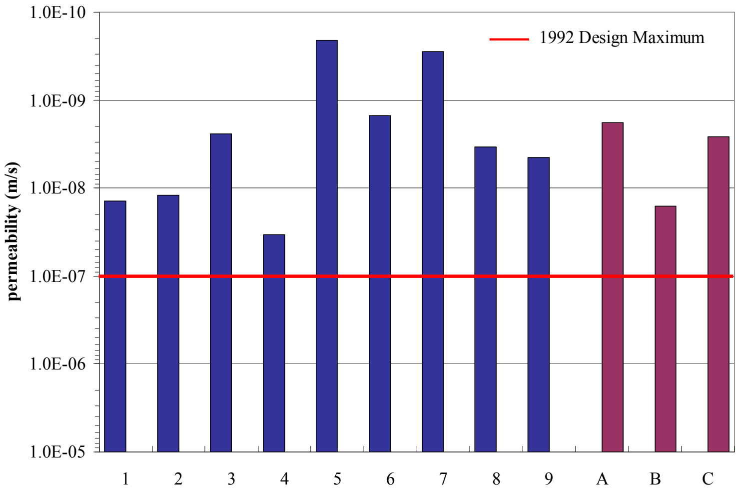

Figure 4.61: Permeability Results for the 2002 sampling of the Columbus MGP site

The Columbus MGP material was tested for total and leachable cyanide and total and leachable PAH. There were no performance criteria set the Columbus MGP. The cyanide results showed an average value of 1.4 µg/l for SPLP leaching, below the 200 µg /l MCL, and an average of 19.5 µg /g for total concentration (Table 4.26).

Table 4.26: SPLP leaching Results for the 2004 Sampling of the Columbus MGP

Sample	Cyanide		PAH	
	Total (mg/kg)	Leaching Conc x 10^{-3} (mg/l)	Total (mg/kg)	Leaching Conc x 10^{-3} (mg/l)
1	18	BDL	169	457.1
2	19	0.31	117.5	372.9
3	29	0.07	82.3	398.6
4	25	0.29	97.9	402.2
5	25	4.9	90.4	229.8
average	19.5	1.4	111.42	372.1
quant limit	1	0.02	0.7	0.8
performance criteria	-	-	-	-

Total PAH results show leaching of PAHs in all samples. An average total concentration of 111.42 µg/g and an average SPLP result of 372.1 µg/l were determined. The most predominant PAH contaminants in the leachate were naphthalene, 2-methylnaphthalene and acenaphthylene. Similar results were shown in a 2002 study of the same site, though a different leaching method was employed (EPRI, 2003).

4.7.3 Transversal testing

4.7.3.1 Microstructure and mineralogy

The saprolitic soil at the Columbus site was examined by XRD eleven years after S/S with Portland cement and was dominated by the presence of clay minerals, quartz and feldspar (Figure 4.62).

No cement crystalline hydration products or secondary phases were observed in any of the three samples analysed. Hydration products were of a non-crystalline nature.

Smectite was readily identified, however, calcium carbonate was absent, despite vaterite and calcite being reported as present in the past (EPRI, 2003). Although, vaterite is unstable, and rarely found in nature, it may result from the natural carbonation of C-S-H gel, before conversion to calcite (Fernandez-Bertos et al., 2004). The discrepancy with results previously reported may reflect the inhomogeneous nature of the cement-stabilised waste form.

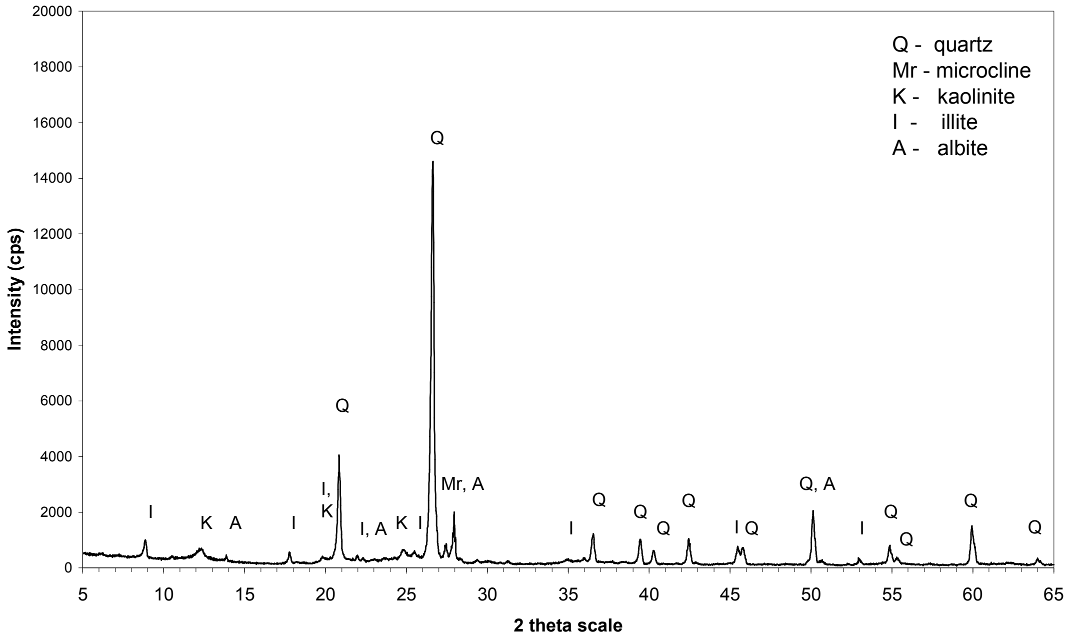

Figure 4.62: X-ray Diffractogram of Columbus MGP soils

The cores recovered from the site were largely intact. However, under closer scrutiny (and with the aid of a microscope) a large number of porosity was present, up to 500 µm in diameter. Calcium carbonate was commonly found infilling larger pores and microcracks, as illustrated in Figure 4.63. Ettringite was also observed partially or completely infilling voids, as shown in Figure 4.64.

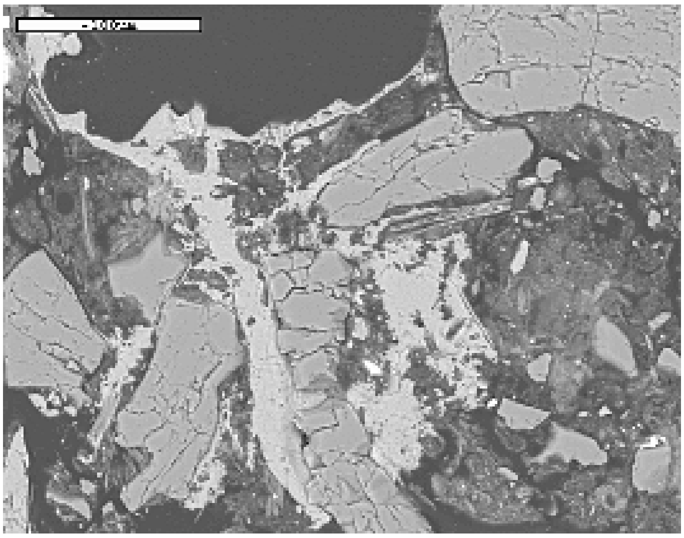

Figure 4.63: Backscattered electron image of calcium carbonate infilling in voids and cracks in Columbus MGP soils

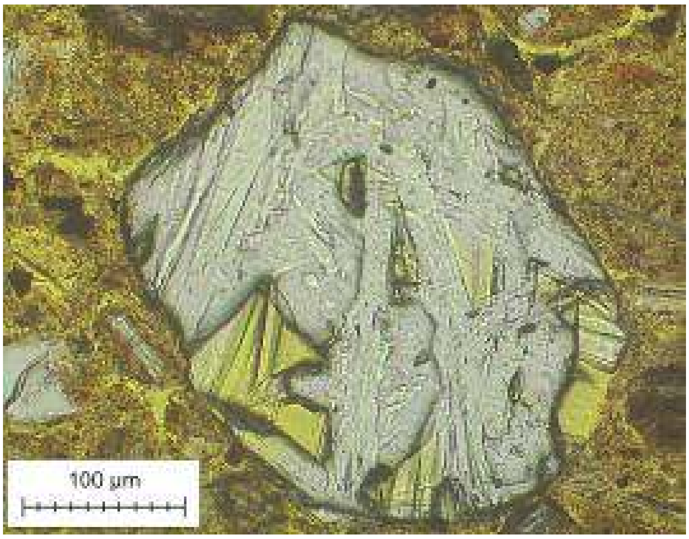

Figure 4.64: Transmitted light micrograph of ettringite infilling a large void in Columbus MGP soils

The Columbus MGP material was tested for total and leachable cyanide and total and leachable PAH. There were no performance criteria set the Columbus MGP. The cyanide results showed an average value of 1.4 µg/l for SPLP leaching, below the 200 µg /l MCL, and an average of 19.5 µg /g for total concentration (Table 4.27). Total PAH results show leaching of PAHs in all samples. An average total concentration of 111.42 mg/kg and an average SPLP result of 372.1 µg/l were determined. The most predominant PAH contaminants in the leachate were naphthalene, 2-methylnaphthalene and acenaphthylene. Similar results were shown in a 2002 study of the same site, though a different leaching method was employed (EPRI, 2003).

Table 4.27: SPLP leaching results for the 2004 sampling of the Columbus MGP

Sample	Cyanide		PAH	
	Total (mg/kg)	Leaching Conc x 10^{-3} (mg/l)	Total (mg/kg)	Leaching Conc x 10^{-3} (mg/l)
1	18	BDL	169	457.1
2	19	0.31	117.5	372.9
3	29	0.07	82.3	398.6
4	25	0.29	97.9	402.2
5	25	4.9	90.4	229.8
average	19.5	1.4	111.42	372.1
quant limit	1	0.02	0.7	0.8
performance criteria	-	-	-	-

4.7.4 Summary

The Columbus site was one of the oldest sites evaluated in this study, being remediated in 1992. During a privately funded ten-year study the site was shown to be exceeding performance specifications. The results of the 2004 sampling showed higher strengths that the design minimum.

The leaching of cyanide was also shown to be below drinking water limits and PAHs leaching was similar to previous 2002 levels, despite different procedures being used. Permeability results were marginal, most likely due to fracturing of samples during extraction. The results indicate that the Columbus site continues to perform satisfactorily with time.

4.8 Caerphilly

The Castle Mews site is located in Caerphilly, South Wales and covers an area of 0.27 ha. A variety of metals (arsenic, cadmium, lead, mercury) and organics (polyaromatic hydrocarbons-PAHs and other petroleum hydrocarbons) were present, with the metal contaminants generally being below the acceptable limits (ICRCL, 1983). The organic contaminants, however, exceeded the regulatory limits. The site was treated in -situ by a cement-based binder system in early 2006. Treatment was applied to a maximum depth of 1.5 m and the waste form was covered by 0.5 m of made ground (CELTIC, 2006). The site has undergone redevelopment for residential use.

4.8.1 Historical compliance results

There were no specific remedial targets established for final strength of the treated material or its permeability. However, the guide values for strength were 100 to 200 kPa and for a permeability of 10^{-8} m/s. The performance indicators for leaching of organic contaminants (using the NEN 7375 tank test) were 0.8 mg/l TPH and 0.1 mg/l PAH, although it should be noted that these were indicative only. Six-month tank leaching tests were performed on the treated soil by Celtic Technologies Ltd as part of the validation process, between 28 days and 6 months. The results are shown in Table 4.28 (CELTIC, 2006).

Table 4.28: Six-month tank test (NEN 7375) leaching results

Contaminant	28 days	2 months	3 months	6 months
PAH (mg/l)	0.47	0.44	0.31	0.18
TPH (mg/l)	0.47	0.81	0.66	0.48

4.8.2 Sampling / new physical and leaching results

The Caerphilly site was sampled shortly after completion, in June 2006. A window corer with an air mist was used to recover cores (1.5 m long and 9.8 cm diameter) to the full depth of the treated soil (Figure 4.65). The majority of the cores recovered were visibly cracked (Figure 4.66).

Figure 4.65: Window corer used to extract the soil samples

Figure 4.66: Core recovered from Caerphilly site; scale 30 cm

4.8.3 Transversal testing

4.8.3.1 Microstructure and mineralogy

The Caerphilly site was the ‘youngest’ site examined during this study, at 6 months after the remedial operation. The mineralogy of the waste form was dominated by the soil-derived minerals quartz, feldspar, kaolinite, and by ettringite, resulting from the cement-based binder (Figure 4.67). Calcite was present and may have been derived from the soil. The presence of portlandite was identified by thermogravimetry (TG) through the characteristic thermal event at approximately 480ºC. Crystalline and poorly crystalline calcium carbonate, were present, as indicated by endotherms at 580 and 700ºC respectively.

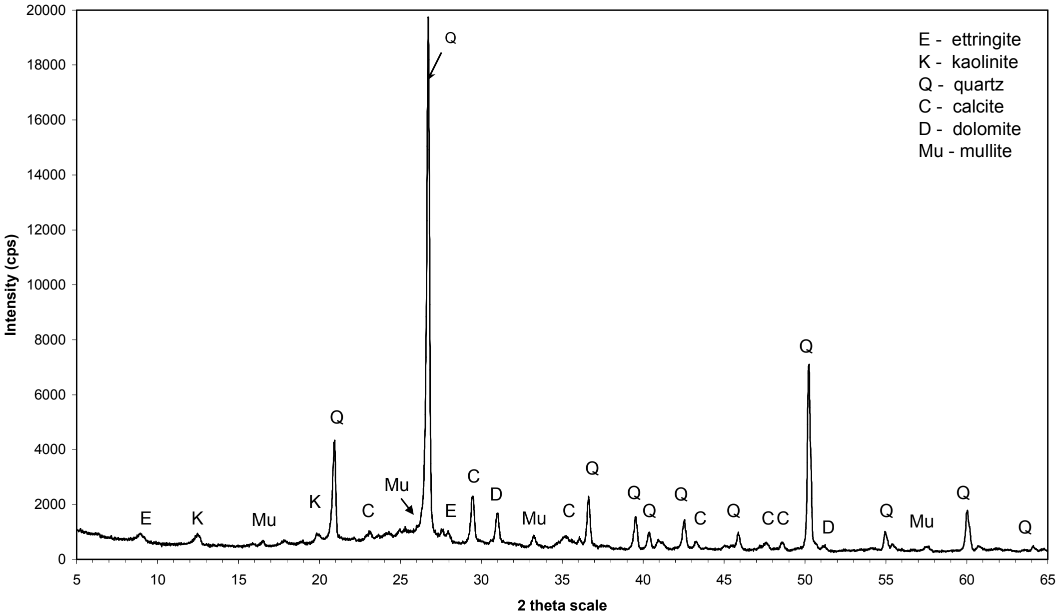

Figure 4.67: X-ray diffractogram from the treated Caerphilly soil

The cement-treated soils were finely grained, with numerous fragments of quartz, dolomite and calcite (Figure 4.68). Other remnants of the binder blend were also observed. The cores retrieved from the ground were poorly indurated and contained numerous visible fractures and those were observed by optical and scanning electron microscopy as clean, wide (up to 50 µm) cracks.

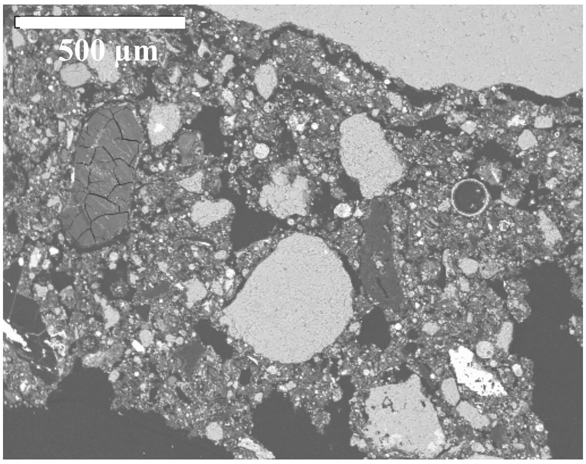

Figure 4.68: Backscattered electron micrograph of the treated soil and x-ray spectra of the iron sulfide particles of interest

Euhedral calcium carbonate was seen infilling the voids between the larger grains of quartz (up to 0.5 mm), limestone and the hydrated cement grains. Figure 4.69 shows an iron-rich particle and the re-precipitation around the grain boundary (as iron sulfide) up to 100 µm away, resulting in its cementation to adjacent quartz grains. This phenomenon was observed isolated in the microstructure of the stabilised soil.

Microcrystalline ettringite was identified in the matrix at high magnification. The formation of ettringite at early age is not normally deleterious in nature.

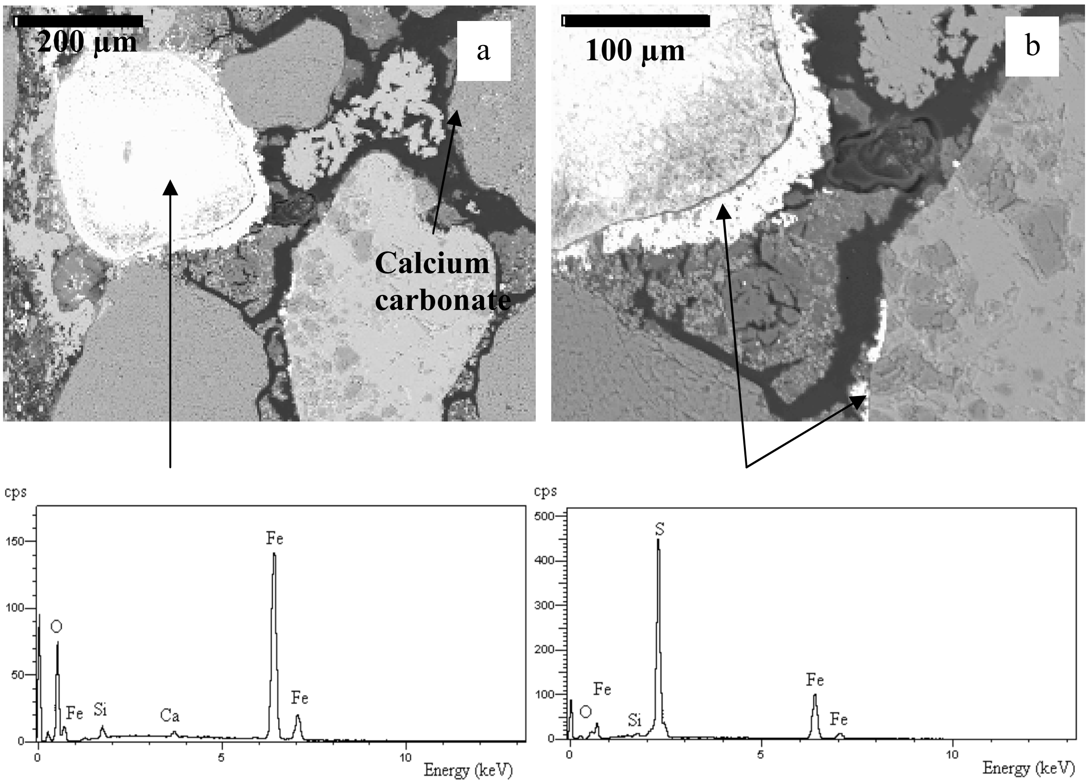

Figure 4.69: Backscattered electron micrograph and corresponding X-ray spectra of iron sulfide particles/precipitates in the Caerphilly soils

4.8.3.2 Chemical characterisation

The results of the elemental analysis carried out on the Caerphilly samples are shown in Table 4.29.

Table 4.29: Total content analyses of the treated soils from Caerphilly (mg/kg)

Depth	0.5 m	1.5 m	2.5 m	Depth	0.5 m	1.5 m	2.5 m
Dry matter (%)	75.82	78.23	76.55	Insoluble residue (%)	22.5	25.22	39.05
Al	36 904	37 516	34 907	Mo	<5	<5	<5
As	10	11	<5	Na	2 316	3 803	1 672
Ba	817	782	241	Ni	42	38	30
Ca	55 436	52 713	2 287	P_tot	1 353	1 096	183
Cd	<5	<5	<5	Pb	236	179	19
Co	16	14	11	S_tot	2 354	2 041	992
Cr	57	49	52	Sb	<5	<5	<5
Cu	93	80	29	Se	<5	<5	<5
Fe	30 500	30 533	10 271	Si	79 774	75 703	84 857
Hg	<10	<10	<10	Sn	41	30	<10
K	8 266	8 160	10 032	Ti	2 229	1 919	2 166
Mg	8 229	10 625	2 165	V	69	61	71
Mn	558	515	136	Zn	506	334	112
Loss on ignition (%)	16.1	15.53	15.18				

4.8.4 Summary

The Caerphilly site was the youngest site examined during this investigation, at an age of less than 1 year old. The material was of relatively low strength, and was not investigated by leaching. Examination of the retrieved material by SEM indicated the presence of ettringite and carbonate, but the latter is unlikely to result from the effects of carbonation. These observations are in accordance with those obtained from many of the other sites and indicate that the treated material at the Caerphilly site, is behaving similarly.

5. Site by site study: Wastes

5.1 Bellegarde

The Bellegarde site is located in the south of France, near Nîmes. Until 1979 this was the site of a quarry. The extraction of marls left a pit underlain by 500 m of impermeable natural clay. In 1993, part of the site was licensed for the disposal of hazardous waste, with a stabilisation unit being operational from 1995. Disposal activities ceased in 2001 and the site has been subject to restoration and re-development, partially for the biological treatment of organically contaminated soil. A second area of the site, covering 36 ha has been actively receiving S/S waste since 2001. The wastes treated were mainly ashes from MSW incineration, which contained high levels of chloride, sulfate, lead and zinc. The treated waste was disposed in storage cells incorporating a geomembrane, integral drainage and a leachate collection facility, and covered with membrane, clay and topsoil.

The waste treatment objectives are governed by French law and are presented in Table 5.1.

Figure 5.1: Aerial photograph of the Bellegarde site

Table 5.1: Waste acceptance criteria for Bellegarde

Parameter	1992 threshold	Parameter	1992 threshold
TDS	< 10 % DM	Cr tot	< 50 mg/kg WM
pH	4-13	Hg	< 5 mg/kg WM
COD	< 2000 mg/kg WM	Ni	< 50 mg/kg WM
As	< 10 mg/kg WM	Pb	< 50 mg/kg WM
Cd	< 25 mg/kg WM	Zn	< 250 mg/kg WM
Cr6	< 5 mg/kg WM	CN	< 5 mg/kg WM
Phenol index	< 100 mg/kg WM		

DM : dry mass, WM : wet mass

5.1.1 Historical compliance results

Results obtained on samples are summarized in the Table 5.2. These results showed that the Bellegarde samples complied with the stabilization/solidification objectives.

Table 5.2: Compliance results obtained from testing the core samples obtained from Bellegarde

Parameter	Limit values	Historical data	Current data
DENSITY (G/CM^3)			1.46-1.7
TDS (% DM)	< 10	4.4-9.5	3.5-9.2
pH	4 to 13		10.9-11.8
UCS (MPa)	> 1	1.1-10.5	1.5-9.3
COD	< 2000	< 300-1140	< 300-570
Phenol index	< 100	< 1.5-1.6	< 1.5
CN	< 5	< 4.5	< 4.5
As	< 10	< 1.5	< 1.5
Cd	< 25	< 1.5	< 1.5
Cr	< 50	1.6	< 1.5
Hg	< 5	3	< 1.5-2.1
Ni	< 50	8	< 1.5
Pb	< 50	< 1.5	< 1.5
Zn	< 250	< 1.5	< 1.5

Average of three replicates. Values expressed in mg/kg of wet matter, except otherwise specified.

5.1.2 Sampling/new physical and leaching results

The sampling of the Bellegarde site was carried out in October 2005. The area selected for sampling on the Bellegarde site is the one of the first cell that was not yet redeveloped at that time (Figure 5.2). The area allows having access to relatively old (before 2001) stabilized waste, which was left without any cover since the disposal, therefore left in very unfavorable conditions as compared with the usual conditions of working in storage centers. The two sampling points were selected from topographical plans in order to avoid location in the edge of daily plots.

Figure 5.2: Aerial photograph of the sampling area and the sampled cells

The sampling method was selected after consultation with several drilling companies according to the site conditions and the testing requirements:

- Carrying out non-destructive drilling, as the aim is the recovery of cores;
- Drilling depth of at least 5 meters;
- Hardness of stabilized waste to be cored: compressive strength between 1 and 10 MPa.

Given these conditions, the method selected was water coring using a 10 cm diameter core barrel (Figure 5.3).

For the reproduction of the compliance tests in place at the time where the stabilized waste was treated (i.e. before 2001), it was necessary to prepare the core bored samples in order to bring them to the standardized test pieces size, i.e. 8 cm in height and 4 cm in diameter. Dry cutting in 4 cm diameter was thus made in February/March 2006 over different sections of cores (Figure 5.4).

Figure 5.3: Image of the drilling machine used and an example of typical cores extracted

Figure 5.4: Photograph of a fragment of core after dry cutting operation to obtain the specimens for laboratory testing

The cut samples were kept in a waterproof bag before carrying out the mechanical tests and the leaching tests.

5.1.3 Transversal testing

For interpretation purpose, transversal testing and conclusions will be presented together with SEDA site results in the following section.

5.2. SEDA

The SEDA site is located in West part of France, near Angers and, as Bellegarde site, operated by SITA company under the same rules and processes.

Part of the site was exploited between 1978 and 1996 for the disposal of mixed, but zoned storage for sanitary refuse, non-hazardous and hazardous waste. The site was closed in 1996 and landscaped. The active part of this site began taking waste in 1993, and from 1995 this material has been pre-treated by S/S. Since 2004, approximately one third of the 10 ha site has been dedicated to the disposal of household refuse and is exploited separately. For hazardous waste, the regulation and waste treatment criteria are the same ones as in Bellegarde site.

5.2.1 Historical compliance results

Results obtained on samples are summarized in the Table 5.3. The results are complying with the stabilization/solidification treatment objectives and are in the range of results generally obtained on the site.

Table 5.3: Compliance results obtained from testing the core samples obtained from Bellegarde

Parameter	Limit values	Historical data	Current data
DENSITY (G/CM^3)	< 10	2.1-10	1.31-1.78
TDS (% DM)	4 to 13		4.29-10
pH	> 1	1.1-12.3	11.0-11.5
UCS (MPa)	< 2000	< 300-1300	3.6-11.8
COD	< 100	< 1.5-1.6	< 300-690
Phenol index	< 5	< 4.5	< 1.5
CN	< 10	< 1.5	< 4.5
As	< 25	< 1.5	< 1.5
Cd	< 50	< 1.5	< 1.5
Cr	< 5	< 1.5-3	< 1.5
Hg	< 50	< 1.5-8	< 1.5
Ni	< 50	< 1.5	< 1.5
Pb	< 1.5	< 1.5	< 1.5
Zn	< 250	< 1.5	< 1.5

Average of three replicates. Values expressed in mg/kg of wet matter, except otherwise specified.

5.2.2 Sampling/new physical and leaching results

Sampling operation took place in 2005 on an area which was not yet redeveloped. The stabilised material was just covered by about 30 cm of top soil as an intermediate cover, which has been removed for final cover installation.

The same methodology as for the Bellegarde site was followed (Figure 5.5):

-Water coring using a 10 cm diameter core barrel on site;

-Dry coring in laboratory to prepare adequate samples for compliance testing (4 cm diameter x 8 cm height).

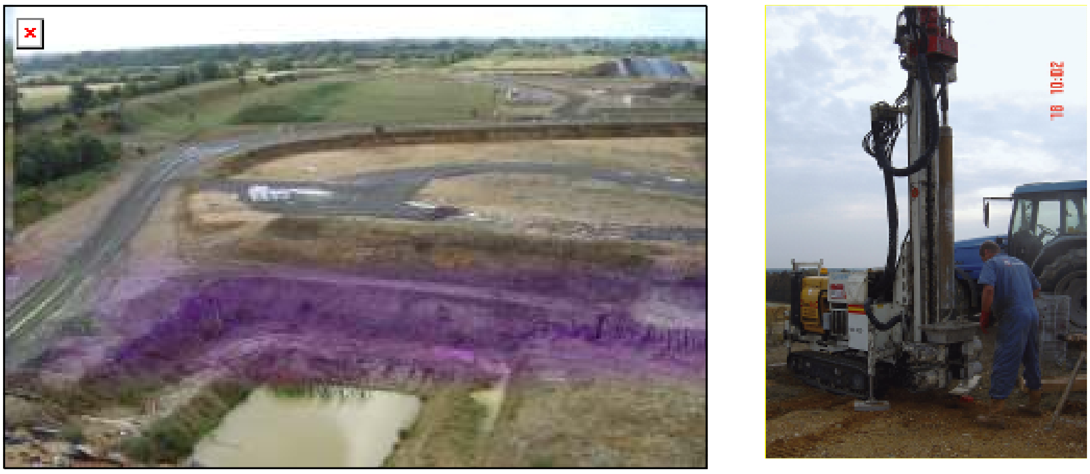

Figure 5.5: SEDA site and the drilling equipment used

5.2.3 Transversal testing

5.2.3.1 Sample selection

According the large number of samples obtained from both sites, it was very important for transversal testing to choose a reduced number of samples to be able to perform deep examinations.

As the processes applied on both sites are quite similar and according to the historical data and compliance results, it was not considered as relevant to examine each site separately for the next steps of the study (which would have lead to study similar samples from both sites).

On the contrary all samples were considered together as a “picture” of stabilised / solidified hazardous waste, treated following French rules, which could be compared to the laboratory samples examined in previous studies performed during the development of treatment processes (SITINERT, Magnié and al 1998, Lambolez-Michel 2000 and 2001, Brault 2001), specially concerning mineralogical species and long term leaching behaviour, with, as a general objective, to determine whether and how the properties of SS waste are changing after several years of storage on site in real conditions.

A multicriteria approach was used by INERTEC and LEM to select this reduced number ofsamples, in order to have the widest possible range of stabilised/solidified hazardous waste. The type of treated waste, the evolution of compliance results compared to historical quality control data provided by the site owner (see Figs 5.6, 5.7) and the estimated time of exposure to air were considered for this selection.

For the type of treated waste on both sites, TDS is the most sensitive parameter on compliance leaching test. Therefore evolution of TDS and UCS between historical results and 2006 results was considered in the multicriteria approach. Finally, five samples were selected for the detailed study and are presented in Table 5.5, in order to cover a wide range of stabilised / solidified waste materials.

Table 5.5: Samples selected for the study (MSW: Wet MSWI fly ashes and APC residues; MSS: Semi-wet MSWI fly ashes and APC residues semi wet; IS: ISWI fly ashes and APC residues)

Sample	Date of treatment	Type of mixed waste	Time of exposure to air
1569	28/12/2000	MSS/IS/industrial sludge: 40/40/20	2.5 months
1586	31/08/1999	MSS + MSW/industrial sludge: 60/40	1 year
2076	19/05/1999	MSS/industrial sludge: 80/20	0 month
2086	26/07/2000	MSS+MSW/industrial sludge: 90/10	3 months
2087	29/07/1998	IS/industrial sludge: 70/30	10 months

5.2.3.2 Microstructure and mineralogy

A number of mineral phasess were identified by XRD, including soluble salts, hydrocalumite, calcite and Portlandite (see Appendix A).

One major observation is that, despite their high solubility, halite and other salts remain in the site for over 6 years. Figure 5.8 shows that the various samples analyzed are relatively homogeneous as far as the presence of major phases is concerned. Therefore, despite the variability of the waste, the same phases are found after stabilization/solidification.

Hydrocalumite represents one of the hydration products commonly formed at the treatment of MSWIs by S/S, which was identified frequently even at low magnifications. In some samples, ettringite was abundant and was observed in different locations in the microstructure lining voids and cracks, in the matrix or within fly ash cenospheres (Figure 5.9).

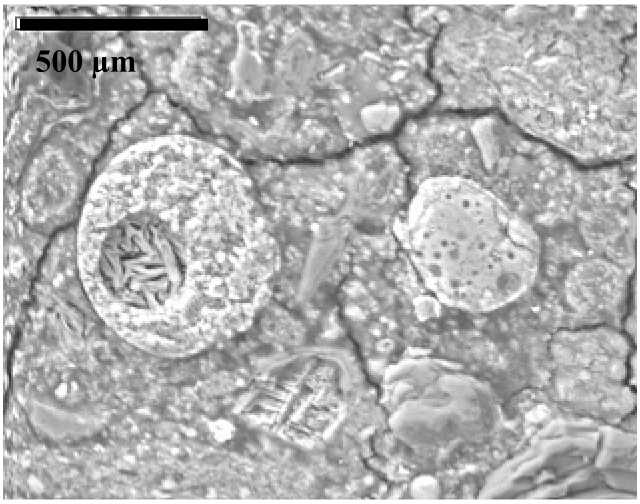

Figure 5.9: Ettringite needles growing inside fly ash cenosphere

The particular sample was criss-crossed by numerous microcracks, believed to be caused by drying shrinkage during sample preparation. However, pre-existing microcraking was also identified in the microstructure by the presence of calcium depletion in immediate adjacent matrix, as illustrated in Figure 5.10.

Where alumina was deficient and sulfate levels high, ettringite was observed, together with euhedral crystals of gypsum growing in adjacent voids or at aggregate edges (Figure 5.11). Calcite formed localized in the matrix, along microcraks and at the aggregate boundary.

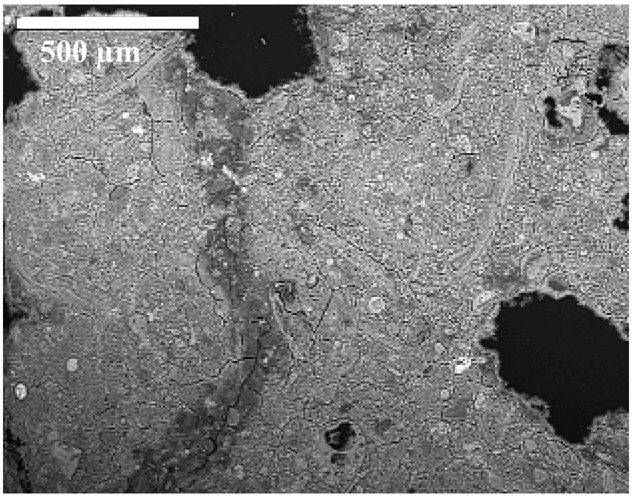

Figure 5.10: Backscattered electron image of a microcrack and decalcified matrix around the microcrack

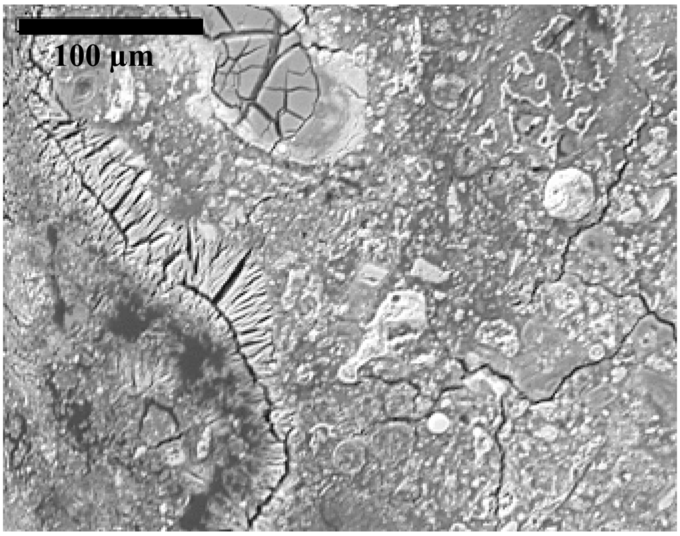

Figure 5.11: Backcattered electron image of ettringite growing along a microcrack

5.2.3.3 Modelling

LeachXS results

Geochemical speciation modelling was conducted for French sample 2087. One of the unique aspects of this modelling exercise was that the details of the treatment were not known. Modelling conducted with the aqueous phase species measured in the leach tests was unsuccessful for some typically well-described elements such as Pb. Figure 5.12 shows the agreement between the model and measured data for Pb from sample 2087, and demonstrates a significant deviation at low pH values (from approximately 4 to 8). In order to attempt to describe this data, hydrous ferric oxide (HFO) was added as a sorptive phase. Concentrations of HFO were varied in order to attempt to match trace element data to that measured (N.B. extraction procedures are available to measure this adsorptive phase, although they were not used in this work to provide an independent measure of the HFO concentration).

Figures 5.12 through 5.17 show modelling results for sample 2087 with addition of HFO as a sorptive phase. Addition of HFO permitted the ability to more closely match experimental data particularly at low pH values (between 3 and 8). The solid-liquid partitioning graphs show the significance of HFO sorption in reducing the aqueous phase concentrations of Cu, Pb, and Zn. It should be noted that the detection limits for Cu, Pb, and Zn are reflected in the graphs where each graph levels off (approximately $1x10^{-6}$ M for Cu and Zn and $2x10^{-7}$ M for Pb. Regardless of whether iron was added as part of the S/S formulation for this sample, it is clear from this modelling work that addition of HFO can have significant benefits in reducing the leaching concentration of these three elements.

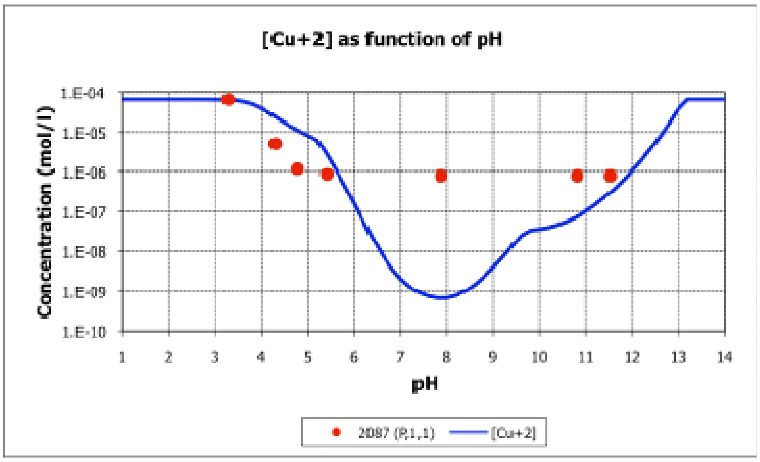

Figure 5.12: pH-dependence leaching data and modeling results for Cu

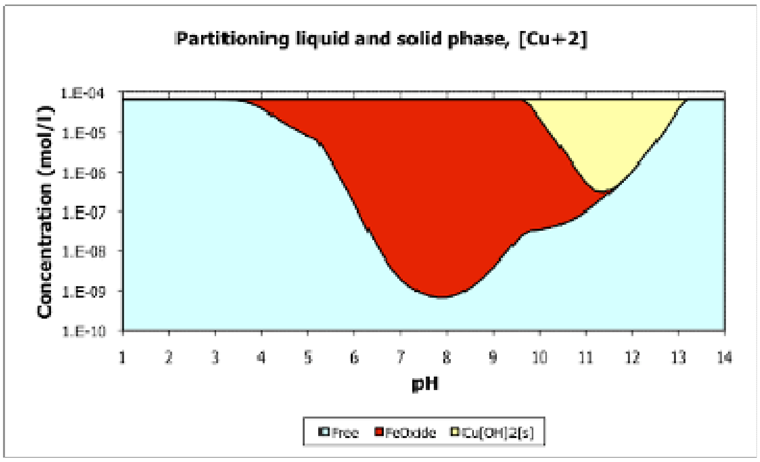

Figure 5.13: Model prediction of the solubility limiting phases for Cu leaching,

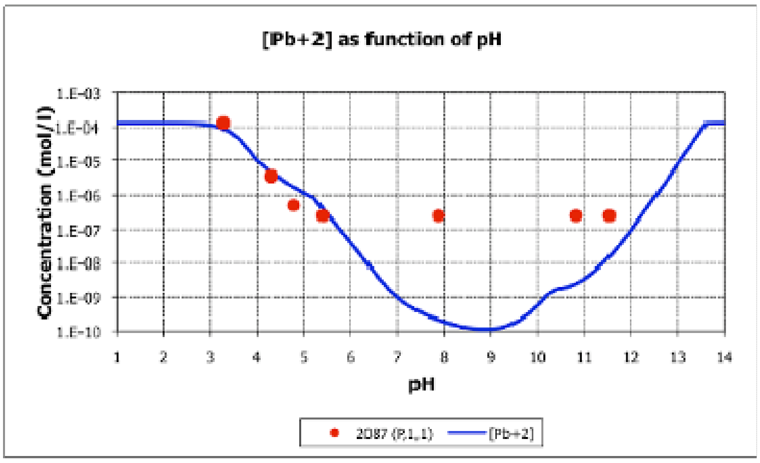

Figure 5.14: pH-dependence leaching data and modeling results for Pb

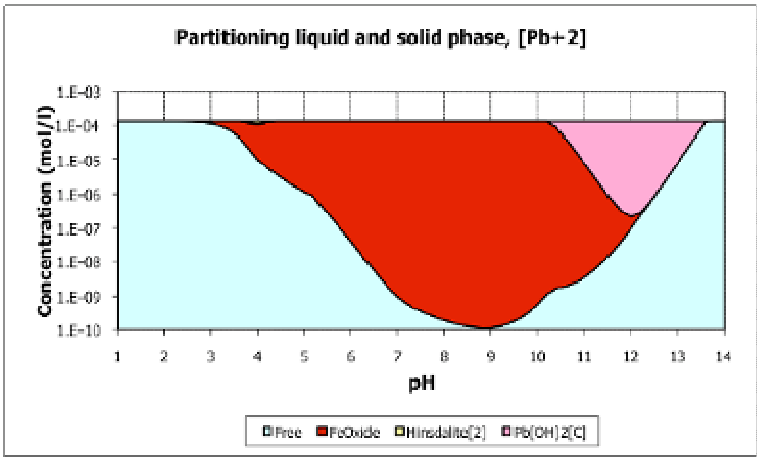

Figure 5.15: Model prediction of the solubility limiting phases for Pb leaching, in function of pH

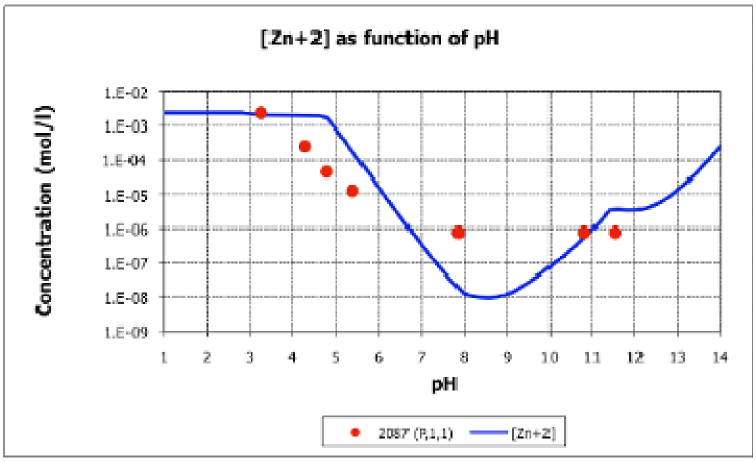

Figure 5.16: pH-dependence leaching data and modeling results for Zn

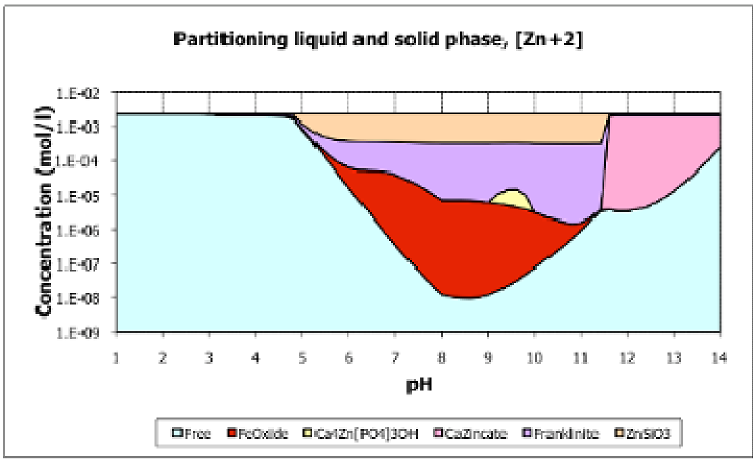

Figure 5.17: Model prediction of the solubility limiting phases for Zn leaching, in function of pH

Visual Minteq results

The modeling results obtained for two samples believed to come from Bellgarde (samples A and B) using Visual Minteq are reported in Figure 5.18 and Figure 5.19, respectively. The plots compare the measured concentrations of major elements and sulfate in the leachate as a function of pH with the predicted solubility curves of solid phases selected as potential candidates for solubility control.

A number of solid phases, including (hydr)oxides (gibbsite [$Al(OH)_3$], boehmite [$AlO(OH)$], diaspore [$AlO(OH)$]) and gehlenite hydrate (also known as strätlingite, an AFm phase having the composition $2CaO{\cdot}Al_2O_3{\cdot}SiO_2{\cdot}8H_2O$) were selected as potential solubility-controlling phases for Al. Considering that the data points in the pH range 6–10 were plotted at the analytical detection limit for Al and therefore may actually represent lower concentrations in solutions, boehmite and diaspore are both considered good candidates for leaching control of Al even though the eluates appear to be oversaturated in such phases in this pH interval. Solubility control be gehlenite hydrate may occur at high pH values (≥ 11) only.

The leaching of Si appears to be controlled by either tobermorite (a calcium silicate hydrate of the C-S-H solid solution series having a Ca/Si ratio of 0.83) or gehlenite hydrate at alkaline pH values. In this range the same phases along with Friedel's salt were also selected as potential solubility-controlling minerals for Ca; Friedel's salt, also known as hydrocalumite, was also detected by XRD analyses (see above), thus indicating the role of chloride-containing phases in dictating the leaching behavior of elements in the S/S material.

In the acidic pH range, Ca leaching was found to be governed by sulfate phases, with anhydrite giving the best fit with the measured leachate concentrations. Anhydrite was also shown to match the experimental sulfate release data up to pH 10. At higher pH values the eluates were found to be slightly oversaturated in ettringite, although the shape of the solubility curve for this phase appeared to adequately describe the measured sulfate concentrations in solution.

The leaching of Mg was observed to be described by either brucite ($Mg(OH)_2$) or forsterite (Mg_2SiO_4, a nesosilicate of the olivine group).

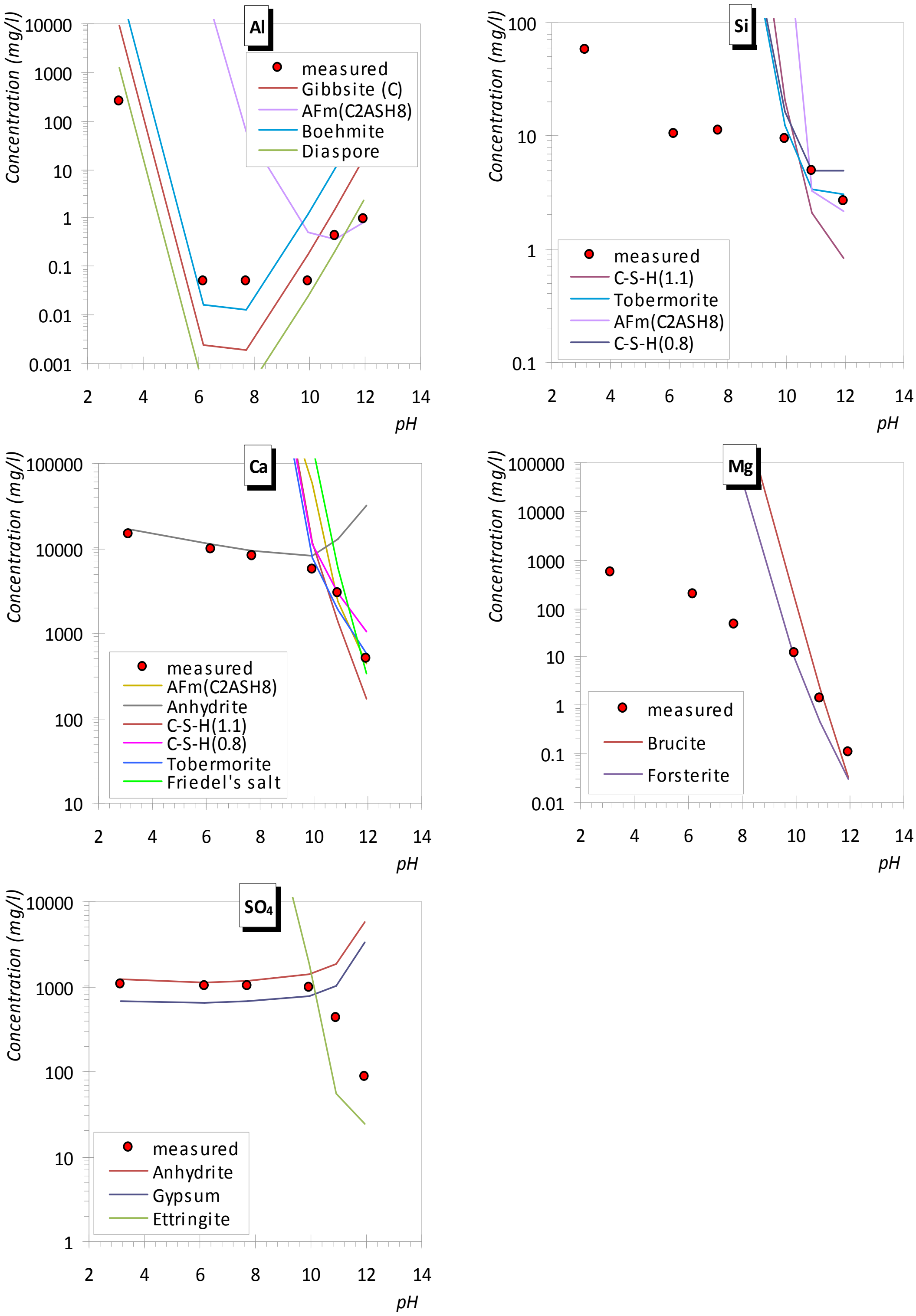

Figure 5.18: pH-dependent leaching of Al, Si, Ca, Mg and SO_4 in Bellgarde sample A and model predictions

As previously noted for the treated Halton soil, even in this case it was not possible to derive any indication about the potential solubility-controlling minerals for heavy metals, since the respective concentrations were below the analytical detection limit in a wide pH range. While on one hand this does not allow to infer about the geochemical mechanisms governing contaminant mobility from the S/S French site

(2076 sample), on the other hand it is an indication of the efficient immobilization of metals within the solidified matrix.

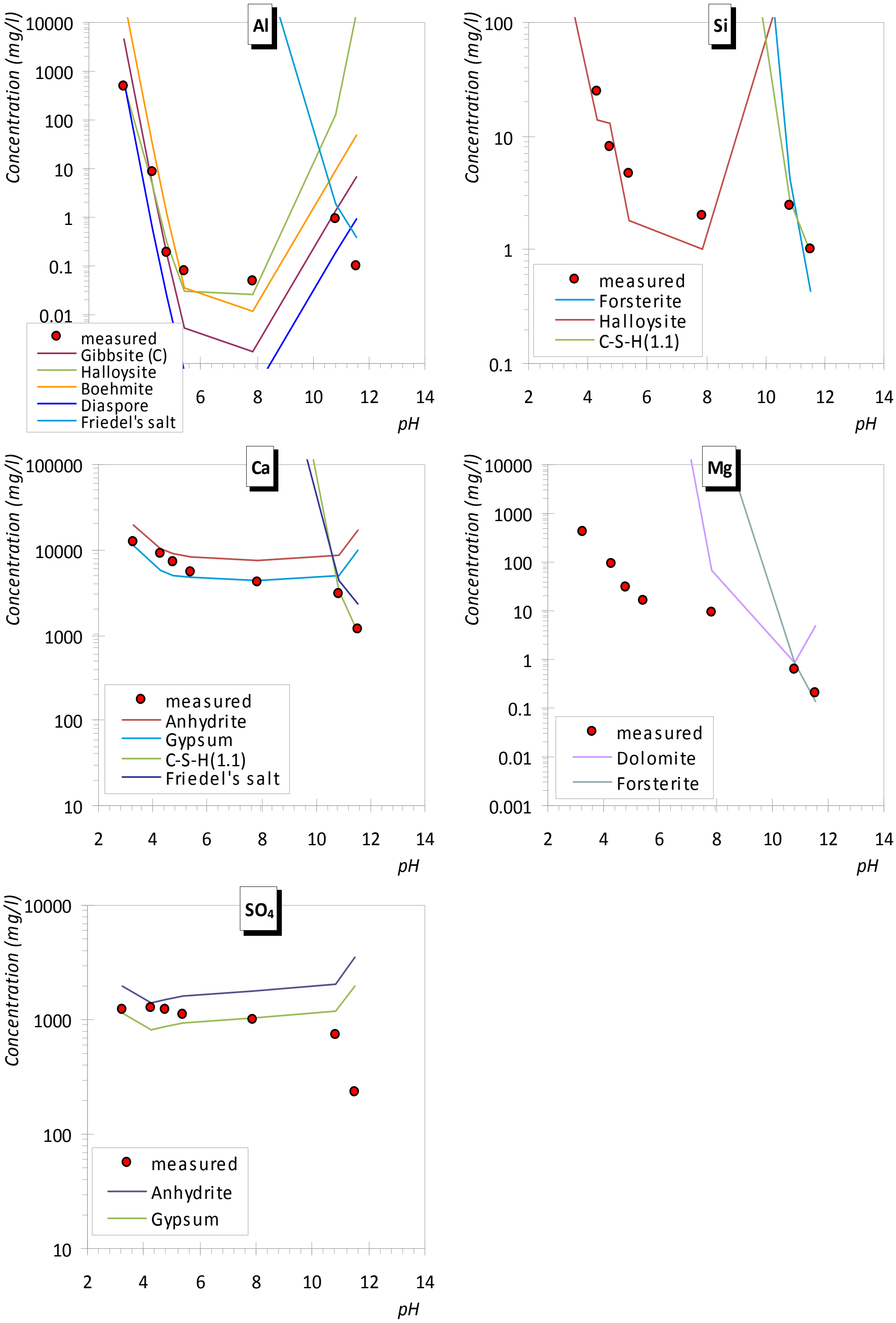

Figure 5.19: pH-dependent leaching of Al, Si, Ca, Mg and SO_4 in Belgarde sample B and model predictions

Among the solid phases selected as possible candidates for solubility control of the elements of concern in sample B, halloysite ($Al_2Si_2O_5(OH)_4$, a phyllosilicate mineral of the kaolinite group) showed the best fit with the measured leachate concentrations for Al at pH values up to 8. However, for the same reason explained above for sample 2076, gibbsite, boehmite and diaspore may still be considered good candidates for leaching control of Al even though the eluates appear to be oversaturated in such phases in this pH interval. This is due to the fact that the analytical detection limit of 0.05 mg Al/l did not allow to further investigate the actual concentrations in solution in the range of minimum solubility, which typically occurs at pH values in the range 6−6.5 for Al (hydr)oxide phases. In the highly alkaline region there was some evidence for solubility control of Al by Friedel's salt, which was also identified by XRD investigations (see above for details).

Other than for Al, halloysite also showed a good fit of the experimental data of Si release in the same pH range. Under more strongly alkaline conditions, either forsterite or C-S-H at a Ca/Si ratio of 1.1 matched the measured data points. In this pH range, 1.1 Ca/Si C-S-H along with Friedel's salt appeared to describe the leaching of Ca, with such phases being replaced by gypsum (which was also found to govern sulfate leaching under the same conditions) for solubility control at pH values ≤ 8.

As for Mg leaching, the two minerals forsterite (at higher pHs) and – possibly – dolomite (at pH $\cong 8-10$) were selected as the most probable solubility-controlling solids. No evidence for leaching control by carbonate minerals was gained for the other elements investigated.

Similarly to what was pointed out for heavy metal leaching for sample A (see above), the measured concentrations for the contaminants analyzed (Cd, Cr, Cu, Pb, Zn, Sb, Mo) were below the analytical detection limit in a large part of the pH range investigated. As a consequence, no significant conclusion could be drawn on the mechanisms governing their release from the S/S matrix.

5.3 Summary

The two hazardous waste treatment sites are different from the contaminated sites investigated elsewhere in this work. They utilise proprietary S/S systems to treat incoming waste.

The Bellgarde and Seda sites primarily stabilise municipal waste incinerator ash and a gel-rich product is produced. In the present and substantial previous work cited, the S/S systems are performing to meet design and regulatory criteria, despite exposure to the environment during placement and burial.

The sites have been subject to independent study that suggests that a variety of heavy metals are effectively encapsulated in a monolithic product that has continued to increase in strength with time.

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Appendix A
Supporting data for the Waste sites

The data contained within this appendix was supplied by INERTEC

1. Comparison of results with historical data

The results obtained from an examination of strength compare well with historical data obtained from SITA FD (Figure 1).

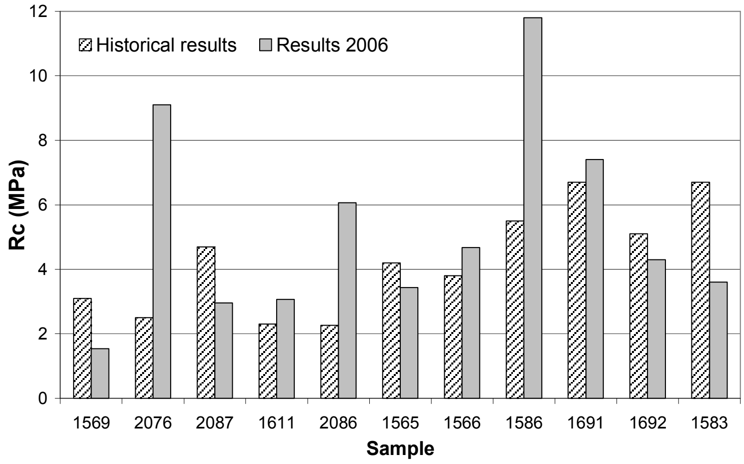


Figure 1: Comparison of the UCS results with the historical data (NF X31.212 standard method)

2. Leaching tests

The leachates obtained from 24 samples from the standard X31.211 leaching test were analysed for the mandatory parameters of the French regulation of 1992 and 2002: As, Cd, Cr, Cu, Ni, Pb, Zn, Hg, Sb, Se, Mo, but also cyanide, aromatic compounds (phenol index) and total organic carbon (TOC).

From the analysed metals only Hg and Se were detected once (2.2 and 2.3 mg/kg WM respectively) while the regulatory threshold are 5 mg/kg WM and 7 mg/kg DM. Sb and Mo were detected twice (the higher releases were 4.8 and 2.5 mg/kg WM respectively) while the regulatory threshold are 5 mg/kg DM and 30 mg/kg DM.

Phenol was detected once at 1.9 mg/kg WM using the NF T90-109 standardised method by spectrocolorimetry and is well below the regulatory limit of 100 mg/kg. The maximum total organic carbon (TOC) released was 500 mg/kg, less than the regulatory threshold (1000 mg/kg DM) showing that the eluates met the prescribed regulatory values.

Five samples were selected for a further detailed study (Table 1).

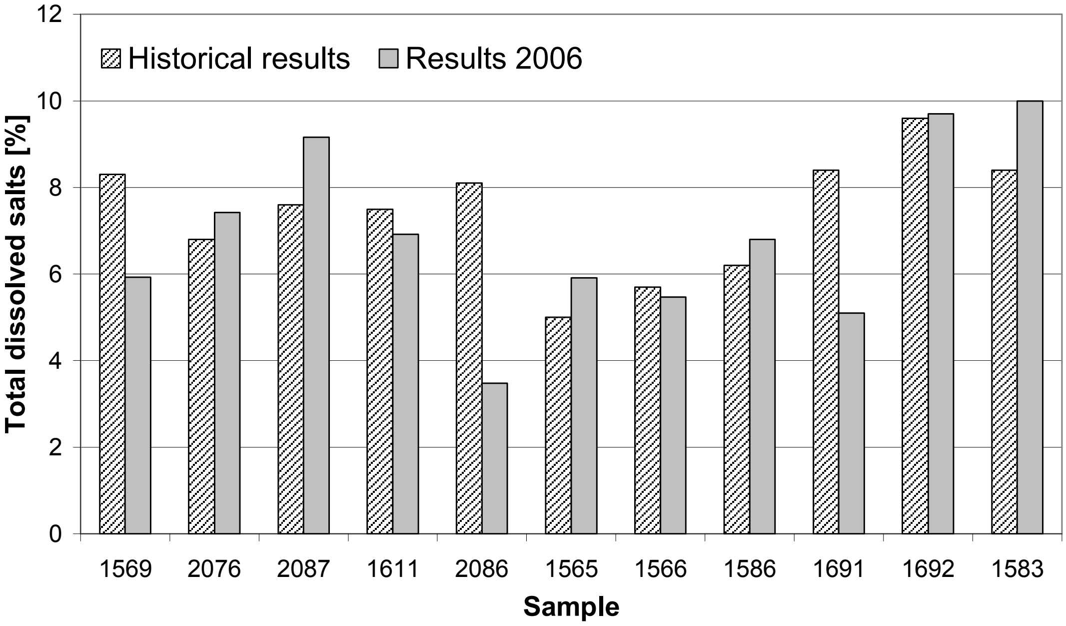


Figure 2: Comparison of the results obtained with the historical data. Total dissolved salts - leaching test according to the standard NF X31.211

Table 3: Samples selected for the study (MSW: Wet MSWI fly ashes and APC residues; MSS: Semi-wet MSWI fly ashes and APC residues semi wet; IS: ISWI fly ashes and APC residues)

Sample	Date of treatment	Type of mixed waste	Time of exposure to air
1569	28/12/2000	MSS/IS/industrial sludge: 40/40/20	2.5 months
1586	31/08/1999	MSS + MSW/industrial sludge: 60/40	1 year
2076	19/05/1999	MSS/industrial sludge: 80/20	0 month
2086	26/07/2000	MSS+MSW/industrial sludge: 90/10	3 months

2087	29/07/1998	IS/industrial sludge: 70/30	10 months

3. X-ray diffractometry

The following minerals were identified by XRD and some are shown in the diffractograms given in Figure 3: hydrocalumite [$Ca_2Al(OH)_6(Cl,OH,).xH_2O$], calcite [$CaCO_3$], halite [NaCl], sylvite [KCl], anhydrite [$CaSO_4$], bassanite [$CaSO_4.0.5H_2O$] and quartz [SiO_2]. Portlandite [$Ca(OH)_2$], hematite [Fe_2O_3] and magnetite [Fe_2O_4].

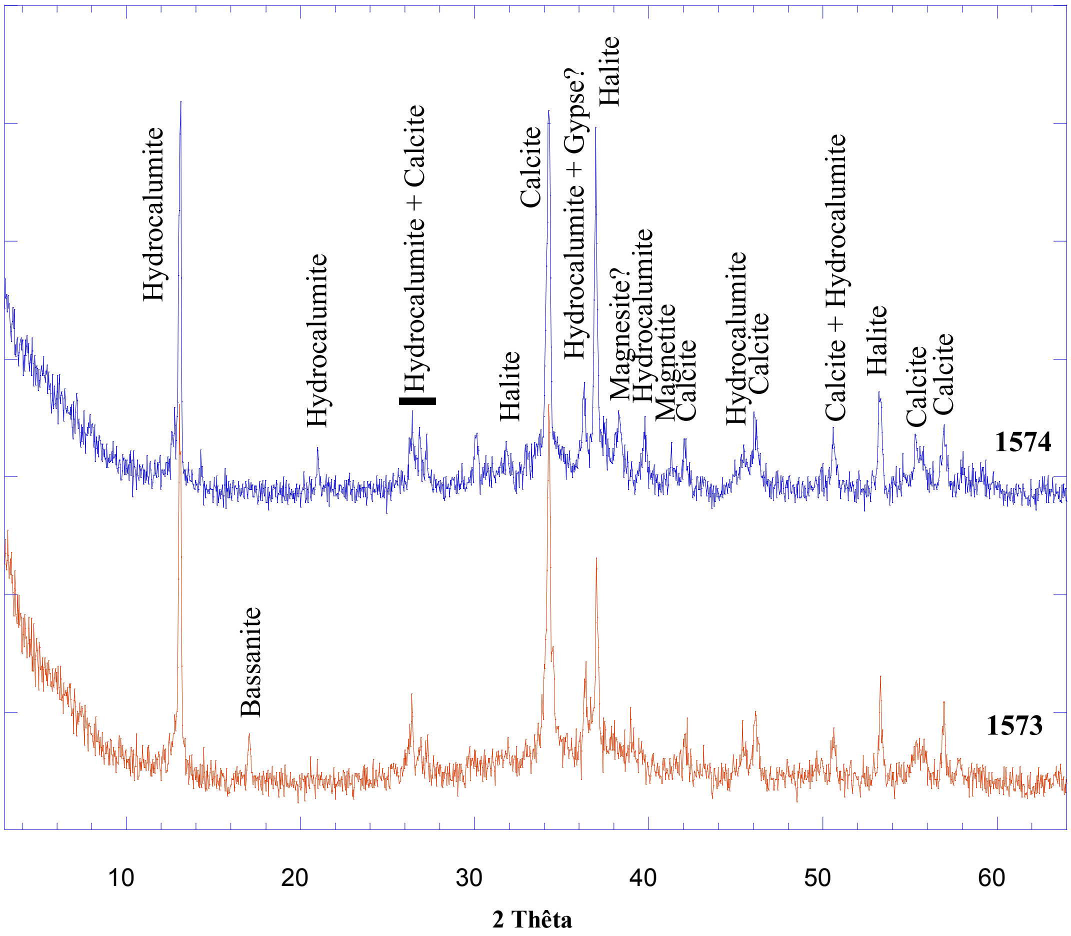


Figure 2: Example of XRD result – samples 2076 (1573) and 2087 (1574) (courtesy of LEM)

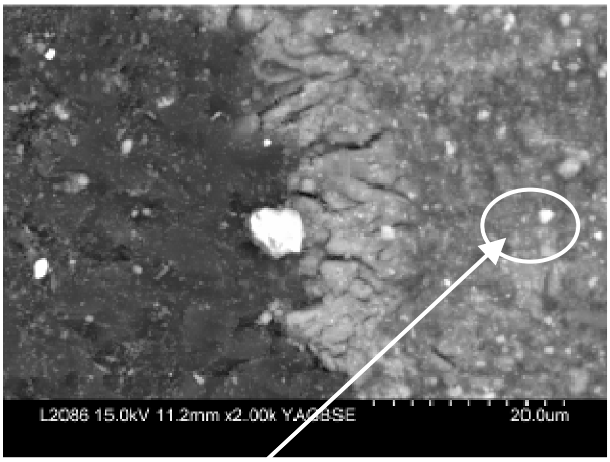
4. Electron microscopy

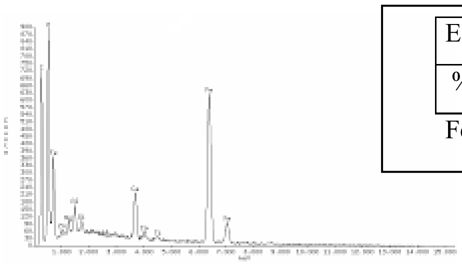
SEM and TEM analyses lead to the following conclusions:

- Heavy metals, including, zinc and lead were incorporated in the C-S-H during treatment by S/S,

- Other s such as spinel or alloy-type metalliferous phases were inherited from the APC residues, being formed at high temperatures of combustion.

All of the observations showed the absence of C-S-H re-crystallization phenomena, and the expulsion of metals from the ordered calcium bearing phases, which can be caused by the circulation of high temperature fluids on damaged deposits. Despite the presence of lead chloride and, probably chromate paragenesis, the metals were in stable forms, similar to those observed during previous studies on stabilized/solidified waste.

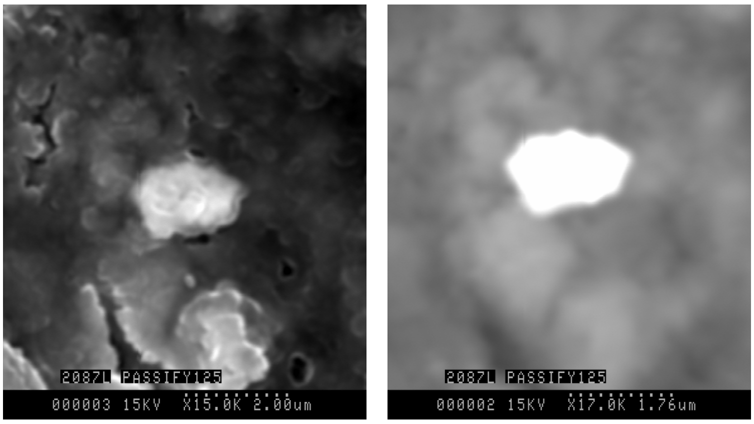




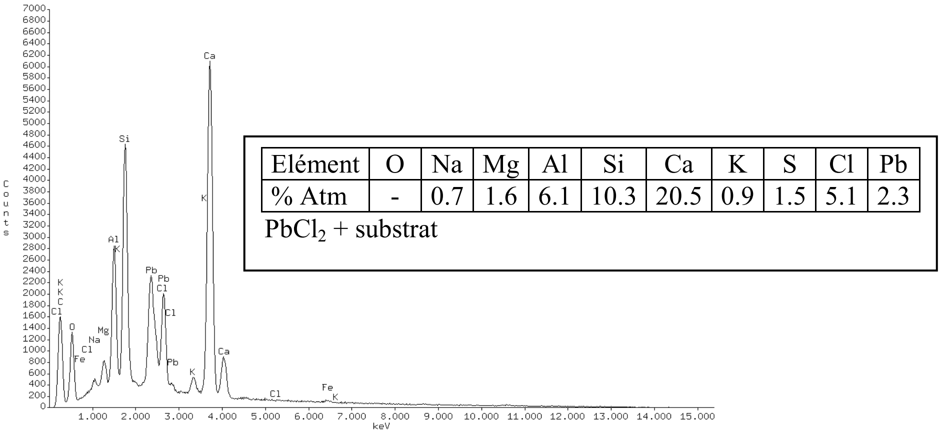
Elément	O	Mg	Al	Si	Ca	Ti	Fe	Zn
% Atm	61	1.3	1.9	0.7	3.8	0.2	30.1	1

$Fe_{0.59}Ca_{0.33}Zn_{0.08}Fe_2O_4$

Figure 3: Example of metallic contaminant – sample 2086 (courtesy of LEM)



ES BSE



Elément	O	Na	Mg	Al	Si	Ca	K	S	Cl	Pb
% Atm	-	0.7	1.6	6.1	10.3	20.5	0.9	1.5	5.1	2.3

$PbCl_2$ + substrat

Figure 4: Example of metallic contaminant – sample 2087 (courtesy of LEM)

5. Equilibrium tests

The results of the equilibrium tests are shown in

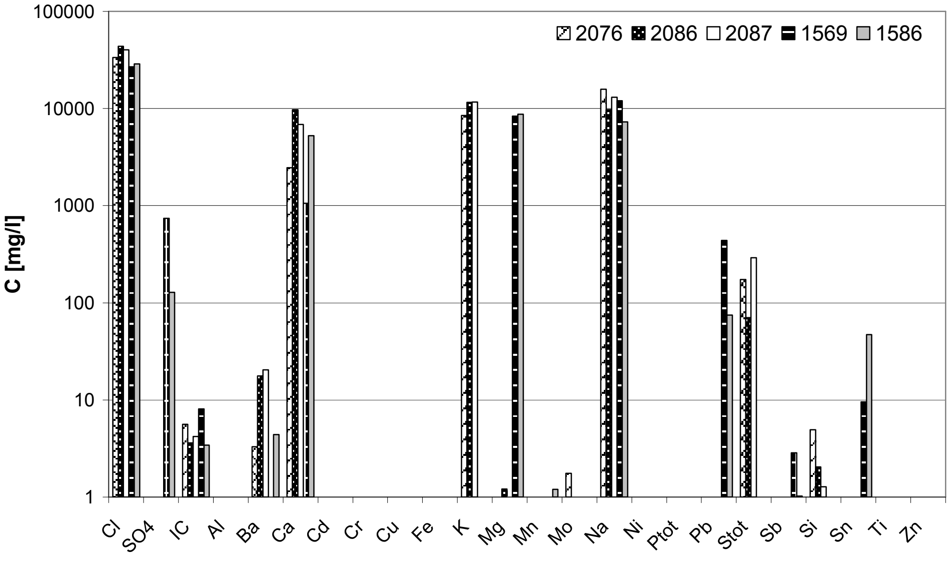


Figure 5. The two ordinate axes are shown on a logarithmic scale.

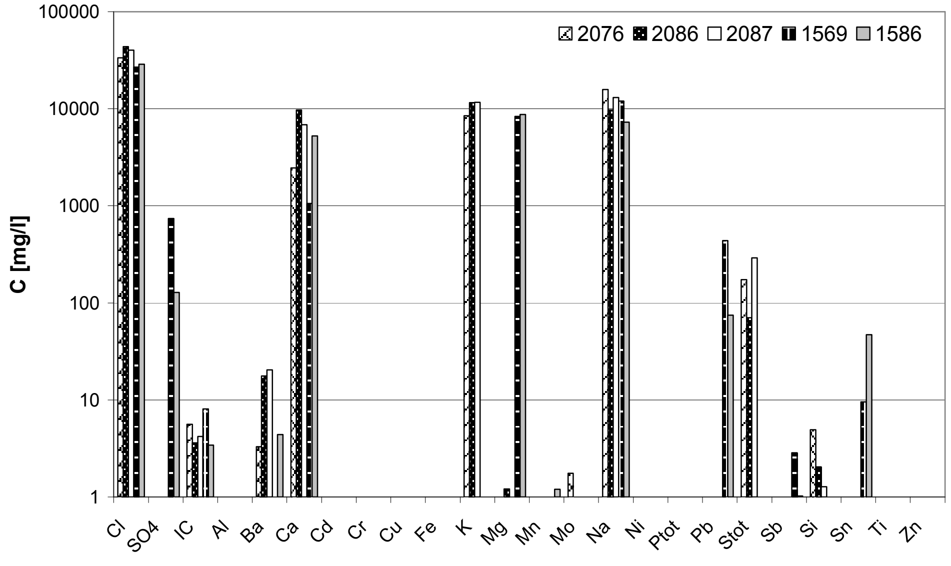


Figure 5: Equilibrium tests: results for L/S = 2

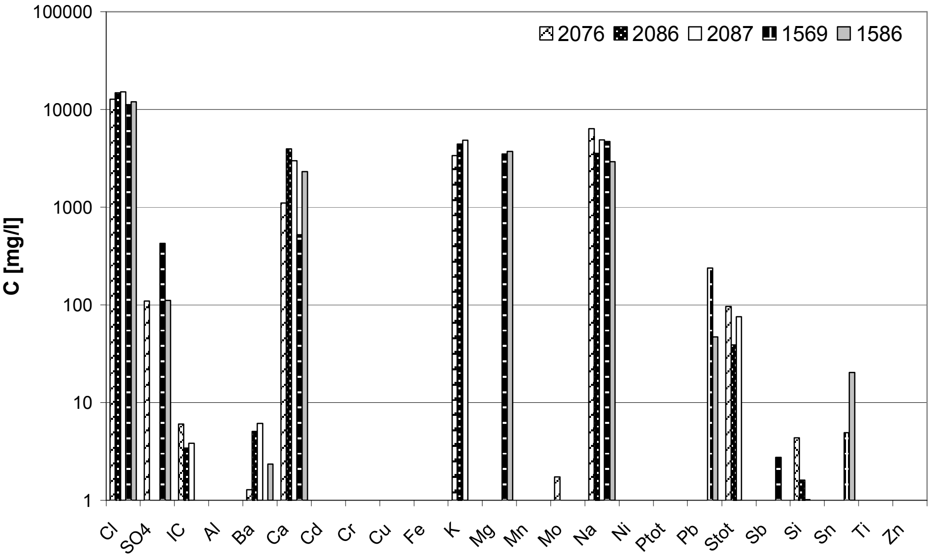


Figure 6: Equilibrium tests: results for L/S = 5

The equilibrium tests show that for all of the samples, the equilibrium pH was around 11, which corresponded well with the pH of the cements. The species mobilized from the materials in contact with deionised water were Cl^-, SO_4^{2-}, CO_3^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}, derived from soluble salts. No heavy metal was detected in the equilibrium solution. The only consequence of the difference between the L/S ratios is the dilution of the final equilibrium solution.

6. ANC tests

This test aims to characterize two behavioural parameters of the material studied: their acid or basic neutralization capacity and the availability of the pH dependent pollutants. The acid-neutralising capacity of the material was relatively high. Depending on the sample, it varied between 7 and 9 mol of H^+/kg of dry material. This was determined by the cementing phases (C-S-H) and the carbonates in the materials studied. As far as the availability of the elements monitored is concerned, the results showed that:

- sodium, potassium and chlorides were released, in equivalent quantities, whatever the imposed pH. These results tally with the literature [Stumm *et al.,* 1996].
- most of the metallic pollutants analyzed (Cr, Cu, Ni, Cd, Sb, Mo, Zn, Pb) remained below the quantification limits (0.05mg/l), with the exception of very acid environments with a pH lower than 4.

7. MMF tests

The objective of this test was to estimate the maximum amount extractable for a given type in imposed physico-chemical conditions (natural pH, 4 and 12). Overall, the results of the tests confirmed the results obtained during the ANC tests. Therefore, for all the samples, sodium, potassium and chloride were released in the three pH conditions, whereas the metals were not leached in the basic medium (natural pH and pH = 12). On the other hand, during tests with an imposed pH of 4, the cementing phases dissolved and the metals present in the waste were released as a result. The average quantities dissolved were approximately 24 % for lead, 54 % for copper and 100 % for zinc.

8. Modified “soxhlet” type dynamic leaching tests

“Soxhlet” type tests were carried out for the five French samples and the following conclusions were drawn:

Monitoring the evolution of the pellet mass during the tests showed that in each of the waste samples tested, the mass rapidly increased at the beginning of the experiment, and, after that, decreased. This can be explained by a first rapid leaching of the surface salts of the pellet, and after that by the entering of the solution in the porosity of the samples, observed by optical microscope. The loss of dry mass was partly compensated for by the entry of water into the pellets. The loss of dry mass is approximately 15 %.

The pH increased from the second renewal at the beginning of the experiment, to the contrary the conductivity rapidly decreased, with a consequent depletion of the salts (NaCl, KCl) in the output solution (Figure 7). Similar results were obtained during other studies [Brault, 2001; INERTEC, 2001]. Table 4 shows a comparison of the quantities contained in the five waste samples before and after leaching.

The mass balance calculations showed that for all the samples studied under the same conditions, chloride, sodium and potassium were completely leached. In fact, the soluble fraction in the waste, during the "soxhlet" varied from 11 to 17%. Approximately 10 % of the sulfates initially present were released from each of the waste samples, except for waste N°1586, where the quantity leached was 33 %. Tin, titanium, cadmium, copper and nickel were not leached (or were leached in quantities lower that the quantification limits – 0.05mg/l).

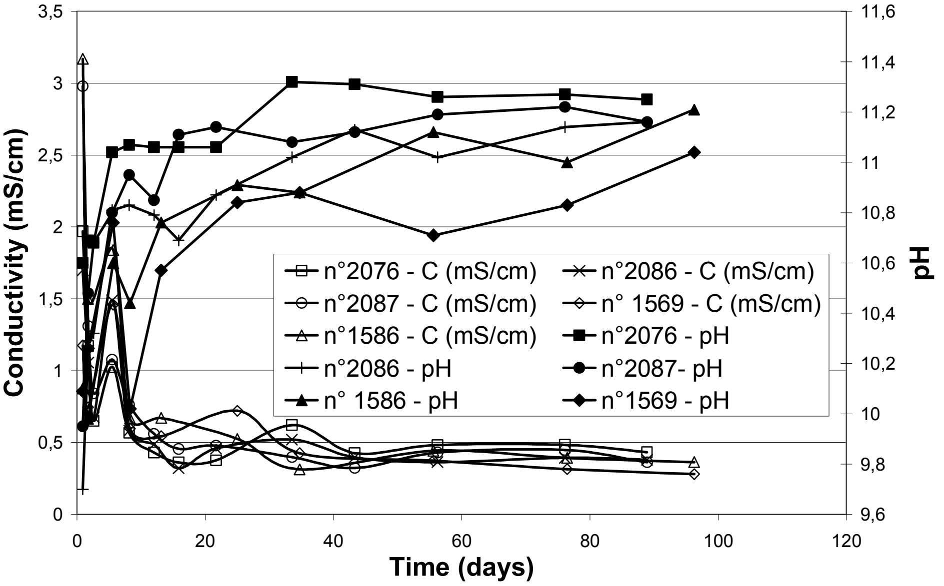


Figure 7: Evolution of pH and conductivity during the "Soxhlet" test

After the soxhlet experiment, total content analyses were carried out on one of the two pellets, at the same time as mineralogical observations.

No lead was leached out from the waste, whereas the dissolution rate of zinc was between 1 and 2.5 % of the initial content. The concentrations of the other metals monitored were below the quantification limit.

Concerning the major elements which make up the cementing phases, about 15% of the initial quantity of calcium, 6 % for silicon and approximately 4% for aluminium are leached out.

It should be noted that during the soxhlet tests, the quantifications limits for the metals were 0.05 mg/l and for the salts, 1 mg/l. Taking these limits into consideration, the quantities of elements extracted which remain constantly above the detection thresholds appear to be a maximum of 0.78 mg for metals and 15 mg for salts in the 13 renewals.

The mineralogical characterization by XRD, SEM and TEM were also carried out on thin sections cut from the pellets destined for dynamic "soxhlet" tests. In order to assess the evolution of the minerals present in the samples, observations were made before and after the "soxhlet" tests. According to the XRD the major minerals in the pellets before and after the "soxhlet" test were almost the same, except for halite (NaCl) and sylvite (KCl), which were absent from the pellets after leaching.

Table 4: Total content analyses, before and after the "soxhlet" test

	2076 before leaching	**2076 after leaching**	**2086/2 before leaching**	**2086 after leaching**	**2087/2 before leaching**	**2087 after leaching**	**1569 before leaching**	**1569 after leaching**	**1586 before leaching**	**1586 after leaching**
water	29.65	38.89	33.08	44.96	30.24	41.7	31.96	41.7	23.43	41.7
Insoluble residue	2.34	1.04	4.76	5.16	3.85	2.98	5.22	7.03	23.22	23.21
SiO_2	11.21	11.25	10.48	10.06	9.62	11.96	10.25	11.67	14.42	16.59
Al_2O_3	2.59	3.18	4.25	3.07	3.68	4.04	3.95	2.90	4.07	4.41
CaO	22.25	21.88	20.25	17.23	21.63	18.20	18.64	17.02	15.80	14.31
MgO	1.77	2.15	2.09	1.81	1.97	2.37	1.94	2.06	1.85	1.84
Fe_2O_3	1.25	0.90	0.60	0.92	0.90	0.61	1.30	1.01	1.95	1.97
MnO	0.05	0.05	0.05	0.05	0.05	0.05	0.06	0.06	0.06	0.07
Na_2O	2.06	0.10	1.27	0.11	1.34	0.09	1.30	0.15	2.28	0.39
K_2O	0.92	0.08	0.96	0.08	1.33	0.09	0.90	0.12	0.70	0.53
SO_4	3.80	4.10	3.53	4.13	4.80	3.49	3.54	3.33	3.27	2.75
P_2O_5	0.29	0.27	0.44	0.49	0.48	0.46	0.51	0.57	0.77	0.77
PbO	0.24	0.16	0.19	0.16	0.16	0.21	0.12	0.10	0.12	0.14
ZnO	0.27	0.28	0.68	0.56	0.63	0.70	0.51	0.39	0.51	0.58
TiO_2	0.25	0.26	0.40	0.41	0.43	0.40	0.00	0.00	0.68	0.68
CuO	0.33	0.14	0.03	0.04	0.04	0.04	0.20	0.13	0.04	0.04
Cl	3.12	0.06	4.27	0.10	4.58	0.06	4.02	0.09	4.98	0.07
trace metals	0.12	0.09	0.10	0.10	0.12	0.09	0.08	0.09	0.15	0.15
total %	82.49	84.91	81.86	89.44	85.05	87.55	84.50	88.43	98.30	110.22

In some pellets, it was observed that during the soxhlet test, the hydrocalumite, initially present, was replaced by ettringite. As hydrocalumite is a relatively mobile phase, it is therefore possible that it dissolved dring the “soxhlet” test and the ettringite precipitated in its place. The necessary sulfates are without doubt mobilized from the sulfate phases, such as calcium sulfate, initially present.

The major minerals present also suggest that the pH was buffered by the hydroxy-carbonates from the stabilized waste.

SEM and TEM observations of the pellets showed that, at the end of the soxhlet test, the heavy metals initially present in the form of oxides (ZnO, PbO) or chlorides ($PbCl_2$) were mobilized after a reaction with water. The fact that the metal concentration in these leaching solutions was negligible, probably results from the re-trapping of these elements in the cementitious phases. This hypothesis is supported by the observation of zinc and lead C-S-H containing phases in the pellets after the “soxhlet” test. The presence of metal oxides and chlorides in the samples characterized before the soxhlet test confirms the hypothesis that the stored stabilized waste has reached a state where it evolves over time. The other phases containing heavy metals are stable, and are therefore difficult to mobilise.

The mobilization curves of the soluble elements during the soxhlet test were used to determine the apparent diffusion coefficient values. The results obtained here and those of previous studies are shown in Table 5.

Table 5: Apparent diffusion coefficient (MSW: Wet MSWI fly ashes and APC residues; MSS: Semi-wet MSWI fly ashes and APC residues semi humid; IS: ISWI fly ashes and APC residues)

Sample	Diffusion coeff. (m^2/s)	Waste	Diffusion coeff. (m^2/s)
n°2076	$5{,}0.10^{-11}$ - $1{,}0.10^{-10}$	MSW	$2{,}4.10^{-13}$ - $7{,}5.10^{-12}$
n°1569	$1{,}5.10^{-11}$ - $2{,}5.10^{-11}$	MSS	$1{,}3.10^{-11}$ - $3{,}0.10^{-10}$
n°1586	$3{,}0.10^{-11}$ - $5{,}0.10^{-11}$	Industrial sludge	$1{,}0.10^{-11}$ - $3{,}0.10^{-11}$
n°2086	$2{,}0.10^{-11}$ - $5{,}0.10^{-11}$		
n°2087	$3{,}0.10^{-11}$ - $1{,}0.10^{-10}$		

In the light of these results, the diffusion coefficients from pellets were of the same order of magnitude as those obtained on samples produced in the laboratory during the "TK1 study” (INERTEC, 2002). This confirms, once again, our hypothesis that the stabilized waste do not undergone significant changes over time after landfilling and that the laboratory results can be taken as representative of the "field" material.

CONCLUSIONS

The results obtained lead to the following conclusions:

- The S/S waste placed in landfill are still complying with the regulations after being buried for 8 year.
- The mineralogical observations showed, that despite the heterogeneity of the samples, that the ageing of the S/S waste has very little influence on the mineralogical composition. Moreover, the very soluble minerals such as halite and sylvite are always present in the waste, showing no significant change over time.
- The batch leaching tests revealed that the metallic pollutants do not leach off the matter confined to their natural pH and that in order to mobilise them, the pH must be lower than 4.5. On the other hand, leaching of the salts present in the waste is not pH dependent. These results tally with the literature and previous data of INERTEC and SITA.
- The results obtained for the soxhlet-type tests provides kinetic data on the changes taking place in the waste during landfill. The salts are quickly leached (approximately 20 days in test conditions), whereas the metallic pollutants are always retained by the matrix.

- In a landfill, significant dissolution of the salts does not occur, as shown by the mineralogical investigation of samples, because contact with water is very limited compared to laboratory tests.

Finally, this study shows the efficiency of the solidification/stabilization processes used in France for the storage of hazardous waste. All of the current observations confirm the results obtained in the laboratories in previous studies and the stability of the S/S waste in onsite storage conditions.