STABILIZATION/SOLIDIFICATION PROCESSES FOR THE TREATMENT OF CONTAMINATED SOIL AND WASTE

PROCESSI DI STABILIZZAZIONE/SOLIDIFICAZIONE PER IL TRATTAMENTO DI SUOLI E RIFIUTI CONTAMINATI

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"Twenty years from now you will be more disappointed by the things that you didn't do than by the ones you did do.

So throw off the bowlines. Sail away from the safe harbor.

Catch the trade winds in your sails.

Explore. Dream. Discover."

Mark Twain

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ABSTRACT

Recovering industrial waste and contaminated soil is one of the main objectives in environmental management. Nowadays in Italy, landfilling is responsible for up to 40% of total soil contamination and up to 50% of the used remediation techniques involves excavation and disposal. On the other hand, the European Legislation has set key drivers to improve waste management, as setting recycling targets and limiting the use of landfilling with its rising cost. In this scenario, new technologies to reduce the toxicity of contaminated soil and hazardous waste before their disposal or to reuse them as aggregates are of great interest.

Stabilisation/solidification (S/S) is a treatment for wastes and soils which mainly uses cementitious or pozzolanic binders to produce a solid monolith that incorporates the contaminants. This process is particularly effective on heavy-metals contaminated soils. Other additives/fillers can also be used during a pre-treatment phase to amend adverse chemical and physical characteristics, e.g. high moisture content. Alternative methods to treat contaminated waste and soil exploited the application of accelerated carbonation to cement-based S/S. This process can improve the characteristics of the stabilized products in terms of leaching, strengths or pH.

Accelerated carbonation (ACT) is an enhanced form of natural carbonation that has been developed during the last years at industrial scale for the treatment of contaminated soil and industrial wastes. Accelerated carbonation induces a rapid reaction exposing the mineral or the reactive waste to a controlled atmosphere containing CO_2 and promotes rapid hardening of the product. The resultant precipitation of calcium carbonate reduces the porosity of the material, and leads to further changes at the microstructure, aiding the retention of contaminants and improving the mechanical properties. The pH is also lowered with the result of reduced solubility of many heavy metals.

Waste can be formed into aggregate by agglomeration. If the two processes are combined, it is feasible to produce hardened aggregate. The final product can be reused as aggregate in engineering fill or in concrete production.

The aim of the research project conducted during the Ph.D. programme is the development of an innovative approach for the enhancing of stabilization/solidification treatment of contaminated soils and wastes. The research aimed at the identification of innovative formulation using cement and thermal wastes for heavy-metals contaminated soil treatment and at the investigation of the effect of the accelerated carbonation applied to cement-based stabilization/solidification.

Tests of cement-based stabilization/solidification using Portland cement and the effect of accelerated carbonation on metals mobility were investigated on artificial heavy-metals contaminated soil at the *Sanitary Environmental Engineering Division* (SEED) at the *University of Salerno*. The process was assessed with further investigations on soil washing residues blended with thermal ashes and cement for the production of lightweight recycled aggregate. This part was conducted within the *LLP Erasmus Placement Programme* at the *Centre for Contaminated Land Remediation (CCLR)* of the *University of Greenwich* (UK). The process investigated entailed the mixing of soil washing residues with paper incineration ashes, reactive to carbon dioxide, or sewage sludge ashes followed by accelerated carbonation to produce the aggregate. Portland cement was used as the binder, which also has an ability to combine with CO_2.

The effect of accelerated carbonation on the cemented contaminated soil was evaluated by mineralogical and structural properties. Chemical stability was measured by leaching of heavy metals from the raw materials and the final products. The aggregates produced showed comparable strength to commercially lightweight aggregates. Accelerated carbonation increased the strength and the density of the aggregate compared to the hydrated one. Heavy metals leaching were substantially unaffected by carbonation, apart for copper and barium. Further investigation tested the aggregates for using in lightweight concrete block and for green roofing. The use of a synthetic CO_2 flue gas lead to a capture of the carbon dioxide leading to a "low carbon" product. The study showed the applicability of the process for manufacturing lightweight aggregates from soil washing residues and ashes by enhanced cement based S/S as a good alternative for a wide range of civil engineering applications. The effect of accelerated carbonation has to be further explained. Future investigations are needed to enhance the process based on the variability of the wastes. Other waste and alternative carbon dioxide reactive fillers can be considered to be treated by the process.

SOMMARIO

Il recupero di suoli contaminati e di rifiuti industriali è uno degli obiettivi prioritari della gestione dell'ambiente. Ad oggi, lo smaltimento in discarica rappresenta il metodo più utilizzato sia nella gestione dei rifiuti pericolosi che negli interventi di bonifica, dove, previa l'escavazione del terreno contaminato, rappresenta ancora il 50% dei metodi optati. L'aumento del costo per lo smaltimento in discarica, insieme agli obiettivi di recupero e di riciclaggio imposti dalla normativa europea e l'attuazione di diverse direttive per la protezione del suolo, come la *Soil Strategy*, ha indirizzato l'attenzione verso lo sviluppo di nuovi e immediati metodi di intervento e di gestione che riducono la pericolosità del materiale e ne consentono il recupero. Il suolo contaminato delle operazioni di bonifica, quando è escavato per essere trattato, è considerato un rifiuto. Il suo trattamento e il recupero immediato rappresenta uno degli aspetti più rilevanti negli interventi di bonifica.

La stabilizzazione/solidificazione è una tecnologia utilizzata per il trattamento di suoli e rifiuti contaminati che consiste nella miscelazione del rifiuto o terreno contaminato con leganti che, attraverso reazioni di tipo chimico-fisico, riducono la mobilità dei contaminanti e garantiscono resistenza meccanica. Il processo è particolarmente efficace per la stabilizzazione di metalli pesanti. Metodi alternativi prevedono l'utilizzo della carbonatazione accelerata ai processi di stabilizzazione/solidficazione a base cementizia. Tale processo può migliorare le caratteristiche del materiale trattato in termini di lisciviazione dei contaminanti, resistenza meccanica e pH.

La carbonatazione accelerata (ACT) è la forma accelerata della carbonatazione naturale ed è stata sviluppata negli ultimi anni come tecnologia di trattamento di rifiuti industriali e applicata successivamente anche a suoli contaminati. Il processo comporta una rapida reazione tra i minerali o i rifiuti reattivi alla CO_2 esponendoli ad una atmosfera controllata contenente questo gas. La reazione comporta un rapido indurimento del prodotto. La conseguente precipitazione di carbonato di calcio riduce la porosità del materiale e induce ulteriori modifiche alla microstruttura che favoriscono l'immobilizzazione dei contaminanti ed il

miglioramento delle proprietà meccaniche del prodotto. La riduzione del pH, inoltre, può comportare una ridotta solubilità di molti metalli pesanti.

I rifiuti in forma fine, come ceneri e residui da impianti di soil washings, posso essere recuperati attraverso un processo di agglomerazione per produrre aggregati. Se si combinano i processi di stabilizzazione/solidificazione, carbonatazione accelerata e agglomerazione è possibile produrre aggregati con caratteristiche di resistenza specifica. Tale prodotto può essere riutilizzato in diverse applicazioni ingegneristiche come mezzo di riempimento o per la produzione di calcestruzzo.

Obiettivo del progetto di ricerca, condotto nell'ambito del *dottorato in Ingegneria per l'Ambiente e il Territorio* presso *l'Università di Salerno*, è stato lo studio dei processi di stabilizzazione/solidificazione per il trattamento di suoli e rifiuti contaminati. L'attività si è incentrata sulla formulazione di miscele innovative a base di cemento e ceneri di scarto provenienti da trattamenti termici per il recupero di terreni contaminati da metalli pesanti. Prove di stabilizzazione/solidificazione con cemento Portland e l'effetto della carbonatazione accelerata sul processo sono state condotte su terreni contaminati da metalli pesanti preparati artificialmente in laboratorio. L'attività sperimentale è stata effettuata presso il *Laboratorio di Ingegneria Sanitaria Ambientale (SEED)* dell'*Università di Salerno*.

Il processo è stato valutato con ulteriori prove effettuate su residui fini contaminati da impianti di soil washig per la produzione di un aggregato riciclato. Tale attività è stata svolta presso il *Centre for Contaminated Land Remediation* della *University of Greenwich* (UK) nell'ambito di un accodo *Erasmus Placement*. Il processo implementato consiste nella miscelazione dei residui da impianti di soil washing con ceneri da trattamento termico di fanghi e cemento Portland, seguito da una fase di granulazione per la produzione dell'aggregato. Il cemento Portland è stato utilizzato come legante alla base del processo e per la sua reattività all'anidride carbonica. Prima del trattamento i residui contaminanti, sulla base del test di cessione, sono stati classificati come rifiuti stabili-non reattivi o pericolosi, mentre a seguito del trattamento la pericolosità è stata ridotta comportando valori dei metalli negli eluati del test di cessione inferiori a quelli per rifiuti inerti. L'effetto della carbonatazione accelerata sul suolo contaminato trattato con stabilizzazione/solidificazione è stato valutato con analisi mineralogiche e strutturali. La stabilità chimica del materiale è

stata valutata attraverso test di cessione. Gli aggregati prodotti hanno mostrato proprietà comparabili con gli aggregati disponibili in commercio. La carbonatazione accelerata ha comportato un aumento della resistenza e della densità dei granuli, rispetto al quelli sottoposti a normale processo di idratazione. La lisciviazione dei metalli pesanti è stata scarsamente influenzata dalla carbonatazione accelerata.

Ulteriori test sugli aggregati prodotti hanno dimostrato la loro potenziale applicazione nella produzione di blocchi di calcestruzzo leggero. Il conseguente abbassamento del pH a valori vicino la neutralità, oltre a caratteristiche specifiche del materiale, lo rendono adatto per applicazioni come substrato per coperture ("green roofing").

L'utilizzo nel processo di un gas sintetico di CO_2 ha comportato anche la cattura di anidride carbonica rendendo l'aggregato prodotto "low-carbon".

La ricerca ha dimostrato l'applicazione del processo di stabilizzazione/solidificazione con carbonatazione accelerata per il recupero di residui di soil washing e ceneri per la produzione di aggregati da riutilizzare in differenti applicazioni ingegneristiche. Studi successivi sono necessari per valutare in dettaglio l'effetto della carbonatazione accelerata sul processo. Inoltre è necessario effettuare valutazioni sulla variabilità del rifiuto in ingresso. L'applicazione del processo può essere valutata per il recupero di altre tipologie di rifiuti, come ad esempio sedimenti contaminati e altre ceneri reattive all'anidride carbonica.

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ABOUT THE AUTHOR

Roberta Maffettone graduated in Environmental Engineering cum laude in 2011 discussing a thesis entitled "MBR design and operation impacts of performance". She conducted her research at the Centre for Water Science Institute at Cranfield University (UK) as a visiting research student within the LLP Erasmus Programme.

She began the Ph.D. programme in the same year at the Department of Civil Engineering of University of Salerno. Her research activity has been focused on stabilization/solidification processes for the treatment of contaminated soil and waste. During the Ph.D. she was a visiting research at University of Greenwich where she studied the application of Accelerated Carbonation Technology for the valorisation of contaminated soil and waste within the $SAPICO_2$ project. She has also been involved in several activities promoted by the Sanitary Environmental Engineering Division (SEED) group in the area of sanitary engineering.

Roberta Maffettone ha conseguito con lode la laurea specialistica in Ingegneria per l'Ambiente e il Territorio nel 2011 presso l'Università degli Studi di Salerno con una tesi dal titolo "Verifica delle prestazioni di impianti MBR in riferimento a parametri di progetto e gestione" al termine dell'attività svolta nell'ambito del programma Erasmus presso il *Center for Water Science Institute* della *Cranfield University* (Regno Unito).

Nello stesso anno è stata vincitrice con borsa del XIII ciclo del Dottorato di ricerca in Ingegneria Civile per l'Ambiente e il Territorio. La sua attività di ricerca si è incentrata sullo studio dei processi di Stabilizzazione/Solidificazione per il trattamento di suoli contaminati e rifiuti. Durante il dottorato ha svolto attività di ricerca presso la *University of Greenwich* come visiting research nell'ambito del progetto $SAPICO_2$ per la valorizzazione e il recupero di suoli e rifiuti contaminati tramite trattamento di carbonatazione accelerata. Ha inoltre collaborato attivamente alle attività promosse dal gruppo di Ingegneria Sanitaria Ambientale dell'Università di Salerno.

LIST OF ABBREVIATIONS

ACT Accelerated Carbonation Technology
ASTM American Society for Testing and Materials
BAA British Aggregate Association
BGS British Geological Survey
BS British Standard
BSE Backscattered Secondary Electrons
CEM I Ordinary Portland Cement
C-S-H Calcium Silicate Hydrate
EA Environment Agency
EDAX Electron Dispersive X-Ray Analysis
EU European Union
EWC European Waste Catalogue
ICP-OES Inductively Couple Plasma Optical Emission Spectroscopy
ISPRA Istituto Superiore per la Protezione e la Ricerca Ambientale
LOI Loss On Ignition
LWA Lightweight Aggregate
Mpa Megapascals
MSWI Municipal Solid Waste Incineration
PA Paper Ashes
SEM Scanning Electron Microscopy
S/S Stabilisation/Solidification
SSA Sewage Sludge Ash
WAC Waste Acceptance Criteria
WRAP Waste Resources Action Programme
W/S Water/Solid Ratio
XRF X-Ray Fluorescence
XRD X-Ray Diffraction

1 INTRODUCTION

Recovery and reuse of contaminated soil and waste against landfilling is a priority in Europe. Disposal to landfill continues to be the easiest and most economical waste management solution but it is considered unsustainable. The European legislation is a major driver for the development of other treatment options. Recovering industrial waste and contaminated soil is a main objective in the last years in environmental management. European legislation has set objectives and targets to improve waste management, stimulate innovation in recycling, limit the use of landfilling and create incentives. The EU, with the implementation of several Directive or Proposal for the managing of contaminated land and waste, among them the *Soil Strategy* and the *Waste Framework Directive 2008/98/CE*, is driving the decisions in this direction. Soil contamination is a widespread environmental problem due to the occurrence of pollutants in soil from a wide range of industries or also from the landfilling of waste, breaking of storage tanks or illegal direct dumping of industrial waste in the soil. Depending on the concentration and speciation of contaminants, contaminated soils are of concern for the risk associated to the human health and to the ecological system as a whole. Contaminated soil, when is a by-products of the remediation activity or it is excavated to be treated ex-situ, is handling as a waste. Reduction of waste soil volumes and its classification as hazardous waste are of concern for the site owners and consultants.

Stabilisation/solidification (S/S), which usually employs the addition of cementitious binders to the contaminated soils in order to immobilize the contaminants present, has emerged as a cost effective and efficient remedial measure for contaminated soils. S/S treatment entails chemical fixation and physical encapsulation of contaminants. Therefore it reduces the migration of contaminants, both organics and heavy metals, into the wider environment; common binders include Portland cement, pulverised fly ash, lime or ground granulated blast furnace slag.
Stabilization/Solidification by hydraulic or pozzolanic binders with cement is used for the immobilisation of soils and sludges containing a

variety of metal pollutants. Cement-based solidification is attractive for the easy application and cost and because it offers an assurance of chemical stabilisation at high pH of many compounds producing a mechanically stable waste form. Commonly used cementitious materials and cementitious waste mixture are affected by carbonation. Carbonation has been used in a "speed" way in combination with hydraulic and pozzolanic binders to overcome inhibiting effects of complex waste material reactions responsible for effective solidification.

Accelerated Carbonation Technology (ACT) is being investigated as a carbon capture solution since carbon dioxide is permanently bound into solid carbonate minerals. Accelerated carbonation can be used to induce a rapid reaction between mineral or reactive waste materials and carbon dioxide. This is achieved by exposing the material to a controlled atmosphere containing CO_2 to promote rapid harden of the product. This process promotes rapid solidification of the material treated binding toxic metals. ACT has been used to treat hazardous waste using hydraulic binder in a combined process with granulation to produce recycled and "low-carbon" lightweight aggregate. Contaminated soil and industrial residues treated with accelerated carbonation have been reused as aggregates, engineering fill or for concrete production.

Combining Accelerated Carbonation and cement-based stabilization/solidification using a reactive hydraulic binder, as cement, can be a solution for the recovery of contaminated soil and waste as aggregates. The process can allow the recover and the reuse of the contaminated material treated as a construction material incorporated into a structure such as a road or building. This requires that the material does not have a potential risk for the environment or human health, with a proper risk assessment. Furthermore, its reuse requires specification to meet the indications set by the CEN series of European Standard and the End of Waste criteria developed by the European Union.
The aim of this study is to investigate the feasibility of treating contaminated soil using an accelerated carbonation induced cement-based stabilization/solidification. Moreover soil washing residues have been studied to be recovered by this process in the form of a recycled aggregate.

This aspect of the research has been conducted on soil washing residues collected from different soil washing plants. The residues have been blended with paper ashes from a local incineration treatment plant to obtain a granular material potentially reusable as aggregate. Different mixes have been tested for mechanical and chemical characteristics and selected based on the leaching of contaminants and strength of the pellets. The material has been treated with natural carbonation and accelerated carbonation using a flow of CO_2 during the pelletising or curing stage. The effect of the carbonation on the materials was evaluated with mineralogical and structural properties by XRD and SEM analysis. Chemical stability was measured by leaching of heavy metals of the hydrated and carbonated pellets. Treatment by forced carbonation of cement-based stabilization/solidification showed a reduction of the leaching of certain metals and the improving of the strength of the pellets. The research aimed at the proposal of a process to produce lightweight aggregate from waste and from a source of CO_2 gas for a "low carbon" product.

1.1 OBJECTIVES

The aim of the research project conducted during the Ph.D. programme was the developing of innovative processes for the enhancing of stabilization/solidification treatment of contaminated soils and wastes.
The research aimed at the identification of innovative formulation using cement and thermal wastes heavy-metals contaminated soil treatment and at the investigation of the effect of Accelerated Carbonation applied to cement-based stabilization/solidification.
The process was assessed with investigations on soil washing residues for the production of innovative lightweight recycled aggregate blended with thermal ashes and cement.

The objectives achieved during the research programme were:

1. Evaluate the effect of accelerated carbonation on heavy-metal contaminated soil treated by cement based-stabilization/solidification.

2. Examine the use of accelerated carbonation for the treatment of soil washing residues using thermal ashes waste in substitution of conventional filler and cement.

3. Assess the treated product for the potential re-use as aggregate for chemical and physical stability.

4. Test the aggregate to the regulatory standards, and consider potential end-uses.

Activities to reach the objectives were divided in two parts of the research. Preliminary tests on cement-based stabilization/solidification using Portland cement CEM I and the effect of accelerated carbonation on heavy metals mobility were investigated on artificial heavy-metal contaminated soil at different conditions. The research was conducted at the *Sanitary Environmental Engineering Division* at the *University of Salerno* within a *Ph.D. programme in Environmental Engineering.*

In the second part of the study, conducted at the *Centre for Contaminated Land Remediation of University of Greenwich (UK)*, contaminated residues from soil washing process were treated by a combined process of cement-based stabilization/solidification and accelerated carbonation. The process was investigated mixing soil washing residues with paper incineration ashes, reactive to carbon dioxide and sewage sludge ashes and treated by accelerated carbonation to produce a recycled lightweight aggregates. Portland cement (CEM I) was used as binder. It also reacts with CO_2. The aggregates produced have been tested for different applications.

1.2 THESIS STRUCTURE

This thesis comprises of six chapters. The introductory chapter (Chapter 1) gives an overview of the problems addressed, and the aims and objectives of this research. An overview of contaminated land and waste management under the legislative and technical aspect, including the criteria of End of Waste is presented in Chapter 2. Also the recycling of waste as aggregate and specification standards for their testing are reviewed here.

The relevant literature and background to the project is examined in Chapter 3. In this chapter the stabilization/solidification processes are presented. Cement based stabilization/solidification is explored in details including the variables of the process, as strength and leaching, chemical and physical effect and potential applications. Accelerated carbonation is presented both as a technology to treat hazardous reactive waste and a way to enhance cement-based stabilization/solidification processes to treat contaminated soil and waste. A novel and patented method for the production of aggregates by accelerated carbonation is also discussed in this chapter.

Chapter 4 presents the details of the materials used in the experiments with the experimental procedures employed both in the assessment of the performance of the S/S treated soils and in the production of recycled aggregate. This chapter describes all the analytical methods for the physical and chemical characterization of the materials used and the testing of the final stabilized/solidified and carbonated product. Standard test used for testing aggregates are also reported.

In Chapter 5 the results of the project are presented in two sections. The first part focuses on the effect of stabilization/solidification process on heavy metals contaminated soil under different conditions, included the effect of accelerated carbonation. In the second part the results of the aggregates produced from soil washing residues and ashes are discussed. This includes the results of the mechanical and leaching properties of the different binder formulations considered, the leaching of contaminants and the microstructural changes for the effect of accelerated carbonation. The results are compared against European legislation to evaluate the effectiveness of the process to reduce hazardous properties and facilitate cost-effective disposal and potential re-use. The properties of the aggregates under the relevant Standards are presented alongside commercial lightweight aggregates and discussed based on the two analysed application: lightweight concrete blocks and green roofing application.

Chapter 6, the conclusive part, provides an overall discussion of the results. The main findings of both aspects of this research are presented together with recommendations for further researches and the final

conclusions are drawn. Questions remaining unanswered and suggestions for further works are also outlined.

2 RECOVERING OF CONTAMINATED SOIL AND WASTE

2.1 INTRODUCTION

Across Europe recovery and reuse for managing contaminated soil and waste against landfilling is becoming a priority. European legislation, with the implementation of the Landfill Directive, the waste treatment and acceptance criteria (WAC; EU Council Decision 2003/33/EC) with also other specific measures, the limited number of hazardous landfills and the landfill tax, is leading the research to new solutions.

Contaminated soil, when is a by-products of the remediation activity or it is excavated to be treated, is handling as a waste. Soil contamination and waste management are also linked. A large number of contaminated site, for example, find their origin in an improper waste management. Reduction of waste soil volumes and its classification as hazardous waste are also of concern for the site owners and consultants. There is also still uncertainty regarding the handling of contaminated soils, both in the ground or excavated onto a site, in their transport as a waste, and also their ultimate home. The 2008/98/CE Directive considers the excavated contaminated soil as a waste when its treatment and reuse is not part of the remediation project. Its classification is under the EWC (European Waste Code) codes 19 13 01* and 19 13 02 and it is subject to the requirements of the Waste Framework Directive (WFD). Moreover the Landfill Directive regulates that the excavated material reused back into the ground has to be construed as waste disposal and be subject to a landfill licence.

A method for recovering soil and waste could be, for example, their management as construction material (AWE, 2007), but in Europe only recent waste guidance documents, such as those issued by the UK EA, (2004) allow characterisation of soils and assessment for re-use. This is particularly relevant to the process of treating contaminated soils by thermal/physical/biological processes on-site and re-internment.

One method to treat contaminated soil is through a process such as screening or crushing and reusing it as an aggregate/construction

material incorporated into a structure, a road, concrete blocks for building or filter medium.

This treatment also requires that the material does not have a potential risk to the environment or human health- i.e. under the terms of risk assessment the waste can no longer form a link to the receptor or pathway. Furthermore, the reuse of the treated materials requires specification for definite applications, as for example to meet the indications set by the CEN series of European Standard. Together the EU Thematic Strategy for Soil Protection, the Waste Directive and the CEN series of European Standards for aggregates can focus on these aspects and provide opportunities to use treated contaminated soil or contaminated waste as secondary aggregate.

2.2 CONTAMINATED SOIL MANAGEMENT

The term "soil" usually refers to the top layer of the earth's crust formed by mineral particles, organic matter, water, air and living organisms, which give it many vital functions. In the EU and at global level soil is increasingly degrading with erosion, loss of organic matter, compaction, salinization, landslides and contamination with negative impacts on human health, natural ecosystems, climate, as well as on economy (EEA JRC, 2012). Soil protection is extremely important because of the socio-economic and environmental importance of its functions.

The handling of contaminated soils may have two approaches: hazard-based and risk-based. The risk-approach assesses the probability of exposure of the receptor through pathway from the source and it is used to determine the measures taken to remediate the land.

The hazardous approach considers the presence of "dangerous substances" exceeding particular thresholds, and it is not dependant on site specific risk assessment factors such as the source or disposal point of the waste.

Management of contaminated sites is based on the reduction of the risk associated to the contamination to the receptors to an acceptable level. The management process starts with an historical investigation of the site, which may lead to more detailed site investigations and, depending on the outcome of these, to the implementation of risk reduction

measures. In this approach the term 'Potentially Contaminated Site' (PCS) refers to sites where unacceptable soil contamination is suspected but not verified, and where detailed investigations need to be carried out to verify whether there is an unacceptable risk of adverse impacts on receptors. In Italy this is established by the level of the concentration of contaminants compared to threshold values. 'Contaminated Site' (CS) refers to a well-defined area where the presence of soil contamination has been recognised and this presents a potential risk to humans, water, ecosystems or other receptors. Risk management measures, such as remediation, may be needed depending on the severity of the risk of adverse impacts to receptors under the current or planned use of the site (JRC, 2014).

2.2.1   European and National Legislation

At the moment soil protection is not subject to a coherent set of legislation in the European Union; legal requirements for its general protection only exist in a few of the Member States. However, there are substantial differences in the underlying site definitions and interpretations used in different countries.

An indirect contribute to the protection of this resource is given by EU policies in areas such as agriculture, water, waste, chemicals, and prevention of industrial pollution (e.g. the Integrated Pollution and Prevention Control Directive (IPPC 2008/1/ EC), the Water Framework Directive (WFD 2000/60/EC), the Waste Framework Directive (2008/98/EC) and Landfill Directive (99/31/EC)). Although the specific aims of these areas are not sufficient to ensure an adequate level of protection for all soils in Europe.

Notwithstanding these policies, significant new site contamination still occurs as a result of accidents and illegal activities and while the managing of new contaminated sites is constrained by regulation, a very large number of sites exist with historical contamination that may present unacceptable risks and need to be properly managed.

For all this reasons the Commission adopted the *Soil Thematic Strategy for Soil Protection* (COM (2006) 231) on 22 September 2006, a proposal for a Soil Framework Directive with the objective to protect soils across the EU. Further in May 2014 the Commission decided to withdraw a

proposal that recognises soil degradation as a serious challenge. It provides that by 2020 in the European Union soil is adequately protected and the remediation of contaminated sites is well underway. It commits the EU and its Member States to increasing efforts to reduce soil erosion and to remediate contaminated sites. For the reduction of soil contamination no European targets have yet been established, whereas national targets were established in many European Economic Area countries.

In 2004 Directive 2004/35/EC Directive on the Environmental Liability with regard to the prevention and remedying of environmental damage (ELD) establishes a framework based on the polluter pays principle to prevent and remedy environmental damage. The Directive defines "environmental damage" as damage to protected species and natural habitats, damage to water and to soil. The ELD gives a definition to "land damage", which is any land contamination that creates a significant risk on human health being adversely affected as a result of the direct or indirect introduction, in, on or under land, of substances, preparations, organisms or micro-organisms.

In Italy the management of contaminated sites is ruled by the Government Decree, D. Lgs. 152/2006 (Environmental norms), Part IV, Title V: "Remediation of contaminated sites". The law establishes risk-based and site-specific criteria for the management of contaminated soil and groundwater to be integrated with first screening generic criteria, based on threshold concentration levels. It also gives a definition to "potentially contaminated site", in the case the concentration of the contaminants is above the threshold level (CSC) for soil and ground water. Risk assessment gives the definition of the "contaminated site" in the case the concentrations are above the site-specific risk concentration levels (CSR). It also introduces flexible criteria for the management of contamination at active sites and explains administrative and operational procedures and criteria for restoration/requalification aimed at site redevelopment.

2.2.2   State of contaminated soil in Europe

In many areas of Europe, soil is being irreversibly lost and degraded by the consumer behaviour and the industrial sector, which are contributing

to the increase of potential sources of contamination: municipal waste disposal, energy production and transport, mainly in urban areas.

The estimated number of Potentially Contaminated Sites in Europe in 2011 is around 2.5 million, which about 14 % (340,000 sites) are expected to be contaminated and likely to require remediation (JRC, 2014). On the 27 States Members about 1,170,000 Potentially Contaminated Sites have been identified. About one third of the estimated total of 342,000 Contaminated Sites has already been identified and about 15 % of the estimated total has been remediated.

About one third of the management practise of contaminated soil continues to be using "traditional" techniques. In-situ and ex-situ remediation techniques are applied more or less equally, while ex-situ physical and/or chemical remediation techniques account for 37 % of the contaminated groundwater treatments. The excavation of contaminated soil and its disposal at landfills still remains the most common remediation technique. However the increasing of regulatory control of landfill operations and rising tax, with the development of improved ex-situ and in-situ remediation techniques, is changing the pattern of these practices. In Italy up to 50 % of the remediation technics are excavation and disposal (Figure 2.1).

Most frequently applied remediation techniques for contaminated soil
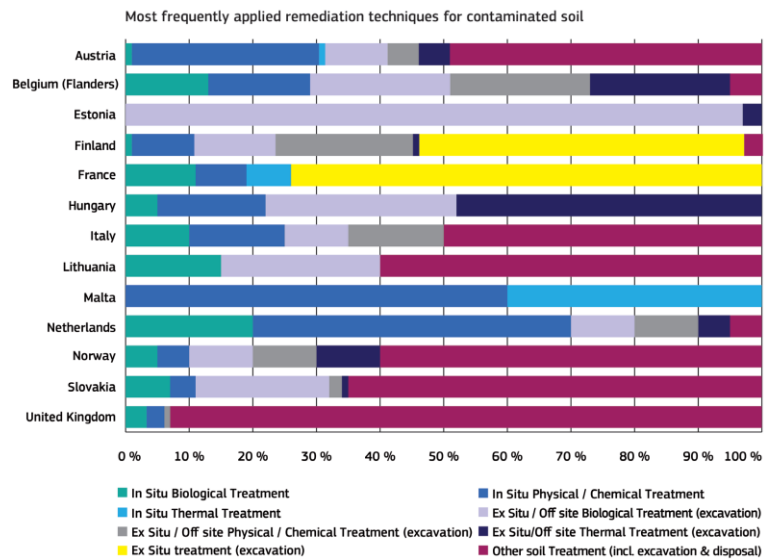
Figure 2.1 Dominant remediation technologies for contaminated soil reported in 2011 (JRC, 2014)

As shown in the Figure 2.2 waste disposal and treatment is the first type of source of contamination and, together with industrial and commercial activities, have caused almost two thirds of the local contamination. Overall, the production sectors contribute up to 60 % to the local soil contamination in which metal industries are most frequently reported to be important sources of contamination (13 %). In particular in Italy the main activity causing contamination is the industrial and commercial sector, while contamination by waste disposal is responsible for up to 40 % of the total local contamination (JRC, 2014).
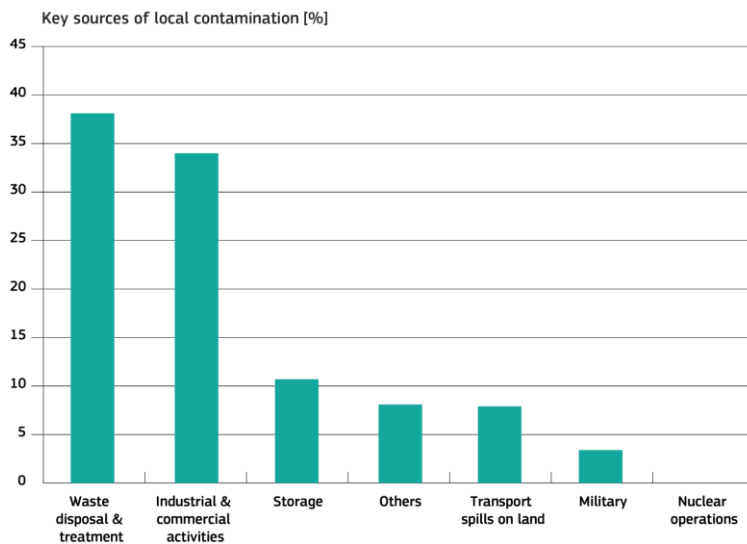
Figure 2.2 Key sources of contamination in 2011 (JRC, 2014)

The Figure 2.3 shows the distribution of contaminants affecting solid and liquid matrix in Europe. Heavy metals are the most frequent contaminants (35 % in the soil matrix) followed by the mineral oil, while phenols and cyanides make a negligible contribution to total contaminant loading.

Most frequently applied occurring contaminants
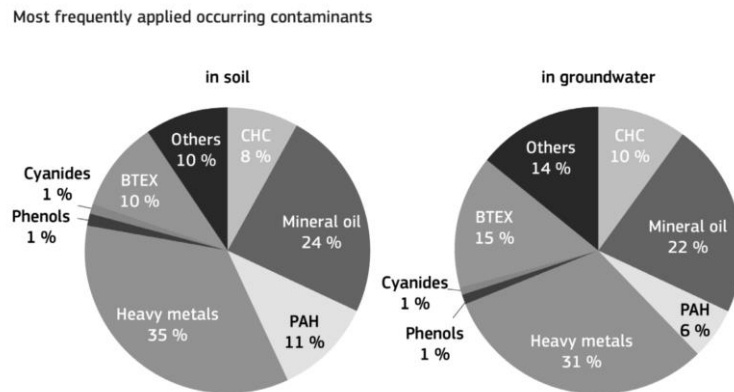
Figure 2.3 Contaminants in soil and groundwater in 2011 (JRC, 2014)

2.3 WASTE MANAGEMENT AND RECOVERING

The European Union produces up to 3 billion tonnes of waste every year (EU, 2010), of which around 100 million tonnes (4.1%) made of hazardous waste. On average of the 500 million people living in the EU half a tonne of household waste is produced every year. This is on top of huge amounts of waste generated from activities such as manufacturing (360 million tonnes) and construction (900 million tonnes), while water supply and energy production generate another 95 million tonnes (EU, 2010). In 2010 Italy produced 161 million tonnes of not hazardous waste and 9.7 million tonnes of hazardous waste, while in the U.K. was respectively of around 250 million tonnes and 9.5 million tonnes. (ISPRA, 2012).

In Italy, in 2010, 42.3% of the total of not-household waste was from Construction and Demolition wastes (including excavated soil from contaminated sites) (EWC code 17). In particular, around 13 million tonnes of these were "soil and stones containing dangerous substance" (EWC 17 05 03*) and "soil and stones other than those mentioned in 17 05 03" (EWC 17 05 04) (ISPRA 2012).

One of the main aims regarding waste is turning it into a resource and reduces its landfilling. For these reasons the European Legislation has set objectives and targets to improve waste management, stimulate innovation in recycling, limit the use of landfilling and create incentives

to change consumer behaviour. The reuse, recycle and re-manufacture of waste materials into new materials can move to a more circular economy where waste is eliminated and resources are used in an efficient and sustainable way.

Moreover waste management can help to reduce health and environmental problems, reduce greenhouse gas emissions (directly by cutting emissions from landfills and indirectly by recycling materials which would otherwise be extracted and processed), and avoid negative impacts at local level such as landscape deterioration due to landfilling, local water and air pollution, as well as littering.

2.3.1 European and National Legislation

The European Union's approach to waste management is based on a "waste hierarchy" and, with the 7th Environment Action Programme, has been set the following priority objectives for waste policy:

- reduce the amount of waste generated;
- maximise recycling and re-use;
- limit incineration to non-recyclable materials;
- phase out landfilling to non-recyclable and non-recoverable waste
- ensure full implementation of the waste policy targets in all Member States.

The main EU directive on waste is the European Waste Framework Directive 2008/98/EC, with other specific directives, among them the Landfill Directive 1999//31/EC and the Packaging and Packaging Waste Directive 94/62/EC.

The Waste Framework Directive contains a list of potentially hazardous wastes, and those not identified are deemed non-hazardous. Nearly all household, commercial and industrial waste is listed and should be assessed to determine if it should be designated as hazardous. The European Waste Catalogue is a directory classifying wastes by mode of production, which also separates wastes as hazardous or non-hazardous. Each waste has a unique six-digit identification code (EWC or CER in Italian), with the first two digits denoting the European Waste Catalogue Chapter.

Waste is classified into three categories based upon the severity of designated hazardous properties and the appropriate class of Landfill: inert, non-hazardous or stable-non reactive and hazardous waste. Wastes sent for landfill are tested by comparing water leachate concentrations against Waste Acceptance Criteria (WAC). Only wastes meeting the specified criteria for the particular landfill class are permitted to be disposed. Hazardous wastes are subjected to WAC assessment to determine if they have lower levels of toxicity and can be landfilled in specially engineered non-hazardous facilities as stable non-reactive wastes, or can only be disposed at a hazardous landfill.

To improve diversion of waste from landfill, Landfill Taxes are applied in a number of EU countries: different countries have taxes with different scopes. In the 27 Member States of Europe the Landfill Tax for hazardous waste is at an average of 80 €/t. In Italy the Landfill Tax, depending on Region Average, varies from 1–10€/t for inert waste to 79 – 94€/t for hazardous waste. In UK in 2012 it reached the range 2.5 - 80 £/t (3-97.3 €/t) (ETC/SCP, 2012; CEWEP, 2015).

In Italy the national framework law on waste was amended on the 3rd April 2006 by the Legislative Decree 152/06 (Testo Unico Ambientale), which regulates the Italian environmental framework. The regulations concerning waste topics are included in part 4 (Parte Quarta) of the decree. There is also a wide range of different instruments implemented to promote the recovery of material at national level: targets of separate collection, recycling and recovery targets (Packaging, End of live vehicles, WEEE), landfill bans for certain waste streams (D.Lgs.36/2003), obligation of use of recycled materials (D.Lgs. 203/2003), simplified procedures and regulations (D.Lgs.152/2006, DM 5 February 1998 e DM 161/2002).

2.3.2 End of waste criteria

End-of-waste criteria specify when certain waste ceases to be waste and obtain a status of a product or a secondary raw material. According to Article 6 of the Waste Framework Directive 2008/98/EC, certain specified waste shall cease to be waste when, after a recovery or recycling operation, meets specific criteria:

1. the substance or object is commonly used for specific purposes;
2. there is an existing market or demand for the substance or object;
3. the use is lawful (substance or object fulfils the technical requirements for the specific purposes and meets the existing legislation and standards applicable to products);
4. the use will not lead to overall adverse environmental or human health impacts.

End-of-waste criteria were introduced to provide a high level of environmental protection and an environmental and economic benefit in the recycling of materials. The environmental compatibility of the treated waste can be assess by the hazard assessment approach, even if it can be onerous with much soil analysis and eluate testing required under the terms of the EWC code and hazardous waste list. Various report provided by the Joint Research Centre of the European Commission have proposed procedures to streamline the hazard assessment (JRC, 2009). Several methodologies have also been proposed to recover waste under the "End of Waste" criteria, such as one by Hjelmar et al., (2013) for waste-derived aggregates.

In Italy the article 6 of the Waste Directive has been adopted by the 205/2010 Legislative Decree which added to the 152/2066 Legislative Decree the article 184-ter, which specifies the criteria for "End of Waste" in a transitory phase during which the Ministry of the Environment should identify the correct criteria. In the meanwhile national legislation for the recovering of waste still refers to the previous laws (www.reteambiente.it):

- Simplified procedures for the recovery of not-hazardous waste (DM 5/2/1998)
- Simplified procedures for the recovery of hazardous waste (DM 12/6/2002, n.161)
- Simplified procedures for the recovery of ship waste (DM 17/11/2005 n.169)
- Article 9-bis of the law 30/12/2008 n.210 that regulates the characteristics of the materials to be considered "Mps" (Secondary raw materials).

Italian Ministerial Decree 5/2/1998 is the relevant legislation for the environmental compatibility of the waste treated to be recovered. The reuse as inert material of industrial wastes is generally based on the results of the leaching tests, aimed to evaluate the potential impact produced by the soil or waste in a natural context. Leaching tests are employed to evaluate the waste acceptance criteria for landfill. A leaching test determines the release of pollutants from the solid phase to the leachate, simulating the environmental conditions of which the waste would become part.

At the moment Italian law concerning leaching tests to evaluate the reuse of not dangerous wastes in direct contact with the environment is in a transition phase; in fact the leaching test established by DM 5/2/98 has been replaced in 2006 by UNI 10802 test, equivalent to EN 12457/2 test (Italian law DM 186/2006). This test is the one also adopted by the European Community to evaluate the required landfill disposal (Decision of European Community Council 2003/33) and Italian Law for the waste acceptance criteria (DM 3/8/2005).

Table 2.1 shows the concentration limits of the contaminants considered by the laws.

Table 2.1 European Community (2003/33) and Italian law (DM 3/8/2005) requirements for landfill disposal, at L/S=10.

	Inert waste	Not hazardous wastes	Hazardous waste
TOC	3 %	5 %	6 %
LOI	-	-	10 %
pH	-	>6	
As (mg/kg)	0.5	2	25
Ba (mg/kg)	20	100	300
Cd (mg/kg)	0.04	1/0.2 *	5
tot Cr (mg/kg)	0.5	10	70
Cu (mg/kg)	2	50	100
Hg (mg/kg)	0.01	0.2/0.05 *	2
Mo (mg/kg)	0.5	10	30
Ni (mg/kg)	0.4	10	40
Pb (mg/kg)	0.5	10	50
Sb (mg/kg)	0.06	0.7	5
Se (mg/kg)	0.1	0.5	7
Zn (mg/kg)	4	50	200
Cl⁻ (mg/kg)	800	15,000	25,000
F⁻ (mg/kg)	10	150	50
SO_4^- (mg/kg)	1,000	20,000	50,000

* Italian law foresees lower requirements concerning Cd and Hg about not dangerous wastes landfill disposal.

The inert waste concentration limits are usually used for a first screening for the recovering of the waste treated to be reused.

Italian limits concerning the reuse of not dangerous wastes are comparable to European Community limits for the landfilling of inert wastes considering a solid/liquid ratio equal to 1:10 and are shown in the Table 2.2.

Table 2.2 Italian limits concerning the reuse of not dangerous wastes as inert material (Italian Law DM 5/2/98 and DM 186/2006)

	Limit		Limit
NO_3^- (mg/l)	50	V (µg/l)	250
F^- (mg/l)	1.5	As (µg/l)l)	50
SO_4^- (mg/l)	250	Cd (µg/l)l)	5
Cl^- (mg/l)	200/100 *	Tot Cr (µg/l)	50
CN^- (mg/l)	50	Pb (µg/l)	50
Ba (mg/l)	1	Se (µg/l)	10
Cu (mg/l)	0.05	Hg (µg/l)	1
Zn (mg/l)	3	Asbestos (µg/l)	30
Be (µg/l)	10	COD (µg/l)	30
Co (µg/l))	250	pH	5.5-12.0
Ni (µg/l)1)	10		

* DM 186/2006 maintained all DM 5/2/98 limits, with the exception of chlorides, for which the limit was halved.

2.4 RECOVERING SOIL AND WASTE AS RECYCLED AGGREGATES

The decreasing availability of natural resources for the construction industry supply chain necessitates the use of alternative materials such as wastes or industrial by products. The manufacture of aggregates from waste is a way to recover contaminated soil and waste and to reduce the amount of material going to landfill (C. R. Cheeseman, 2005; Gunning et al., 2009). The demand for aggregate in the European Union in 2012 was 2.7 Gte. Only 183 Mte comprised recycled aggregates and 51 Mte manufactured aggregates (UEPG, 2014). In the UK for example aggregates production is in the region of 300 Mte each year (ONS, 2014), with only 25% of this demand being satisfied by recycled or secondary materials (WRAP, 2008).

With a proper implementation of hazard assessment on the excavated contaminated soils and the move towards classifying the waste as

aggregate, the treated contaminated soils or waste can be widely used as secondary aggregate if the outputs meet the standards.

2.4.1 Aggregates

Aggregates are defined as granular material used in construction (UNI (BS) EN 12620:2002). Their applications include concrete, mortar, roadstone, asphalt, railway ballast, drainage courses and bulk fill. Aggregates may be natural, manufactured or recycled depending if they are extracted from mineral sources, resulting from the processing of inorganic materials previously used in construction and demolition waste, or from an industrial process involving thermal or other modification (BGS, 2013). Aggregates may also be classified according to particle size. In civil engineering, fine aggregate refers to particles below 4mm in size, and coarse aggregate to those above 4mm in size (UNI (BS) EN 12620, 2002). Aggregates are sub-divided by bulk density into lightweight, normal-weight and heavyweight classes. Natural aggregates typically have dry densities within the range 1400-2000 kg/m^3, but if their bulk density falls below 1200 kg/m^3, they are classified as lightweight in nature, and can include naturally occurring low-density materials such as pumice and scoria, or be manufactured by the thermal treatment of clays, shale, siliceous rock or slate via sintering or firing (BGS, 2013).

Aggregates with a bulk density below 1200 kg/m^3 are classified as lightweight, which are usually produced by pelletising and by sintering or firing (UNI (BS) EN 13055: 2002). These processes are usually energy intensive and form low-density solid pellets by particle fusion and bloating the structure (BGS, 2013). There are different lightweight aggregates currently available, from naturally occurring low-density materials such as pumice, scoria to manufactured by thermally treating expanding clays, shale, siliceous rock or slate.
Some examples of manufactured LWA are shown in the Table 2.3 and Figure 2.4. Lightweight aggregates are utilised in a diverse range of applications including lightweight structural concretes, low-density construction blocks, engineering fill and horticultural growing mediums.

Table 2.3 Examples of commercial manufactured aggregates using in this study for comparison

Aggregate	Description
LECA®	Lightweight aggregate produced by natural clay, pelletised and expanded in a rotary kiln at 1050°C (Saint Gobain, 2015).
Lytag®	Aggregates produced from pulverised fuel ash, pelletised and sintered at 1000-1250°C (Lytag® Ltd, 2015).
C8agg®	Lightweight aggregates produced form MSWI (Municipal Solid Waste Incineration ashes) by pelletising and carbonation (Gunning et al.; 2009)

LECA   Lytag   C8agg

Figure 2.4 Examples of commercial manufactured aggregates

2.4.2   Aggregates from waste and industrial by-products

The construction industry requires the use of alternative materials among recycled waste and industrial by products to substitute the diminishing natural resource. Recovering waste for the manufacture of aggregates leads to the reduction of the landfilling and it preserves natural aggregate resources landfill (C. R. Cheeseman, 2005; Gunning et al., 2009).

Lightweight aggregates can be produced from waste by agglomeration. Agglomeration uses mechanical agitation by tumbling or pelletising, to stick particulates of powered materials with a liquid binder. The process is governed by several parameters: physico-chemical properties of waste, the moisture content of the feed and machineries parameters such as rotation speed (Gunning et al., 2009).

A number of previous studies have examined different manufacturing methods and materials for the production of artificial lightweight aggregates, examples of which are outlined in Table 2.4.

Table 2.4 Selected examples of novel aggregate manufacturing methods

Waste used	Manufacturing Process	Notes	Reference
Municipal solid waste incinerator (MSWI) residues and aggregates derived from contaminated soil washing	Raw material	Concrete production	Sorlini et al. (2011)
SSA **River sediments**	Sintering at temperatures above 1100 °C	Binding of Cd, Cr, Cu and Pb	Xu et al. (2013)
Incinerator bottom ash	Rapid sintering between 900 and 1080 °C.	Reuse of waste Concrete and construction application	Cheeseman et al., 2005
Sewage sludge **Waste glass powder**	Palletisation and sintering	-	Tuan et al., (2013)
Air pollution control residues form municipal solid waste incineration	Firing at 1090 °C	Different wastes mixes Using of natural clay	Quina et al.,(2014)
Quarry fines **Different thermal ashes**	Palletisation with Accelerated Carbonation	Cold process	Gunning et al., (2009)
Harbour sediments **Waste glass**	Sintering/bloating at 1000, 1050, 1100,and 1150°C	-	Wei et al., (2011)
Dredged silt	-	Using of a superplasticizer	Wang & Tsai, (2006)
Lignite coal fly ash **Recycled glass**	Sintered at 1040 and 1120°C in a rotary furnace	-	Kourti & Cheeseman et al. (2010)

2.4.3   Aggregates specifications

The production of aggregates from recovered treated soil waste is now becoming more common and it is necessary to identify the limits at which the waste can be fully recovered – for example when it ceases to be a waste and becomes a product. Aggregate recovery has a strong basis, enabled by the CEN European Standards for aggregates, effective from 1 January 2004. In the construction sector, the CEN standards accept secondary/recycled materials on an equal basis with natural aggregates, hence facilitating a standardised recovery process throughout Europe. Classification of inert waste as a usable aggregate can be based on ISO protocols. The regulation, specification and testing requirements for aggregates are covered in several CEN series of European standards:

- EN 12620 Aggregates for concrete
- EN 13043 Aggregates for bituminous mixtures and surface treatments for roads, airfields and other trafficked areas
- EN 13055 Lightweight aggregates
- EN 13139 Aggregates for mortar
- EN 13242 Aggregates for unbound and hydraulically bound materials for use in civil engineering work and road construction
- EN 13383 Armourstone
- EN 13450 Aggregates for railway ballast

For the End of Waste criteria for recycled aggregates, above the leaching test to assess the environmental compatibility of the product, technical aspect may be considered under:

- EU Construction Products Directive
- Technical standards and guidance
- National building / construction regulations

If an aggregate achieves End-of-Waste (EoW) status, it will become a construction product and hence regulated by the Construction Products Regulation which means that in most EU member states there will be no applicable environmental protection regulation. The EoW criteria must

therefore ensure sufficient protection of the environment and human health. EoW criteria without restrictions and conditions on the use must necessarily include very stringent leaching limit values. Since there is still not a regulated procedure to assess aggregate for End of Waste, some methodologies have been proposed. The one proposed by Hjelmar et al. (2012) includes restrictions and conditions on the use in EoW criteria, and outlines a step-wise methodology for development of leaching limit values for EoW to recover waste in the form of aggregates.

3 STABILIZATION/SOLIDIFICATION PROCESSES

3.1 INTRODUCTION

Solidification/Stabilization (S/S) is a remedial technology which blends treatment reagents into contaminated material to impart physical and/or chemical changes and reduce the flux of contamination that leaches from a contaminant source within acceptable parameters set forth in a site-specific remediation goal. S/S can be effective for metals, asbestos, radioactive materials, oxidizers, PAHs, PCBs, and pesticides and is potentially effective for dioxins/furans, some VOCs and other organics (Dermatas and Al-Tabbaa, 2007; ITRC, 2011).

Stabilization/solidification aims to the chemical stabilization and mechanical solidification of the material treated. It has been widely applied for the treatment of industrial wastes and contaminated land and more recently to wastes prior to landfill disposal (B.D. Bone, LH. Barnard, et al., 2004). The process minimizes the rate of contaminant migration into the environment or reduces the toxicity or hazardous properties of the material. The term "stabilization" refers to the chemical process of converting the contaminants in a soil or waste material into less soluble, mobile, or toxic forms, while "solidification" refers to the physical process which mechanically bind the contaminated soil or waste into a dense monolith with structural integrity suitable for reuse or for storage (B.D. Bone, LH. Barnard, et al., 2004; Dermatas and Al-Tabbaa, 2007; ITRC, 2011). S/S treatment typically involves mixing a binding agent into the contaminated media or waste. These techniques are done either in-situ, by injecting the binder agent into the contaminated media or ex-situ, by excavating the materials and machine mixing them with the agent (Barnett et al., 2009). The process is particularly effective to treat heavy metals contaminated soil and to a lesser extent for organic contaminants because of the detrimental effects on the hydration and structural formation of the materials (Chen et al., 2009). Stabilization/solidification also employs other additives/fillers to pre-treat the materials to, for example, reduce the moisture content (B.D. Bone, LH. Barnard, et al., 2004, ITRC, 2011). The advantages of S/S

include speed of implementation, elimination of off-site disposal and low cost

Stabilization/Solidification using hydraulic or pozzolanic binders with cement is used for the immobilisation of soils and sludges containing a variety of metal pollutants. Cement-based solidification is attractive for the easy application and cost and because it offers an assurance of chemical stabilisation at high pH of many compounds producing a mechanically stable waste form (B.D. Bone, LH. Barnard, et al., 2004; Barnett et al., 2009).

Commonly used cementitious materials and cementitious waste mixture are affected to carbonation. Carbonation is a natural phenomenon known for the detrimental effects on structural concrete, but it can act positively in the immobilisation of heavy metal-contaminated soils and other residues. Carbonation has been used in a "speed" way in combination with hydraulic and pozzolanic material to overcome inhibiting effects of complex waste material reactions responsible for effective solidification. (Hills C.D., 1999; Hills C.D. & MacLeod C.L., 1997; Fernandez Bertos et al. 2004a). Accelerated carbonation of hazardous wastes is a controlled accelerated process during which the solid mixture is carbonated under a gaseous, carbon dioxide (CO_2)-rich environment. This process promotes rapid solidification of the material treated into a structural medium within minutes (Gunning et al., 2009). It also affect the contaminants since binding of toxic metals may occur as the carbonated product rapidly solidifies. ACT has been used to treat hazardous waste using hydraulic binder in a combined process with granulation to produce recycled lightweight aggregate (Gunning et al., 2009Gunning et al, 2010a; Gunning et al., 2011).

At a time when legislation is promoting the recycling and re-use of waste materials, the emergence of technologies that can utilise both gaseous and solid waste products in re-useable materials is fascinating. Contaminated soil and waste can be recovered by stabilization/solidification and/or by accelerated carbonation to produce lightweight aggregates.

3.2 CEMENT-BASED STABILIZATION/SOLIDIFICATION

Cementitious binders are the most used in stabilization/solidification processes and they have been widely used in the world for about 50 years (Malviya & Chaudhary, 2006; ITRC, 2011).

Cement-based solidification/stabilisation improves the handling characteristics and lowers the leaching rates of wastes by a combination of solidification and stabilisation. The high strength, low permeability and relatively high durability of hydraulic cement make it a good binder for this waste management technique (Bone at al., 2004).

3.2.1   Cementitious binders and additives

S/S process options can generally be grouped into cementitious reagent processes and/or surface adsorption reagent processes (Bone at al., 2004; ITRC, 2011). Binders are chosen for the process, depending mainly on the contaminants of interests and the aims of the process. Cementitious reagents are the most common commercially employed S/S process options due, in part, to low cost and availability (Chen et al., 2009; Kogbara et al. 2012). Cement and lime are the most common binders, while cementitious and/or pozzolanic (i.e. materials that react with lime or cement in the presence of water to produce a cementitious compound reagents) include like PFA, GGBS, silica fume, CKD that are industrial by-products reused in concrete production (Bone et al, 2004). These additives can be used in partial substitution of cement to improve chemical and physical properties of the products. For example, PFA leads to reduced hydraulic conductivity, increasing compressive strength and durability, GGBS provides enhanced durability, high resistance to chloride penetration and resistance to sulphate attack as well as improved sustainability. While lime-based S/S processes are able to accommodate large quantities of organics as well as common inorganic sludges (Kogbara et al., 2012). Additives from industrial by-products can vary considerably from source to source and this variability must be taken into consideration in the selection of binder materials. However the contaminated material to be treated is the most important factor to consider as this can affect the physical and chemical properties of the binder systems and lead to poor S/S performance (Ranjit K. Nath, 2012). Organic matter can exhibit an affinity towards cement particles or

cement hydration products by adsorption due to the electrostatic force, hydrogen-bonding interaction, chemical bonding, and hydrophobic force Organics may interfere with the bonding of wastes with cement binders decreasing the strength and impair short-term or long –term durability (Chen et al., 2009). Additives with sorptive properties are used to avoid the detrimental effect that organics may have on cement hydration and improve the efficiency of S/S treatment. They include organophilic clay, bentonite, activated carbon, phosphates, rubber particulates, and chemical gellants (ITRC, 2011). Stabilizing agents and additives may also be recovered from waste or industrial by-products. For example organics waste such as oyster shells, bone mills have been investigated for reducing the leacheability of lead (Moon et al., 2013). Industrial by-products as red mud and steel slag have been found to affect the leacheability of several heavy metals (Garrido et al., 2005; Kumpiene et al., 2008).

Although these reagents may be used singly or in various combinations, Portland cement is by far the most widely used for S/S of contaminated soils and has been applied to a greater variety of wastes than any other binder (Bone et al., 2004; ITRC, 2011). Cement is frequently deployed for S/S works generally, due to its ability to (a) chemically bind free liquids, (b) reduce the permeability of the waste form, (c) encapsulate waste particles surrounding them with an impermeable coating, (d) chemically fix hazardous constituents by reducing their solubility, and (e) facilitate the reduction of the toxicity of some contaminants (Bone et al., 2004; Chen et al., 2009; ITRC, 2011).

Portland cement is a family of cements introduced in EN 197-1: 2000, which are based upon standard strength classes. Class 42.5N. It is produced by calcining a mixture of finely ground limestone and clay in an inclined rotary kiln to a maximum temperature of 1450°C. After cooling, the clinker is ground with $2 - 5\%$ gypsum to control the rate of setting during addition of water (Bone et al., 2004).

The main composition of Portland cement is the Calcium Silicate C_3S (and C_2S). The hydration products of C_3S (and C_2S) are the microcrystalline hydrate, $C_3S_2H_3$, (referred to as C-S-H) and CH, normally referred to as portlandite (Bone et al, 2004; Chen et al., 2009). The formation of the C-S-H gel is important to the setting of cement and to S/S processes as interference with these reactions results in an unsatisfactory set. The C–S–H gel formed during the hydration has a

strong capacity of binding metals (Chen et al., 2009). During hydration of cement, the production of C-S-H is accompanied by a rising of pH to 12-13 as alkalis become solubilised. At this high pH, certain hydroxides can react with silica derived from clayey soils, leading to the production of a gel-phase that cements the soil matrix. Sand particles in the soil are thought to be uninvolved in chemical reactions with cement and the precipitation of $Ca(OH)_2$ crystals on the surface of sand grains forming crystals does not appear to be detrimental. Soil organic matter (SOM) seems to sequester contaminants, immobilize them. The increasing of the pH of a soil by the addition of cement may cause morphological change to the organic matter (Bone et al., 2004).

3.2.1 Heavy-metals stabilization mechanisms

Binders are mixed with wastes or soils containing contaminants with the aim of stabilizing and/or solidifying the contaminants in the final product. Immobilisation of inorganic contaminants involves both stabilisation and solidification. Cement is the most adaptable binder currently available for the immobilization of heavy metals. The overall process of cement hydration is extremely complex, especially in the presence of heavy metals. Immobilization mechanisms involved in the interaction of heavy-metals with soils and cement can be (Bone et al, 2004, Chen et al., 2009):

- pH-dependent precipitation
- redox-controlled precipitation of insoluble compounds
- sorption potential
- incorporation into crystalline components of the cement matrix.

The changing of the pH and of the redox potential (Eh) leads to the variation in the speciation and solubility of contaminants. The precipitation of salts from solution is pH-dependent, an increase in the concentration of OH- ions in solution results in the formation of metal complexes and in the precipitation of metal salts (Bone et al, 2004). Since most metals precipitate as their insoluble hydroxides at high pH, highly alkaline conditions are desirable in S/S treatment. For example the solubility of the Cd, Cu, Pb, Ni and Zn passes through a minimum around a pH of 10 (Figure 3.1) (Stegemann, 2005).
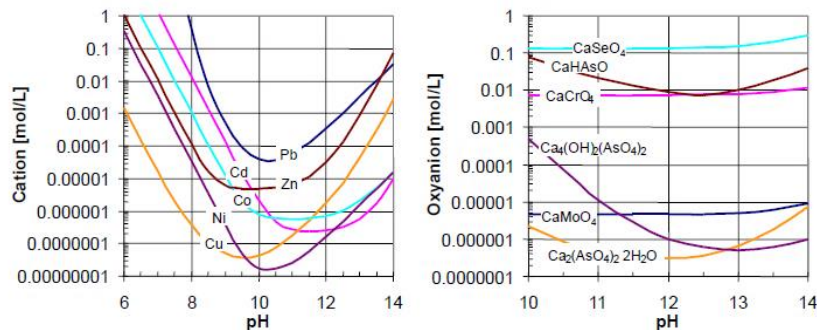
Figure 3.1 Solubility of cation and oxanion with the pH (Stegemann, 2005).

A lower Eh environment leads to a better immobilization of contaminants since multivalent anionic metals can be reduced to less soluble cationic species. Low Eh binders can reduce the mobility of multivalent metals such as Cr and Mn reducing them to lower-valent less soluble species, and increasing sorption onto the C-S-H gel (Glasser, 1993; Bone et al, 2004).

The nano-porous C-S-H gel from hydration mechanism of cement has sorption potential. This generally includes adsorption to binder-soil matrices and absorption/encapsulation into and onto the gel. Adsorption to binder-soil matrices is achieved at high pH and the effectiveness of sorption processes depends on both soil mineralogy and the maintaining of high pH environment. The nano-porous structure of the C-S-H gel with high surface area (between 10 and 50 m^2/g) promotes the sorption of anions and cations. However heavy metals are more likely to be physically encapsulated in the C-S-H gel, which provides another simple mechanism for the effective retention of pollutants (Bonen and Sarkar, 1995; Chen et al., 2009). Contaminants are also incorporated into the solid, crystalline phases of the cementitious matrix. The degree of incorporation depends on the crystalline phases present, which in turn leans on the formulation of the cement-based system and the degree of hydration. Incorporation into the crystalline phase may occurs with the substitution of Ca^{2+} with cations like Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} (Bone et al, 2004; Chen et al., 2009).

3.2.2 Design criteria

Stabilization/Solidification is designed to satisfy mainly two parameters: leacheability and strength. The design criteria of the process, based on treatability tests, is usually governed by the management scenario, which could be defined by the remediation aims: the reuse of the material treated or to the disposing to a landfill, although clearly it is the least desirable option. The design properties of the S/S soil or contaminated material are controlled by the specific reuse application from a number of options (Bone et al. 2004, ITRC, 2011).

Contaminant transport modelling may define the physical properties of the material, which are chosen to guarantee the structural properties, such as load bearing properties of the monolithic nature of a waste form and therefore the diffusion of contaminants by the leaching mechanism (Bone et al., 2004; Al Tabaa et al., 2006; IRTC, 2011).
For example S/S materials have to be strong enough to resist to the load caused by the mass of overlying soil, operational equipment and surface structures. Further diffusion of contaminants from the S/S material by groundwater flow or rain, have to respect the leachate concentration at the point of compliance (POC), that can set as a down-gradient well or a subsurface or surface water body (Figure 3.2).
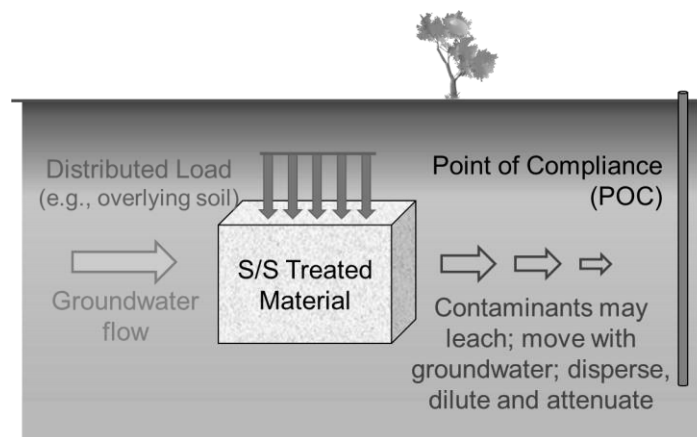
Figure 3.2 Example of a design criteria scenario for S/S material (ITRC, 2011).

There are a minimum of parameters defined to enable handling and treatment during construction and to ensure long-term performance of the material against factors such as weathering, loading and saturation.

Depending on the end use of the S/S treated material, other properties that could be specified include strength, permeability, porosity, compaction, bulk density, freeze-thaw durability, compressibility, California bearing ratio (CBR) and others. Freeze/thaw and wet/dry durability tests for example are conducted to examine the capability of the S/S material to withstand weathering due to temperature and moisture fluctuations.

All the parameters may be pertinent for every site and may be identified based on individual site goals and conditions. However the main primary performance parameters, which can typically be used to define the important performance characteristics for an S/S material, are:

- Strength
- Hydraulic Conductivity or permeability
- Leachability

- **Leachability**

The *leacheability* of the stabilised/solidified (S/S) soil is the most important design parameter. There are now a number of leaching tests, whose application depends on the management scenario. The batch leaching test, UNI (BS) EN 12457, is the most common in Europe and the one proposed in the main regulation discussed in the specified section. This leaching test is suitable for granular material, while monolithic material like S/S soil can be tested with the tank leaching test. The batch leaching represents the worst-case scenario, since the material is crushed prior to testing hence maximising the leaching potential of contaminants. The tank-leaching test assesses the leaching potential due to diffusion processes which is likely to be a more realistic scenario in practice. Sometimes it is used the acid and base neutralisation capacity test (ANC/BNC), DD CEN/TS15364 (BSI, 2006), in which the contaminants in the leachate are assessed based on their availability at pH values of interest.

- **Strength**

The *Strength* of a material is its ability to withstand an applied physical stress without incurring an inelastic damage leading to structural failure.
In S/S processes strength is monitored to ensure that the waste treated has adequate resistance for the specific end use, for example to resist at the load of the surrounding material. Minimum compressive strength criteria are set such that S/S material will support the loads imposed by the equipment used in implementation; however, high strength values may be required depending on other considerations. Strength is also related to the durability of the material treated. Materials with higher initial compressive strength are typically considered to be more resistant to aging and may be used as an indicator to maximize durability, as well as to monitor the performance during S/S application.

Among several measurements of strength, as flexural, tensile and compressive strength, the unconfined compressive strength (UCS), or the capacity of a material to withstand axially-directed pushing forces, is the most commonly utilized for S/S materials. The UCS is used as a measure of the ability of a monolithic S/S material to resist mechanical stresses and it relates to the progress of hydration reactions in the product. For S/S materials treated, which form a monolithic mass an appropriate test method for UCS is the ASTM D1633. This method provides two alternative procedures based on specimen size and component particle size. When S/S treatment results in an encapsulated granular material, ASTM D2166 may be used to provide an approximate measure of the compressive strength in a cohesive molded. Strength is expressed in terms of total stresses. UCS is expressed as the load per unit area in units of pounds per square inch (psi) or kilo-newton per square meter (kN/m^2) at failure (ASTM D1633) or at 15% axial strain (ASTM D1633) (ITRC, 2011). For granular material another strength test may be the CRB (California Bearing Ratio), while the MAPEI company used the Los Angeles test to test their HPSS aggregates (Scanferla et al., 2009).

- **Hydraulic conductivity and permeability**

Hydraulic Conductivity of a material measures the property related to the movement of water through a porous medium under groundwater flow conditions governed by Darcy's Law. This term is often used

interchangeably with the *permeability*, which relates to the ease with which water passes through a porous medium. Hydraulic conductivity depends on the properties of the material structure, while permeability depends on the properties of both the material and the fluid.

S/S treatment aims to reduce the ingress and egress of water in and out of the monolithic mass to reduce leaching potential. Determining the likely permeability of the treated material is therefore linked to the potential of the transportation of leachate bearing contaminants through the treated material into underlying strata and eventually into groundwater. More important is the relative hydraulic conductivity between the S/S material and the surrounding soil. The relative hydraulic conductivity determines if groundwater is diverted around the outside of the S/S mass or if groundwater will percolate through the S/S mass. Hydraulic conductivity can be tested by ASTM D5084 method, which is a common testing procedure for saturated soils and soil-cement materials and contains procedures for a falling head permeameter and a constant head permeameter (Bone et al., 2006; ITRC, 2011). Granular material can also be tested for water permeability and maximum water capacity to assess their suitability as geotechnical medium.

The performance of S/S treated is also governed by several variables including soil type and properties, contaminant type, speciation and concentrations, curing environment, binder type and dosage. These factors complicate the optimisation of treatment process design and as a result, it is important to develop the range of operating conditions that results in acceptable performance for generic S/S of contaminated soils.

3.3 STABILISATION/SOLIDIFICATION BY ACCELERATED CARBONATION

Accelerated carbonation (ACT) is a technology which induces rapid reaction between mineral or reactive waste materials and carbon dioxide. Exposing the material to a rich atmosphere of CO_2 or a slightly positive pressure promotes its rapid harden into a desired structural medium rapidly (Fernández Bertos et al., 2004; Gunning et al., 2009). Precipitation of calcium carbonate reduces the porosity of the waste materials treated, changes the microstructure aiding the retentions of

contaminants and improving the mechanical characteristics. This leads stability and strength development in materials with otherwise comparably poor cementitious properties, and can bind waste together into preformed shapes for use as construction materials (Fernández Bertos et al., 2004). It also lower the pH to values corresponding with the immune-solubility of many heavy metals and to within regulatory defined limits for landfill (Malviya and Chaudhary, 2006; Gunning et al., 2010; Ranjit K. Nath, 2012).

Accelerated Carbonation Technology (ACT) is being investigated as a carbon capture solution since carbon dioxide is permanently bound into solid carbonate minerals. In the last twenty years, ACT has been developed for the treatment of contaminated land and industrial wastes (Araizi et al., 2013; JRC, 2013).

Accelerated carbonation has been used as a stabilization/solidification method for the treatment of contaminated soils and hazardous wastes, giving reaction that can cause rapid hardening and the production of granulated or monolithic materials. This technology provides a route to sustainable waste management and it generates a viable remedy to the problems of a decreasing number of landfill sites, global warming and the depletion of natural aggregate resources, for instance sand and gravel (Gunning et al., 2009, Gunning et al., 2010a). Accelerated carbonation induced stabilization/solidification could also be used to improve the treatment of S/S contaminated soil, since in certain circumstances S/S cannot be used because of the high pH of the final product, the increasing solubility/mobility of some heavy metals, the poisoning on hydraulic activity of some contaminants and the length of time that it could take to obtain a mature product (Ranjit K. Nath, 2012).

Palletisation has been used in combination with accelerated carbonation to produce hardened aggregate by agglomeration (also known as pelletising) in a rotating vessel. Aggregates produced by accelerated carbonation showed strength and durability compared to aggregate exposed to natural carbonation (Padfield et al., 2004; Gunning et al., 2009). This enhanced stabilization/solidification process could therefore be used to produce lightweight aggregate for concrete, pipe bedding, geotechnical and filling applications, filter or drainage and flooring and roofing (Gunning et al., 2010a).

3.3.1 Carbonation reaction

Carbonation is a natural reaction occurring between carbon dioxide and alkaline materials (Fernández Bertos et al., 2004). Atmospheric carbonation is a well-known natural phenomenon affecting commonly used cementitious materials. It can have detrimental effects on structural concrete, or can act positively in the immobilisation of heavy metal-contaminated soils and other residues (Fernándes Bertos et al., 2004; Chen et al., 2009; Gunning et al., 2010b; Ranjit K. Nath, 2012).

In the solid phases ionized carbon dioxide induces salvation of calcium ions, which then re-precipitate in the pore space of the cement mixture as $CaCO_3$, forming a solidified product. The reaction is diffusion-controlled and strongly exothermic. The gas diffuses into the solid resulting in a growing front of carbonated material surrounding an inner zone of non-carbonated material (Figure 3.3).
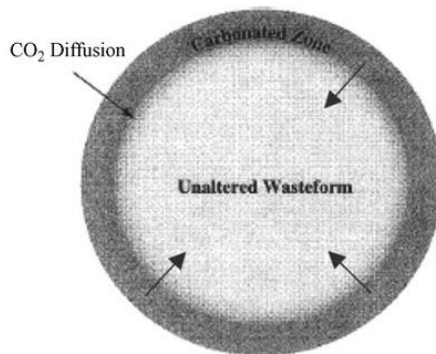
Figure 3.3 Schematic of carbonation process (Fernández Bertos et al., 2004).

The carbonation mechanism can be considered a sequential reaction expressed by the following equations (Freyssinet et al., 2002):

$$H_2O + CO_2 \rightarrow H_2CO_3 \quad (1)$$
$$H_2CO_3 \rightarrow H^+ + HCO_3^- \rightarrow 2H^+ + CO_3^{2-} \quad (2)$$
$$Ca^{2+} + CO_3^{2-} = CaCO_3 \quad (3)$$
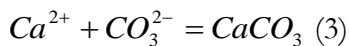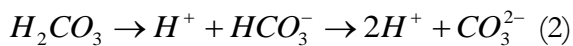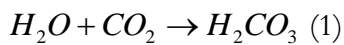
Carbonation and the capacity of the process to stabilize contaminants is controlled by several parameters such as solid composition, compaction and water content of the material; pressure, temperature and partial pressure of the gas during the process.

Water at a right amount is necessary to promote the reaction of CO_2, too much water limits the reaction due to the blockage of the pores in the solid (Fernández Bertos et al., 2004). Hydration and dissolution of CO_2 occur in the presence of water, as well as the dissolution of Ca^{2+} ions from the solid phase, which reacts with the CO_2 to form calcium carbonate. At low water-solid ratios, the gas permeability is high and the CO_2 effectively diffuses into the material (Fernández Bertos et al., 2004; Gunning et al; 2010b).

3.3.2   Accelerated Carbonation Technology (ACT)

Accelerated Carbonation Technology (ACT) is used to treat a wide range of alkaline wastes and metal-contaminated soils by exposing them to a carbon dioxide rich atmosphere in a way that promotes the massive precipitation of calcium carbonate (Gunning et al., 2010b). Mineral carbonation of rocks by ACT is also used and it involves the reaction of carbon dioxide with minerals, mostly constituted by calcium or magnesium silicates. The product of the reaction is an inert carbonates, which may be recovered as an excellent construction materials silicates, since it has improved physical and chemical characteristics (Gunning et al., 2010a; Gunning et al., 2010b; CSLF, 2013; JRC, 2013).

3.3.3   ACT of cement-based stabilization/solidification

C-S-H product in cement-solidified waste is affected by carbonation. The reaction between carbon dioxide and $Ca(OH)_2$ and C–S–H present in the cement material lead to the consumption of them and the lowering of the pH (Lange et al., 1996; Fernández Bertos et al., 2004; Bhaswati et al., 2006; Chen et al., 2009).

In certain circumstances S/S cannot be used for the high pH of the final product, the increasing solubility/mobility of some heavy metals, the poisoning on hydraulic activity of some contaminants and the length of time to obtain a mature product (Ranjit K. Nath, 2012). Carbonation induced S/S could be used to improve the treatment of S/S contaminated soil since it is capable of inducing setting and strength development in the waste forms where hydration is significantly retarded

(Fernández Bertos et al., 2004; Malviya, 2006; Chen et al., 2009; Antemir et al., 2010a; Antemir et al., 2010b; Ranjit K. Nath, 2012).

In cement based materials carbonation leads to the transformation of silicate hydrate of calcium in the form of C-S-H gel and of the Portlandite to calcite as in the reaction reported below (Fernández Bertos et al., 2004).

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \quad (4)$$
$$Ca(OH)_2 + H_2CO_3 \rightarrow CaCO_3 + 2H_2O \quad (5)$$
$$3CaO \cdot 2SiO_2 \cdot 3H_2O + H_2CO_3 \rightarrow CaCO_3 + 2SiO_2 + 6H_2O \quad (6)$$
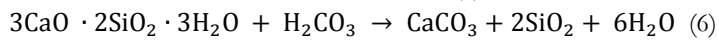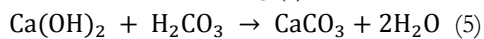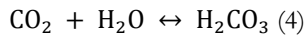
These reactions influence the physical, microstructural and chemical properties of cement-based solidification/stabilisation of waste forms (Lange et al., 1996; Fernández Bertos et al., 2004; Bhaswati et al., 2006). Precipitation of calcium carbonate reduces the porosity of the waste materials treated aiding the retentions of contaminants and improving the mechanical characteristics of the treated materials because of the changing of the microstructure (M.A. Venhuis, E.J. Reardon, 2001; Rendek et al., 2006; Malviya and Chaudhary, 2006; Ranjit K. Nath, 2012).

The Figure 3.4 shows a more dense structure of a carbonated pellet than the natural-carbonated one.
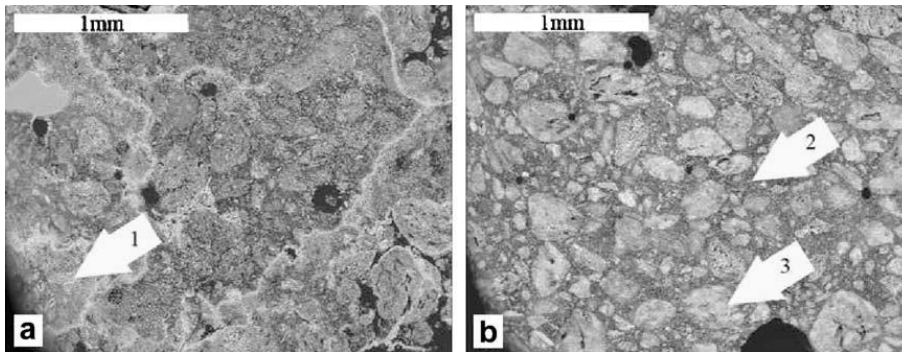
1. calcium carbonate mass; 2. fine crystals of calcium carbonate, 3. gehlenite crystals

Figure 3.4 BSE image of (a) accelerated carbonated pellets (b) naturally carbonated pellets (Gunning et al., 2009).

Despite this general observation there is still disagreement in the studies in the literature about this. In late studies it is reported that degradation of the principal binding phases, the CSH gel, by carbonation will lead to considerable strength loss, while in other studies it is reported that

accelerated carbonation in a waste-binder matrix can lead to strength up to 70 % higher and stabilization improvement (Lange et al., 1996; Fernàndez bertos et al., 2004; Malviya et al., 2006; Chen et al., 2009). Carbonation may alter the rate at which some contaminants leach from industrial wastes or cement solidified/stabilized waste streams (Antemir et al., 2010, Ranjit K. Nath, 2012). The increasing capacity of retention of heavy-metals cations and heavy metal hydroxyl ions carbonation may also be due to the large surface area and meta-stability of decalcified C–S–H gel and calcium carbonate (Chen et al., 2009). The detrimental effect on the trace elements mobility in cement-based system depends on the type of waste and the type and severity of the treatment. The choice of binder is a balance between cost and environmental considerations. The more C_3S or calcium the binder contains, the higher the potential for producing a carbonated product (Fernández Bertos et al., 2004). A reduction of permeability would be a desirable effect in a matrix used to confine toxic wastes (Lange et al., 1996).

Moreover, carbonation reduces the alkaline nature of the hydrated cement paste and reduces the availability of some metals through their precipitation as soluble salts. The pH of the cement-solidified hazardous may drop to values at the minimum solubility of many metals and to within regulatory defined limits (pH<9.5), leading to an improvement in metal immobilization (Lange et al., 1996; Fernàndez bertos et al., 2004; Gunning et al., 2010b; Ranjit K. Nath, 2012). However the reduction of buffering capacity of the solidified matrix, due to the lowered alkalinity, makes the waste more vulnerable to the effects of acid attack and hence to the release of heavy metals in the long term (Fernández Bertos et al., 2004; Ranjit K. Nath, 2012).

Based on dynamic leaching tests using pure water and 0.5 N acetic acid, Shaffique et al. (1998) observed that the accelerated carbonation of mature cement s/s products lead to higher leaching rates of metals, as Cd, Pb and Co respect to the non-carbonated analogues. Also Cr, in leachates associated with non-carbonated samples were observed to be generally higher than those of their carbonated analogues. Higher concentrations of Zn at the low acid addition and similar concentrations at the higher acid addition was observed compared with non-carbonated samples (Hills et al., 1999). The changing of the pH also reduces the buffering capacity of the solidified matrix for the lowering of the alkalinity. This leads that the waste is more vulnerable to the attack of the acid and to the re-mobility of the metals on the long term (Hills et

al., 1999). One positive effect is that accelerated carbonation may overcome the inhibiting effect of complex waste materials on the hydraulic and pozzolanic reaction that are responsible for effective solidification (Fernández Bertos et al., 2004; Ranjit K. Nath, 2012).

3.3.4   Contaminated soil treatment by ACT

In S/S contaminated soil carbonation occurs in years and leads to densification of the treated soil for the precipitation of calcium carbonate within voids and microcracks in the matrix (Antemir et al., 2010a). Contaminated industrial soil has also been tested with a combined treatment of S/S and ACT (Antemir et al., 2010b) and also carbonation has been tested as an in-situ technology to treat alkali industrial soil to improve the environmental leaching behaviour and mineralogy (Capobianco e al., 2014). Contaminated soil and industrial residues that reach specific properties after treatment could be reused within the site as aggregates, filling materials or for concrete production (Scanferla et al., 2009; Gunning et al., 2009).

In recent years Accelerated Carbonation has been tested to enhance stabilization/solidification treatment of contaminated soil (Fernández Bertos et al., 2004; Antemir et al., 2010) and as a technique to increase the compressive strength of compacts formed by residues rich in Ca silicates as steel slag (Johnson et al., 2003). One of the advantages of using accelerated carbonation during cement-based S/S treatment over conventional stabilisation/solidification systems is that the soil is immediately available for development respect to the long term curing time required (Ranjit K. Nath, 2012).

The carbonation technique on contaminated soil underwent successful in a pilot-scale field trials in September 2000 when accelerated carbonation was applied at an ex-pyrotechnics site at Dartford in Kent (George A., 2000; Chen et al., 2009; Antemir et al., 2010a). Contaminated industrial soil has also been treated with a combined S/S and carbonation treatment in an ex-situ process (Antemir et al., 2010b). The soil was treated to obtain pellets whose rapidly harden was observed during a series of studies and pilot scale trials to assess the use of carbonation to promote the rate and extent of setting of stabilisation/solidification treated soils (Antemir et al., 2010a). The improvement of chemical and physical properties of treated material can facilitate the re-use in a variety of construction purpose (Ranjit K. Nath, 2012).

In Brownfield sites redevelopment ACT for contaminated site has been applied in remediation management using the CO_2 emissions resulted as a consequence of treatments for the remediation of groundwater contaminated by organic compounds such as oxidation or CO_2 stripping (Nelson et al., 2009). Moreover CO_2 has been also used in soil for the improvement of the structural properties of the subsoil (Hartog et al., 2013). Accelerated Carbonation for contaminated was used to treat soil characterized by the presence of alkaline mixture, for the presence of former steelmaking on the site, and, due to reaction with the atmospheric carbon dioxide, showed a variable content of $CaCO_3$ (Capobianco et al., 2014). The presence of alkaline earth metal oxides and silicates mixture in soils has been used as an option for the storage of CO_2 into the formation of thermodynamically and chemically stable carbonated phases (Lackner et al., 1995). In the application proposed by Capobianco et al. (2014) the injected CO_2 serves to strip VOCs from groundwater, produced by the reaction between reagents and the resulting volatilization of organic contaminants. Once the CO_2 reaches the layer of alkaline industrial soil was used to stimulate the carbonation of the slag material in the overlying industrial soil, resulting in the improvement of the environmental properties of the carbonated material and CO_2 storage.

3.3.5 Stabilization of waste by ACT

Accelerated carbonation is usually used to treat hazardous wastes. Many thermal wastes, including those from cement, metallurgical and paper processes, were found to be reactive with carbon dioxide (Gunning et al., 2010a). Accelerated carbonation induces rapid reaction between mineral reactive waste materials exposing these to carbon dioxide, promoting rapid harden of the product (Fernández Bertos et al., 2004; Gunning et al., 2010a). The process permit at least to reduce the hazardous properties of wastes as a means of reducing the costs of disposal in landfill or, more important, to reuse the material treated. Also the neutralization of the alkaline nature of these wastes allowing their reclassification as stable non-reactive hazardous wastes (Gunning et al., 2010b). Significant improvement in the chemical and physical properties of the treated materials can facilitate re-use in a variety of construction applications (Fernández Bertos et al., 2004). For this scope carbonated waste can be formed into aggregate by agglomeration, also known as

pelletising, using a rotating vessel to produce hardened aggregate (Padfield et al., 2004; Gunning et al., 2010b; Gunning et al., 2011). This type of innovative and cold energy-saving process has been developed to treat different type of ashes for lightweight aggregate production (Gunning et al., 2009). ACT was also used to recover fine-grained not-reactive wastes that have poor engineering properties and when they are mixed with hydraulic reactive binders in a CO_2-rich atmosphere, they can be bound together to form pellets suitable for use as aggregates. This process can require the combination of two or more types of reactive and not-reactive waste materials and binders. (Gunning et al., 2009; Padfield et al., 2004). Contaminated soil and industrial residues treated with accelerated carbonation can be reused as aggregates, engineering fill or for concrete production (Scanferla et al., 2009; Gunning et al., 2009, 2010a). Aggregates subjected to accelerated carbonation showed improved strength and durability compared to aggregate exposed to natural carbonation (Gunning et al., 2009). The process has been studied first at lab scales and then followed by pilot scale trials to assess the use of carbonation to promote the rate and extent of setting of stabilisation/solidification wastes and treated soils (Gunning et al., 2012a). A typical carbonated-granulates product from waste is shown in the Figure 3.5. The carbonated aggregates produced were classified as LWA based on the specified bulk density limit of 1200 kg/m^3 (EN 13055, 2002).

Figure 3.5 Example of a pelletised product developed by Gunning et al. (2009).

These recycled materials have been tested to be used in lightweight concrete construction blocks (Figure 3.6).

Figure 3.6 Example of block produced from recycled carbonated aggregate by Carbon 8 Aggregates Ltd (Gunnning et al., 2012a).

Other applications can be pipe bedding, geotechnical and filling applications, filter or drainage and flooring and roofing. The latest involves artificially vegetating the tops of buildings by installing drainage and growing layers, resulting in improved aesthetic and building insulation properties, and environmental benefits (Guuning et al., 2010a). For this last possibility a lightweight kind of pellets is required to support plant growth without placing excessive load on the roof structure (FFL Guidelines, 2002).

Although ACT of waste predominantly uses high purity carbon dioxide gas, that is expensive to produce and buy, the enhanced curing of concrete articles typically employs CO_2 at 5-20% by volume. An alternative supply of lower purity, carbon dioxide can be obtained from industrial point source emissions as coal-fired power stations, cement manufacturing and energy from waste plants. The flue gas obtained from a combusted landfill gas of a closed non-hazardous waste landfills is a potential source of CO_2 (Chalvatzaki and Lazaridis, 2010). Using cement, CO_2 and wastes for the production of secondary aggregates could be a solution to the disposal of huge volumes of waste, and at the same time to provide an additional source of aggregates.

3.3.5.1   *Carbonated aggregates by Carbon8 Systems*

The described process is used by Carbon8 Systems ltd, a spinout company from the University of Greenwich, which is developing and

applying accelerated carbonation for the commercial production of aggregates from solid waste incineration (MSWI) air pollution control residues (APCr) with a patented method (Hills C.D. & Carey P.J.; 2007; Gunning et al., 2012a). The ash is solidified and stabilized in carbonate-cemented pellets and the aggregates have mechanical and chemical properties that make them suitable for use in concrete blocks. Hazardous wastes are converted into construction aggregates that meet the regulatory requirements for "end of waste". After a pilot-scale trials at a hazardous waste landfill in 2010, where five tonnes of aggregate were produced and used in a small production construction block by a major UK manufacturer, in early 2012 a full scale carbonation plant (Figure 3.7) for commercial purpose was built and commissioned at Brandon in Suffolk, UK (Gunning et al., 2012a; CSLF, 2013; Carbon8 aggregates ltd, 2015).

Figure 3.7 Illustration of the completed manufacturing plant (Carbon8 aggregates ltd, 2015; figure from: http://c8a.co.uk/)

Carbon8 Aggregates have been subject to the "End of waste" criteria for the commercialization of the product (Gunning et al., 2012b). This was implemented with a series of permission to obtain the Environmental Permitting regime under the control of the Environmental Agency at each stage of the scaling up of the process due to the challenges faced for the European waste legislation and its implementation in the UK to obtain the EoW qualification. The trials had to provide the evidence of the quality of the aggregate and through third part accredited testing of the physical and chemical properties of the product allowed a specification for the aggregate to be devised. At the end an application to the Modernising Waste Panel for "End of Waste" status for the aggregate was submitted to certify that, according to the European Waste Legislation, the produced aggregate did not pose an environmental risk, had a clear end use, and was a suitable replacement for virgin natural aggregate; the latest tested the clear end use of the

material for the production of concrete blocks according to European Standard. Furthermore it had a carbon negative impact at -44kg CO_2/t of product (Gunning et al., 2012a; Gunning et al., 2013; Report, 2013; Carbon8 aggregates ltd, 2015).

4 MATERIALS & METHODS

4.1 INTRODUCTION

The trials of cement-based stabilization/solidification and accelerated carbonation have been conducted on different type of contaminated soils and waste.

The first part of the research focused on the efficacy of the cement stabilization/solidification of heavy metals artificial contaminated soil and investigated the effect of accelerated carbonation on the process.

In the second part different types of soil washing residues, collected from different soil washing plants, were characterized for their chemical and physical properties and treated to be recovered as a reusable product with stabilization/solidification and carbonation. Other wastes used in the process were Paper Ashes and Sewage Sludge Ashes collected from incineration plant. They were characterized and used in combination with Portland cement to treat the residues. A combined process of accelerated carbonation and granulation has been implemented to produce a reusable aggregate from the material treated. All the materials and methods used in the research are described in the following sections.

4.2 MATERIALS

4.2.1 Artificial contaminated soil

Two batches of artificial contaminated soils have been prepared for the stabilization/solidification test. The artificial soils were prepared using sand (*Sabbie Sataf Srl*) with effective size of 0.20 mm and clay (*Linea natura– Termocomposti)*, first crushed and sieved past 2 mm.

Compost (*Fiore vivo – Termocomposti terriccio universale*), sieved past 2 mm with 40 % of organic matter, was added to provide a source of organic matter (OM) in the prepared soils.

The three components where in the sand:clay:compost ratio of:
• Soil 1(S1): of 50 % sand, 40 % clay and 10 % compost

• Soil 2 (S2): of 50% sand, 50% silt and 0% compost

The soil was spiked in small batches of ~2 kg with three heavy metals added as reagent grade chemical compounds of Pb $(NO_3)_2$, Cd $(NO_3)_2$ and Cu $(NO_3)_2$ (all supplied by *Sigma-Aldrich*) at relatively high value. Three samples for each type of soils have been contaminated with the three metals at three different concentrations: 500, 1500 and 3000 mg/kg.

Table 4.1 details the contaminant compounds spiked, which were monitored during the course of the experiments. These heavy-metals were chosen because they are among the most common found on contaminated sites (Kogbara et al., 2013).

The concentrations of contaminants recovered from the spiked soil (particle size < 2 mm), are also shown in Table 4.1 showing a degree of mixing of the contaminants within the soils at about 50 % of the initial values. Concentrations of contaminants were over the threshold value for "potential contaminated soil" by D.Lgs 152/2006. The pH of the spiked contaminated soil is also reported.

Table 4.1 Contaminants concentration of the spiked artificial soils

Sample	OM (%)	Amount of each metal spiked (mg/kg)	Amount of contaminant recovered (mg/kg)			pH
			Cd	Cu	Pb	
S1_C1	10	500	237.2±13.24	318.5±27.31	282.8±29.38	6.71
S2_C1	0		219.4±4.43	325.3±19.83	247.5±19.83	5.75
S1_C2	10	1500	596.1±39.27	775.0±77.03	773.3±132.0	6.45
S2_C2	0		674.2±176.98	846.6±213.4	827.7±253.7	5.54
S1_C3	10	3000	1217±98.72	1436.5±115.8	1384±109.0	6.30
S2_C3	0		1532±331.7	1887.8±383.6	1723±212.3	5.25
D.Lgs 152/2006 Tab.A-B limits (mg/kg)			2 - 15	120 - 600	100 - 1000	

4.2.2 Soil washing residues

Soil washing residues are the fine fractions obtained from the washing out of contaminants from a soil or construction debris. Soil washing uses a series of mechanical process steps utilising water and chemicals additives for removing pollutants from contaminated soil or to recover

excavated soil from construction and demolition works (Figure 4.1 and Figure 4.2) (Griffiths, 1995; Mann, 1996; Dermont et al., 2008; Jensen et al., 2012; Apted et al., 2013).
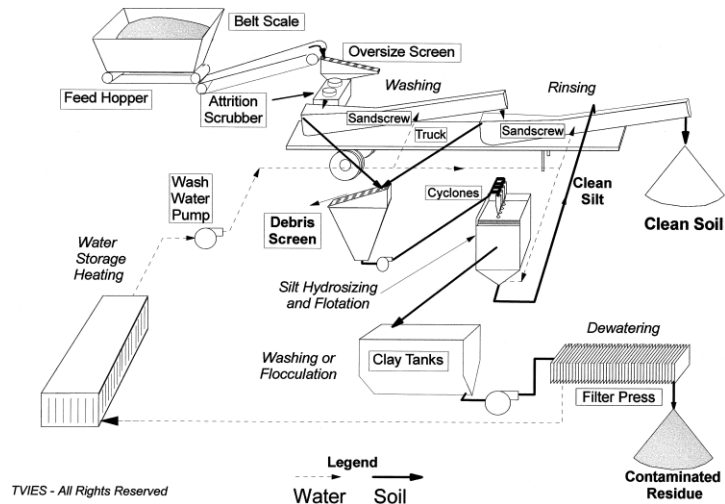
Figure 4.1 Soil washing treatment plant scheme

Figure 4.2 A view of a real soil washing plant in UK

Contaminants are inherently retained in the clay/silt fraction of a soil and can be separated out by processing. The highly contaminated fine-

grained fraction can then be dewatered and caked in a filter press, or discharged into a lagoon to settle. These fines have potential to be recycled, desorbed, bio-remediated or stabilized, or disposed to landfill (Mann, 1996; Khulman, 1999; Jensen et al., 2012). However, landfilling costs can be 50 % of the total cost of the processing (Vaccari et al., 2012), and alternative lower-cost management strategies are desirable for these fine grained residues.

The soil washing residues used in this research were sourced from different soil washing plants located in the UK. (Figure 4.3 and Table 4.2).

| SW1 | SW2 | SW3 | SW4 |

Figure 4.3 Soil washing residues investigated

Table 4.2 Soil washing residues investigated

ID	Source	Treatment method
SW1	Construction and Demolition works soil recycling plant	Lagoon silt
SW2	Organic and inorganics contaminated site soil washing plant	Filter cake
SW3	Road construction works soil recycling plant	Filter cake
SW4	Construction and Demolition works soil recycling plant	Lagoon silt

4.2.1 Paper Ashes

Quicklime (calcium oxide) is often used as a dewatering agent in S/S applications. Paper wastewater incineration ash contains a significant

proportion of calcium oxide, and here is used as a substitute for quicklime. Paper ash arises from the incineration of paper sludge, which contains residual fibres, fillers and chemicals from paper recycling processes (Boni et al., 2004; Mozaffari et al., 2006; WRAP, 2007). Paper production utilises calcium carbonate as a whitening agent, which becomes calcium oxide as a result of calcination during incineration (Boni et al., 2004; Gunning et al., 2010a). Paper ash sometimes exhibits cementitious properties, including during carbonation, and has been previously used to make aggregates, blocks and as a cement replacement (Mozaffari et al., 2006; Gunning et al., 2009). In this work, paper ash (PA) was sourced from a recycling facility in south-east England, UK (Figure 4.4).

Figure 4.4 Paper Ashes sample.

4.2.1 Sewage Sludge Ashes

Sewage sludge ashes are fine ashes from the incineration of sewage sludge from domestic and industrial wastewater treatment process (Cyr et al., 2007; Cheeseman et al., 2003). The use of incineration for dealing with sewage sludge has been steadily increasing, with 260,000 tonnes (dry solids) of sludge being burned in UK in 2010 (DEFRA, 2012). The chemical composition of these ashes is highly variable and may include heavy metals and free cyanide at relatively high concentrations (Lapa et al., 2007; Xu et al., 2013). Although used previously for applications including land spreading, novel uses of sewage sludge (and its ashes) are increasing including partial replacement in cement, bricks and ceramics, in soil stabilization and in sintered lightweight aggregate production (Gunn et al., 2004, Cheeseman and Virdi, 2005, Chiou et al., 2006; Xu et al., 2013; Tuan et al., 2013).

For this work Sewage Sludge Ashes (SSA) was sourced from a sewage incineration plant located near London, UK (Figure 4.5). The plant produces about 8000 tonnes of ash a year, which are placed in the same landfill as the above mentioned silt fines. The combined use of SSA and washing silt are, in a case of waste synergy, where two disposed wastes occur in the same locality and can be combined in a product with potential value.

Figure 4.5 Sewage Sludge Ashes sample.

4.2.1 Portland cement

Portland cement was used as the binder to harden the pellets in the stabilization/solidification process. It also has an ability to combine with CO_2 to produce calcium carbonate. However, in the production of non-carbonated reference aggregates, cement was allowed to harden via 'normal' hydration reactions. Portland cement in stabilization/solidification processes and its reaction to carbonation is described in Chapter 3. The artificial contaminated soil was treated with Portland cement type I 42.5 (COLACEM), while in the recovering of soil washing residues was used Portland cement type I (52.5N).

4.3 EXPERIMENTAL PROCEDURES

4.3.1 S/S and ACT of heavy metals contaminated soils

The cement was employed for treatment of the artificial contaminated soil in 5, 10 and 20% dosages (w/w) in dry form. Water was added to each mix until it was possible to form granules rotating the mixture in a plastic chamber by hand (Figure 4.6).

Figure 4.6 Granular materials obtained mixing artificial contaminated soil and cement.

The mixes (obtained from the two soils, each at three different metal concentrations and mixes each at three cement percentage) have been cured in air, so under natural carbonation, and in dynamic accelerated carbonation, made with a concentrated atmosphere of almost 100 % of CO_2. The samples have been all cured in non-pressurised plastic chamber at 100 % relative humidity, since both the air and the CO_2 flows passes through a humidifier. The CO_2 gas was supplied from a pressurised cylinder, passed through a flowmeter to regulate flow, and through the flask containing deionised water before entering the chamber. The flow of gas was set at the lowest graduation of the flowmeter. An outlet hole in the lid of the chamber allowed the incoming gas to escape, preventing pressure build-up. The experimental set-up with the curing chamber is shown in Figure 4.7 and Figure 4.8.

1a) air pump; 1b) CO_2 supply; 3) flowmeter; 4) pressure reducer; 5) curing chamber
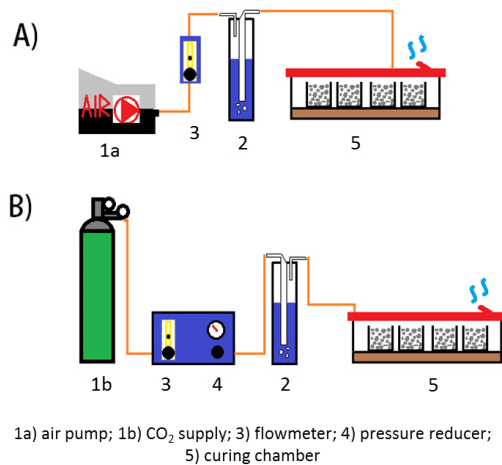
Figure 4.7 Scheme of the dynamic curing chambers

Figure 4.8 Curing chambers for experimental procedures

After 7 days all the mixes were tested for contaminants mobility by leaching test (EN 12457-2) in a rotating apparatus showed in Figure 4.9 and the leachates analysed for metal concentrations. The methods are described in the following section.
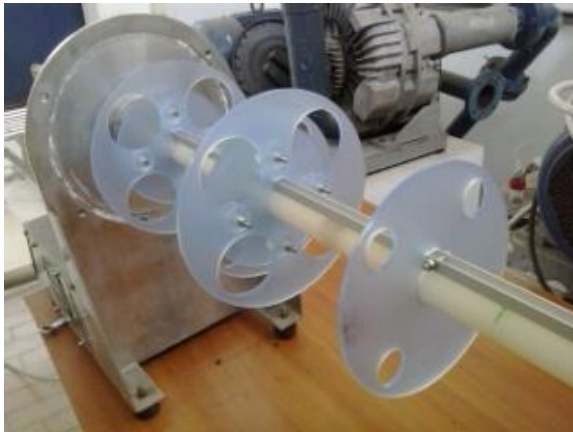
Figure 4.9 Leaching test apparatus

4.3.2   Aggregates production by enhanced S/S

This section presents the methods used to produce carbonation-hardened agglomerates and progressed at University of Greenwich. Manufacture of hardened pellets was obtained by mixing the soil

washing residues with the ashes and the cement and then granulating them by a pelletising step. The mixing and pelletising stages were carried on with an Eirich EL-1 mixer (Figure 4.10) and trials have been conducted varying the mixing recipes and the operational parameters of the mixing and pelletizing stage to produce aggregates as shown in the Figure 4.11.

Figure 4.10 Eirich EL-1 mixer.

Figure 4.11 Examples of pellets at different process parameters

In the first part of the experimental procedure the soil washing residues investigated (SW1, SW2, SW3 and SW4) were mixed with 5, 10 and 20 % by dry weight of CEM I. The soil/cement mixture was then combined with the required amount of paper ash (PA) to remove sufficient moisture to enable pelletising. The speed and residence time in the mixer were adjusted until the desired aggregate product was achieved. The effect of carbonation on the aggregate was evaluated by preparing additional batches under a synthetic flue gas at 20 % of CO_2 according to the process shown in the Figure 4.12.
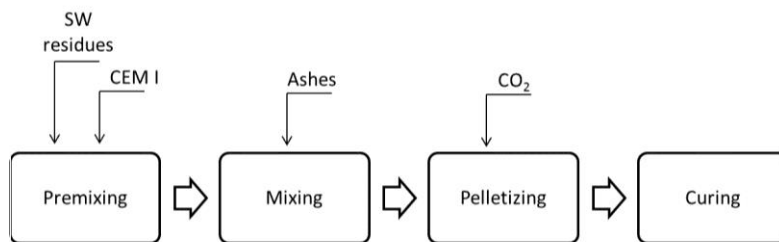
Figure 4.12 Flow chart of the lab-scale process in the first part of experiments

In the second step of the experimental procedure aggregates were produced using one of the residues (SW4) and the SSA previously described. The SSA was used to adjust the water content of SW4 residue and to achieve the required particle size distribution for further processing. The waste residues were mixed together as required, and with 5, 10 and 20 % by dry weight of cement.

Since the SSA were no reactive to carbon dioxide, after a first trial with the flow of carbon dioxide during the pelletising stage, the aggregates were placed in a curing chamber, fed with the synthetic flue gas for up to 6 days. The gas supply contained 20% CO_2 by volume, which is typical of that found in industrial flue gases. The flue gas was used to accentuate the hardening of the pellets, by the 'driving' of normal hydration processes. These are referred to hereafter, as the 'carbonated' aggregates. For comparison, a second set of samples were cured in sealed plastic bags without CO_2 and are referred to as the 'control' aggregates. A scheme of the process is showed in the Figure 4.13.
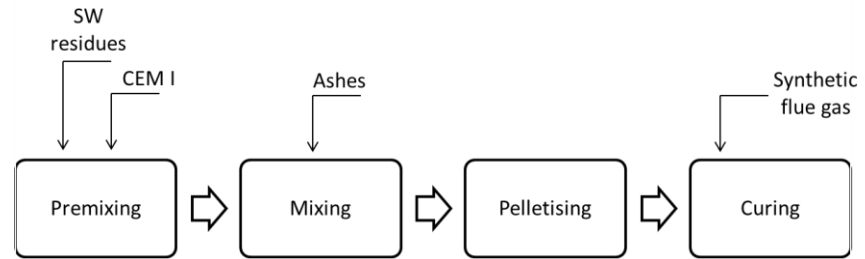
Figure 4.13 Flow chart of the process used in the second part of experiments.

4.4 PHYSICAL-CHEMICAL CHARACTERIZATION

4.4.1 Moisture content

The moisture content of the samples was measured by the weight loss oven drying the material at 105°C for 24 hours. Approximately 10 g of material was weighed in a moisture content tin or 100ml glass beaker. The samples were then placed in the oven at 105°C for 24 hrs and allowed to cool in a desiccator afterward. The moisture content is calculated by subtracting the weight of dry sample from the weight of wet sample and dividing by the weight of dry sample and expressed in %.

$$MC(\%) = ((W_{in} - W_{fin})/W_{in})*100$$

Where MC is the moisture content of the material, W_{in} is the initial weight of the material and W_{fin} is the weight of the material after being oven dried.

4.4.2 pH

The pH of solid materials was measured according to BS 1377-2. Samples of material were air-dried. Three samples of thirty grams were each mixed with 75 grams of water (l/s 2.5) in a clean beaker using a glass rod or shaken for at least 1 minute. Before testing each sample, each container was shacked vigorously for at least 1 minute.

The solution was analysed using an electronic pH meter (Hanna HL4521). Four pre-prepared standards at pH 4, 7, 10, and 13 (VWR Ltd), have been used to calibrate the meter. Each sample was analysed at least three times until a consistent reading within 0.05 was achieved.

4.4.3 Atterberg limits

Atterberg limits were calculated according to the ASTM D 4318, 2012. The liquid limit (LL) is defined as the moisture content at which soil begins to behave as liquid material and begins to flow. Liquid Limit was calculated with a penetrometer (Figure 4.14). The instrument used in this study is formed by a drop-cone penetrometer device, which permits the cone assembly to move vertically in its guide without appreciable friction and which is capable of indicating the depth of penetration to the nearest 0.1 mm. The penetration cone assembly is a stainless steel cone with a cone angle 30°; the conical surfaces shall be polished and the total moving mass shall be 80 g. The test starts permitting the cone to fall freely for a period of 5 seconds. The water content corresponding to a cone penetration of 20 mm defines the liquid limit. Samples of soil at different water contents were used. The results were plotted as water content versus penetration. The liquid limit is read from the plot at a corresponding penetration of the cone of 20 mm.

Figure 4.14 Penetrometer for liquid limit test

The plastic limit (PL) is defined as the moisture content at which soil begins to behave as a plastic material. Experimentally the PL is the water content, in percent, at which soil can no longer be deformed by rolling into 3.2 mm (1/8 in.) diameter threads without crumbling.

Distilled water has been added to the soil until it has a consistency to be rolled without sticking to the hands; the mass was then rolled between the palm or the fingers and the glass plate, using sufficient pressure, until the thread reached a diameter of 3.2 mm (Figure 4.15).

Figure 4.15 Preparation of the thread for the plastic limit.

The Plasticity Index (PI) is the range of the water content within which soil achieves its plastic state and it was evaluated with the following formula:

$$PI = LL - PL$$

4.4.4   Fine Particle Size Distribution

All the washing residues and waste were characterized as fine materials. Particle size analyses aims to characterize the texture of the soils. The particle size distribution of the wastes was measured by laser diffraction (Malvern Mastersizer MS2000, Figure 4.16).The Mastersizer MS2000 was fitted with a wet sample delivery module (Hydro MU) which transports the material in suspension in water.

The samples were soaked in water before the analysis and agitated with a spatula to encourage them to disperse. Immediately before analysis, the dispersed sample is agitated by vigorous stirring, and added drop by drop to the sample holder on the wet delivery module, until the degree of laser obscuration is between 10 and 20%. The default circulating pump speed of 2500rpm was used. The particle size distribution is then obtained by the instrument in terms of the volume expressed in percentage of the particles of different sizes presented in the sample. From the percentage of the particles of different sizes the texture of the materials was obtained using the soil texture USDA triangle.

Figure 4.16 Malvern Mastersizer MS2000

4.4.5 X-Ray Fluorescence

X-Ray Fluorescence (XRF) is used to measure the elemental composition of materials. The composition of the materials is an important indicator of the elemental structure of the contaminants and the carbonation reactivity, and aids the characterization of materials using X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). Oven dried at 105°C samples of the waste were ground in a mortar and 10 g of sample with binder (Cereox, Fluxana) and tableted under a pressure of 2 t/cm^2. The X-ray fluorescence (XRF) analysis was performed on fused beads using a Bruker S4 X-ray fluorescence spectrometer. The measure was replicated twice for each sample (Figure 4.17).

Figure 4.17 Samples in the bruker S4 X-ray fluorescence spectrometer

4.4.6 Loss on Ignition

Sequential loss on ignition (LOI) is a common and widely used method to estimate the organic and carbonate content of soils (Heiri et al., 2000). In a first reaction, organic matter is oxidised at 500–550 °C to carbon dioxide and ash. In a second reaction, carbon dioxide is evolved from carbonate at 900–1000 °C, leaving oxide. The weight loss during the reactions is easily measured by weighing the samples before and after heating and is closely correlated to the organic matter and carbonate content of the soil.

Almost 5 g of three oven dried sample were burned in the furnace at 550 °C and 980 °C for two hours each stage. The samples were cooled down in a desiccator and weight to evaluate the loss during the combustions. Measurements were replicated three times.

The LOI was then calculated using the following equations:

$$LOI_{550} = ((DW_{105}-DW_{550})/DW_{105})*100$$
$$LOI_{950} = ((DW_{550}-DW_{950})/DW_{105})*100$$

where LOI_{550} and LOI_{950} represents LOI at 550 °C and at 950 °C (as a percentage), DW_{105} represents the dry weight of the sample before combustion, DW_{550} the dry weight of the sample after heating to 550 °C and DW_{950} the weight to 950 °C (all in g). The weight loss should then be proportional to the amount of organic carbon contained in the sample. LOI is the sum of LOI_{550} and LOI_{950}.

4.4.7 Trace metals analysis

The metals were extracted by microwave acid digestion according to US EPA 3050B using AnalaR grade nitric and hydrochloric acids and mineralization happened using a CEM Mars 5 Microwave (Figure 4.18) or a Mars Press-Cem. Two certified reference material (LGC6138 and LGC6139) were used to check the degree of metal recovery.

Figure 4.18 CEM Mars 5 Microwave

Almost 1 g of sample and 0.5 g of the controls materials (CRMs) (LGC6138 and LGC6139) were each placed in a vessel. In each sample were added 9 ml HNO3 (65%) and 1 ml of HCl under the protection of a fume cupboard. The vessels were then tightened and afterwards mounted onto a carousel. The carousel is then placed in the microwave

with the control vessel connected to the pressure and temperature controls. After the microwave acid digestion had finished and cooled to 30°C the carousel is extracted. When the samples have cooled down they are filtered through 0.45 μm filter paper into clean volumetric glass flasks and then topped up to 100 ml with deionised water.

The digests were analysed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) on a Perkin Elmer Optima 4300DV or Thermo electron corporation-Icap 6000 series (Figure 4.19).

Figure 4.19 Perkin Elmer Optima 4300DV

Five-point calibration curves are created by analysing standards prepared from single element solutions (BDH SpectrosoL 1000mg/l). Standards were prepared containing 0, 0.2, 2, 5 and 10 ppm of As, Ba, Cd, Cu, Cr, Hg, Mo, Ni, Pb, Sb, Se and Zn. The standards are acidified to achieve a 2% nitric acid solution. The metals analysed are those specified in the UK Landfill Waste Acceptance Criteria (WAC) and DM 5/2/1998.

Detection limits for the elements are measured by repeatedly running a blank solution through the system to determine precision.

4.4.8   Leaching test

Soil and wastes samples were leached in duplicate according to EN 12457-2 (UNI and BS respectively in Italy and UK). EN 12457-2 is a water leaching method for granular materials, which is stipulated as the method required for WAC assessment and according also to the Italian Legislation for the recovering of waste (DM 5/2/1998).

Samples must be of known moisture content and reduced to pass a 4 mm sieve. The material is placed in a clean nitric acid washed plastic bottle, along with two times its dry solid weight of water (minus any water present in the sample), achieving a liquid to solid ratio of 10 l/s as required by the method. In each batch, one blank is prepared by placing deionised water in bottles, to measure any contamination introduced during the method. For 24 hours the bottles were continuously rotated on a roller-table rotation at 10 rpm (Figure 4.20).
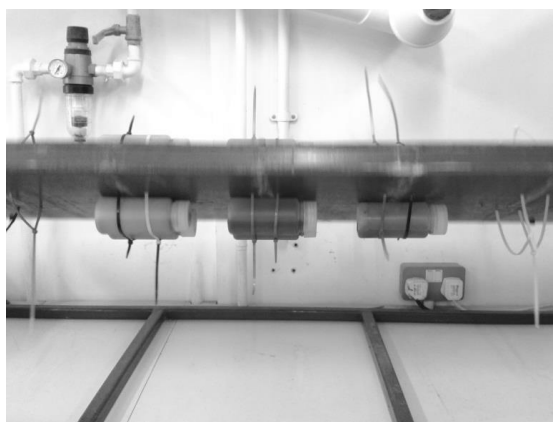
Figure 4.20 Roller-table rotation for leaching test

Once allowed to stand and solid had settled, the liquid is filtered using 0.45µm filter paper into clean plastic vials. Samples are kept refrigerated until analysed. The leachates are prepared to be analysed for heavy metals concentrations: 9.8 ml of each filtered sample are pipetted into a test tube and 0.2 ml ml of HNO_3 are pipetted into each test tube. The leachates are analysed by ICP-OES (Perkin Elmer Optima 4300DV). The resulting concentrations were converted to mg/kg for direct comparison to the WAC regulations for inert limits. The leachates were also analysed for the Dissolved Organic Carbon using the IL 550 TOC-TN analyser fitted with the liquid module and the detector.

4.4.9   XRD

X-Ray Diffraction (XRD) analyses the crystalline phases in solid materials. Pressed powder tablets were prepared from the raw materials and from the carbonated and hydrated pellets. The materials were

ground to less than 40 microns using an agate mortar and pestle. Almost 10 grams of powders was pressed into plastic XRD sample holders using a glass slide to ensure a smooth surface finish. Analysis was performed on a Siemens D500 diffractometer, fitted with a Siemens K710 generator running at 40kV voltage and 40mA current. The tablets were analysed between 5-65° 2θ in 0.02° steps each lasting 2.4 seconds. Diffraction traces were interpreted using DIFFRACplus EVA software (Bruker AXS).

The X-ray fluorescence data import function in EVA was used to filter the phase database and to aid identification. As carbonation results in both the consumption and the growth of new minerals, a shift in peak heights of the phases can be observed.

4.4.10 Carbonation test

A high pressure carbonation method was used to test the reactivity of the ashes and the cement. The materials, already in the form of fine powder, were dried at 105°C before the test and carbonated in stainless steel reaction chamber receiving pressurised CO_2 from a cylinder (Figure 4.21).
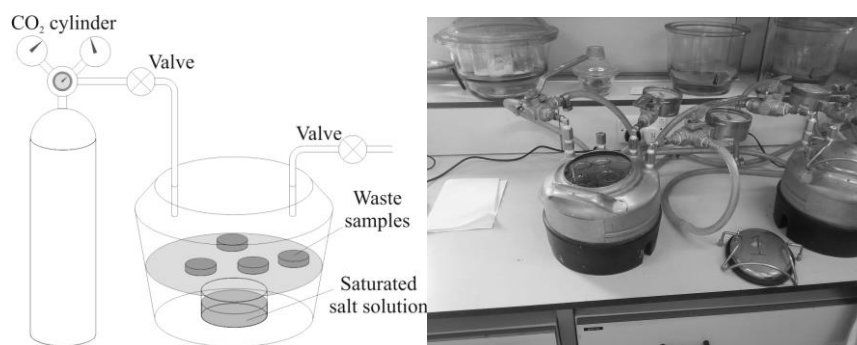
Figure 4.21 Pressurised carbon dioxide reaction chamber

Fifty gram portions of materials were mixed to a water/solid ratio (w/s) of 10 in glass beakers. The samples were placed inside the chamber, and the pressure was adjusted and maintained at the optimum of 2 bar (Gunning et al., 2010b). By opening the exhaust valve for 10 seconds, carbon dioxide was allowed to flow through the chamber to purge any air. Humidity inside the chamber was maintained at the optimum for carbonation at 65% using a saturated sodium chloride solution. After 24

hours, the beakers were removed and placed in a drying oven at 105°C and weighted and the described process was repeated until they reached constant weight. When any increasing of weight were measured the beakers were cooled in a desiccator, and the contents removed and crushed to pass a 125μm sieve. A ten gram sub-sample was taken to measure the carbonate content using an IL 550 TOC-TN analyser using the DSC 1300 module for solid samples. The machine catches the stream of the carbon burnt during the combustion of the samples at 1000°C. Total carbon concentration then converted to carbon dioxide concentration trough their molecular weights. All samples were prepared in triplicate.

The CO_2 uptake of the carbonated material is then obtained by difference with the raw materials' one and by the difference between the natural carbonated and accelerated carbonated pellets.

4.5   AGGREGATES TESTING

Aggregates were first tested for resistance and leacheability to identify the best mix. Single pellet strength was used for the resistance of the pellets, while leaching of the final pellets was determined in accordance with the Waste Acceptance Criteria (WAC) using EN 12457-2 as described in the section 4.4.8. Furthermore the aggregate were tested for XRD (section 4.4.9) and SEM to evaluate the effect of the accelerated carbonation on the process in the first part of the experimental procedure.

4.5.1   Single pellet strength

A simple single pellet crushing test was used to evaluate the strength gain of the aggregate and used to first identify the right mix in the palletisation process. The strength of individual aggregate particles was calculated according to the method described by Li et al. (2000) and used in a previous study (Gunning et al., 2009). Strength was calculated using the following formula:

$$\sigma_c = \frac{F_c}{A_m} = \frac{F_c}{\left(\frac{\pi}{4}d_m^2\right)} \quad (7)$$

Where σ_c the compressive strength in MPa of the single pellet, Fc is the fracture load in KN, Am is the mean area of the aggregate, and d_m is the mean diameter of the pellet. Five pellets from each batch were tested and the average strength calculated. The pellets were measured in the three directions using digital callipers (Figure 4.22), and crushed with a hand-held force meter (Mecmesin MFG250) (Figure 4.23).

Figure 4.22 Digital callipers for single pellet measurement

Figure 4.23 Hand-held force meter (Mecmesin MFG250)

4.5.2 Carbon dioxide uptake

Carbon dioxide uptake was calculated for the carbonated pellets by carbon content analysis as described in the section 4.4.10. The carbon

content was converted to carbon dioxide and the uptake evaluated by difference with the not-carbonated aggregates.

4.5.3   XRD

The effect of carbonation was evaluated by crystalline phase compositions of the pellets. XRD can be used as a tool for measuring carbonation, since carbonation of the material induces changes in the crystalline minerals. A ten gram sample of pellets dried at 105°C was crushed to pass a 40μm sieve. The powder was analysed according to section 4.4.9.

4.5.4   SEM

Microstructural and chemical composition of materials can be detected by Scanning electron microscopy (SEM) technique. SEM analysis can identified any structural changes due to the carbonation. Fragment of the pellets were cast as vacuum-impregnated resin blocks and placed at the base of 30 mm moulds coated with release agent. Liquid epoxy resin (Logitech epoxy 301) was poured into the mould to cover half of the fragment and it was placed in a desiccator connected to a vacuum pump. The air was removed till the bubbles ceased to rise from the sample.

The blocks were then cured for 24 hours at room temperature and pressure and after the curing the block face was ground to expose the embedded fragment using grit paper (Buehler silicon carbide grit paper 300, 600, 1200). This was followed by successive polishing with 3, 1 and 0.25μm diamond paste (Struers DP Sticks) on silk cloths (Buehler Metcloth), using an alcohol based lubricant (Struers DP Yellow) on an Engis MK2a polishing machine. The polished blocks were coated with carbon using an Edwards Carbon Coater. Coated blocks were stored in sealed plastic chambers containing a silica gel desiccant under a continuous flow of nitrogen to prevent further hydration and carbonation.

Electron microscope analysis was performed on a JEOL JSM-5310LV microscope equipped with an Oxford Instruments Energy Dispersive Spectrometer (EDAX). The electron operated at a voltage of 20kV, and the sample surface was maintained at a working distance of 15mm from the detectors to provide a balance between high resolution and depth of

field. Images of the blocks were taken using the backscattered electron (BSE) detector, coupled with chemical analysis using the EDAX. Oxford ISIS software was used for image acquisition and chemical analysis.

4.6   END OF USE AGGREGATE CHARACTERIZATION

The aggregated products were subjected to chemical, mechanical and physical testing. The following tests have been conducted to assess the suitability of the aggregates for different applications. Commercially available lightweight aggregates (LECA, Lytag and C8agg) were tested alongside the manufactured aggregates for comparison. Concrete cubes were made to test the aggregate for lightweight concrete blocks and the method is described. The aggregates were also tested for suitability as a green roof substrate according to the FLL guidelines (2002).

4.6.1   Density

Bulk density was tested by EN 1097-3. In this method un-compacted weight of oven dried aggregate is measured as a unit volume and expressed in kg/m^3 (Figure 4.24).

Figure 4.24 Unit volume for bulk density

Apparent density, saturated density, particle density and water absorption are measured according to EN 1097-6. Density is measured by weighing the aggregate in an oven dried, saturated and water immersed state.

Particle density is defined as the ratio of the oven dried mass to the volume it occupies in water including sealed and water accessible voids.

4.6.1 Particle Size Distribution

The particle size distribution of the pelletised products was measured using a dry sieving technique according to British Standard BS 812-103.1 (1985). A sample of pellets was dried to constant weight at 105°C according to UNI (BS) EN 1377-2 (1990) and was passed through a nest of sieves: 20mm, 14mm, 10mm, 6.3mm, 5mm, 3.35mm, 2.36mm, 1.18mm, and the fraction retained was weighed (Figure 4.25).

The mean diameter of the pellet batches was then calculated by multiplying the mid-point of the class interval (MP) by the frequency (F) in % by weight in that class. The mean particle size in mm is given by the sum of the F*MP column divided by the sum of the frequency column.

Figure 4.25 Aggregates sieved at different sizes

4.6.2 Water permeability and maximum water capacity

Water permeability and maximum water capacity were tested for the aggregates for green roofing applications. This test was done according to the method described in appendix 3 and 4 of the FLL guidelines (2002) for green roof technology. Maximum water capacity identifies the water storage capability of materials used in the layered superstructure in compacted condition. It was measured in a compacted 15 cm cylindrical test samples measuring approximately 10 cm in length (Figure 4.26).

Water permeability was determined measured the time for a known quantity of water to flow in the cylindrical test samples at maximum water capacity.

Figure 4.26 Cylindrical test sample for water permeability and maximum water capacity

4.6.3 Freeze-thaw and crushing resistance

Freeze-thaw and crushing resistance were tested according to UNI (BS) EN 13055. The freeze-thaw test measures the disintegration of aggregate subjected to 20 consecutive cycles of freezing at -18°C and thawing at 20°C.

Crushing resistance is measured putting a sample is in a specified steel cylinder (Figure 4.27) and compacted. A piston is then forced under pressure and the force is expressed as the resistance to crushing.

Figure 4.27 Steel cylinder for crushing resistance

4.6.4 Column leaching test

A column leaching test has been performed to test the mobility of contaminants in the aggregates used as a filter media or for green roof application under long-term conditions. This was performed based on the Upflow Percolation Leaching Test (prEN 14405).

Aggregates were sieved to obtain at least 85 % of particle size less than 4 mm and placed in a small column plastic tube according to the method (Figure 4.28). Eluate is collected using a volumetric pump to ensure the upflow, running at a linear velocity of 15cm/day. The leachates were collected in 7 fraction volumes (at 0.1, 0.3 0.5, 1, 3 and 5 times the dry mass) and the test itself is finished when the L/S ratio of 10 l/kg dry matter is reached. Leachete was analysed for metal concentration as reported in the section and for water soluble chloride using Quantab Chloride Titrator Strips Type with Titration Range 0.05%-1% (300-6000 ppm).

Figure 4.28 Apparatus set up for upflow percolation leaching test (prEN 14405)

4.6.5 Concrete cubes

The fully cured pellets were used for the production of concrete cubes to evaluate their suitability for use in general concrete applications. Cubes were prepared and tested according to BS EN 12390 Parts 1–3 using

100mm moulds. The cubes were demoulded after 24 hours and immersed in water for the remainder of the curing period (Figure 4.29).

Figure 4.29 Concrete moulds and cubes

Concrete cubes were made from the four pellet batches, and from Lytag® and LECA® aggregate for comparison. Mixes were prepared according to a recommended mix for lightweight concrete using Lytag® aggregate (Lytag, 2004), with quartz sharp sand conforming to UNI (BS) EN 12620, and 52.5 Portland. Water doses were altered to account for variations in the bulk density and water absorption of the different aggregates. The water addition was based upon the requirement to achieve a concrete slump of 70mm. Mixes were prepared in a plastic bucket, and blended by hand with a trowel.

5 RESULTS

5.1 INTRODUCTION

This chapter reports the results of the research. The first part focuses on the effect of stabilization/solidification process on heavy metals contaminated soil under different conditions, included the effect of accelerated carbonation. In the second part the results of the aggregates produced from soil washing residues and ashes are discussed. This includes the results of the mechanical and leaching properties of the different binder formulations considered, the leaching of contaminants and the microstructural changes for the effect of accelerated carbonation. The results are compared against European and national legislation to evaluate the effectiveness of the process to reduce hazardous properties and facilitate potential re-use of the materials treated. The properties of the aggregates produced in the second part of the research under the relevant standards are presented alongside commercial lightweight aggregates and discussed based on the two analysed application: lightweight concrete blocks and green roofing application.

5.2 S/S AND ACT OF HEAVY-METALS CONTAMINATED SOIL

5.2.1 Introduction

In this part are reported the results of the stabilization/solidification of the artificial contaminated soils spiked with different concentrations of three heavy metals: cadmium (Cd), copper (Cu) and lead (Pb).
Stabilization of the three spiked heavy metals in the soils are discussed based on the percentage of the binder (5 %, 10 % and 20 % of CEM I), the percentage of organic matter in the two artificial soils (0 % and 10 % of organic matter), the initial concentrations of the three metals (labelled

C1, C2 and C3) and the curing conditions of the cemented samples: normal-hydration and accelerated carbonation.

5.2.2   Contaminated soil characterization

Table 5.1 reports the three heavy metals concentrations in the leachates of the artificial contaminated soils prepared. Metals concentrations are over the concentration limits of the Italian decree DM 5/2/1998 for the recovery of waste. Leachates concentration has been converted from mg/l to mg/kg consider the solid to liquid ratio used during the test at 10 l/kg.

Table 5.1 Leachates concentration of the spiked heavy metals in the soil samples at three concentrations. Values compared with DM 5/2/1998 limits.

Sample	OM (%)	Cd (mg/Kg)	Cu (mg/kg)	Pb (mg/kg)
S1_C1	10	3.97	2.07	1.46
S2 _C1	0	153.5	1.44	1.08
S1_C2	10	86.34	1.78	1.26
S2_C2	0	615.4	86.95	118.7
S1_C3	10	567.0	59.13	11.85
S2_C3	0	1153.	651.55	744.33
D.M. 05/02/1998 limits		0.05	0.50	0.50

By the comparison of the leachates concentration of the spiked metals Cd, Cu and Pb with the total concentrations in the soils it is observed that the mobility of heavy metals is based on the specific contaminant and on the presence of organic matter in the soil. The observed mobility of metals was in the order: Cd>Cu>Pb. The soil with 10 % of organic matter showed a more retain of the heavy-metals than the one without.

5.2.1   Stabilization of the heavy metals

Stabilization of the three spiked heavy metals in the soils are discussed based on the percentage of the binder (5 %, 10 % and 20 % of CEM I), the percentage of organic matter in the two artificial soils (0 % and 10 % of organic matter), the initial concentrations of the three metals (labelled C1, C2 and C3) and the curing conditions of the cemented samples: normal-hydration and accelerated carbonation.

Table 5.2 and Table 5.3 report the concentrations in the eluate of the stabilized/solidifies samples for each samples at the three different concentrations of heavy-metals for 5 % and 10 % of CEM I respectively, both at 7 and 28 days of curing. Accelerated carbonated samples have been cured under carbon dioxide gas for 7 days and tested at 7 and 28 days. Samples at 20 % CEM I have been tested just after 28 days (Table 5.4).

Table 5.2 Leachate concentrations of the spiked heavy metals at 5 % CEM I

			7 days			28 days		
	OM	Curing conditions	Cd (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Cd (mg/kg)	Cu (mg/kg)	Pb (mg/kg)
S1_C1	10 %	Atm	0.39	0.77	0.48	0.55	<0.30	1.07
		CO_2	0.62	<0.30	1.30	0.57	<0.30	0.33
S1_C2	10 %	Atm	<0.30	1.13	0.56	<0.30	0.63	0.68
		CO_2	0.73	0.95	0.98	0.73	0.35	0.60
S1_C3	10 %	Atm	<0.30	6.26	0.83	<0.30	4.00	<0.30
		CO_2	0.95	1.10	0.71	1.19	1.00	0.35
S2_C1	-	Atm	<0.30	<0.30	0.33	<0.30	<0.30	<0.30
		CO_2	<0.30	<0.30	<0.30	<0.30	<0.30	0.35
S2_C2	-	Atm	<0.30	<0.30	<0.30	<0.30	<0.30	0.34
		CO_2	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30
S2_C3	-	Atm	<0.30	<0.03	0.44	<0.30	<0.30	<0.30
		CO_2	<0.30	<0.03	<0.30	<0.30	<0.30	0.74
Limits D.M. 5/02/1998 (mg/kg)			0.05	0.5	0.5	0.05	0.5	0.5

Table 5.3 Leachate concentrations of the spiked heavy metals at 10 % CEM I

			7 days			28 days		
	OM	Curing conditions	Cd (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Cd (mg/kg)	Cu (mg/kg)	Pb (mg/kg)
S1_C1	10 %	Atm	<0.30	0.32	0.74	<0.30	1.24	<0.30
		CO_2	<0.30	<0.30	0.88	<0.30	<0.30	<0.30
S1_C2	10 %	Atm	<0.30	1.43	0.65	0.46	0.85	<0.30
		CO_2	0.96	1.04	0.72	0.44	0.44	<0.30
S1_C3	10 %	Atm	<0.30	2.71	0.54	0.31	2.62	<0.30
		CO_2	0,39	0.73	0.62	2.03	0.97	<0.30
S2_C1	-	Atm	<0.30	<0.30	0.86	<0.30	<0.30	<0.30
		CO_2	<0.30	<0.30	0.36	<0.30	<0.30	<0.30
S2_C2	-	Atm	<0.30	<0.30	0.54	<0.30	<0.30	<0.30
		CO_2	<0.30	<0.30	0.36	<0.30	<0.30	<0.30
S2_C3	-	Atm	<0.30	<0.30	0.61	<0.30	<0.30	<0.30
		CO_2	<0.30	<0.30	0.35	<0.30	<0.30	<0.30
Limits D.M. 5/02/1998 (mg/kg)			0.05	0.5	0.5	0.05	0.5	0.5

Table 5.4 Leachate concentrations of the spiked heavy metals at 20 % CEM I

	OM	Curing conditions	28 days		
			Cd (mg/kg)	Cu (mg/kg)	Pb (mg/kg)
S1_C1	10 %	Atm	<0.30	1.02	0.75
		CO_2	0.62	0.11	<0.30
S1_C2	10 %	Atm	<0.30	1.37	<0.30
		CO_2	<0.30	0.65	0.80
S1_C3	10 %	Atm	<0.30	2.78	0.71
		CO_2	<0.30	0.33	<0.30
S2_C1	-	Atm	<0.30	<0.30	<0.30
		CO_2	<0.30	<0.30	0.32
S2_C2	-	Atm	<0.30	<0.30	<0.30
		CO_2	<0.30	<0.30	0.49
S2_C3	-	Atm	<0.30	<0.30	<0.30
		CO_2	<0.30	<0.30	0.57
Limits D.M. 5/02/1998 (mg/kg)			0.05	0.5	0.5

No measurable levels of cadmium and copper were found in the leachates of the treated S2 sample, with no organic matter, for the three contaminants concentrations and at the two curing conditions. The leaching of lead was below the limit for all the soil samples (S1 and S2) for normal-hydration and accelerated carbonation conditions. The heavy metals were stabilized at 7 days curing and at 28 days no differences in the leachates concentrations have been detected in all the samples.

Copper and cadmium concentrations in the hydrated and accelerated carbonated samples in the sample S2 were over the concentrations of the sample S1, indicating that the organic matter had a detrimental effect on stabilization. Moreover the increasing percentage of cement did not enhance the stabilization of heavy metals and the process was efficient already at 5 % CEM I and for the three concentrations (C1, C2 and C3). Stabilization was independent by the initial concentrations of contaminants and efficient also at high concentrations.

The effective carbonation was confirmed by the variation of the pH of the treated between the normal-hydration and accelerated carbonation curing conditions. The pH has dropped of two-three units from the normal-hydrated and carbonated samples (Table 5.5)

Table 5.5 pH of the untreated and treated soil samples

	OM	0% CEM		5% CEM	10% CEM	20% CEM
				pH		
T1-C1		6,71	*Aria*	9.30	10.16	11.98
			C.A.	7.50	8.75	9.40
T1-C2	10	6,45	*Aria*	10.02	11.5	11.85
			C.A.	7.43	9.20	9.75
T1-C3		6,30	*Aria*	9.70	11.45	12.20
			C.A.	8.24	9.25	10.59
T2-C1		5,75	*Aria*	10.84	11.6	11.71
			C.A.	8.81	9.51	10.57
T2-C2	-	5,54	*Aria*	11.02	11.53	11.60
			C.A.	9.12	8.80	10.33
T2-C3		5,25	*Aria*	10.43	10.97	11.22
			C.A.	7.15	8.74	9.85

Figure 5.1 and Figure 5.2 shows the percentage of stabilization of the three heavy-metals function of the pH respectively for the treated soil sample S1 and S2. Points in the graphs represent the immobilization of heavy metals for all the samples under normal hydration (Air) and accelerated carbonation (100 % CO_2).
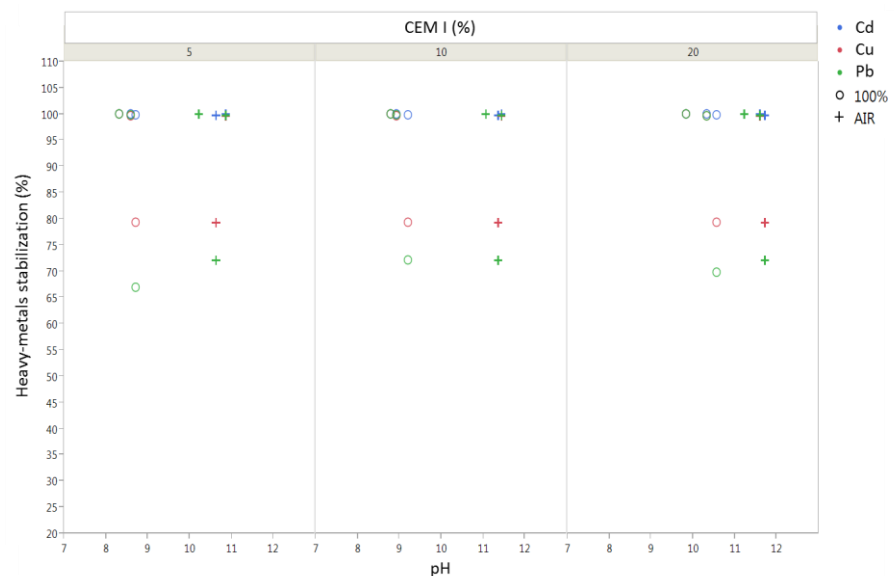
Figure 5.1 Percentage of stabilization in function of the pH of the treated S1 soil sample (10 % OM)
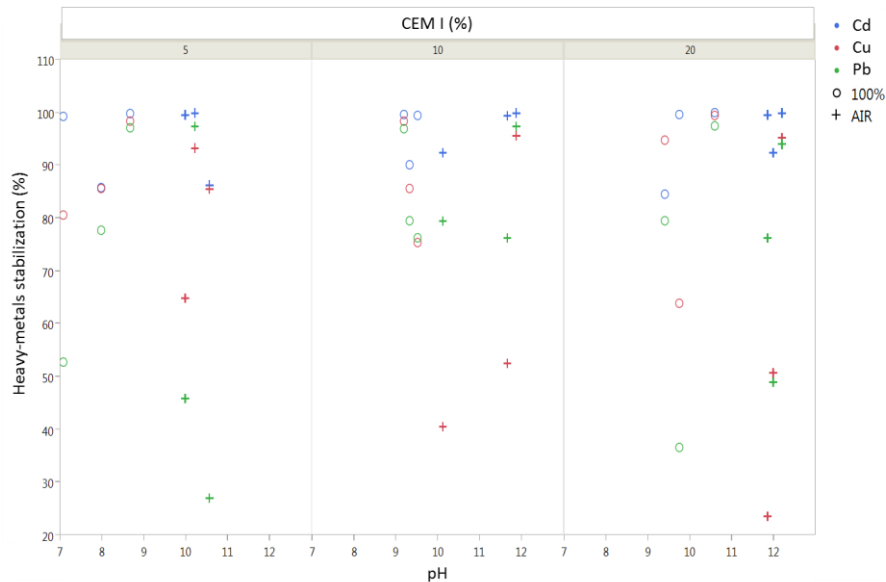
Figure 5.2 Percentage of stabilization in function of the pH of the treated S2 soil sample (No-OM)

In both the treated soil S1 and S2, cement increased the pH at value of 10-11 for 5% and 10 % CEM I and 12 in the 20 % CEM I treated soil samples. Dropping of pH due to the effect of the accelerated carbonation on the samples did not change significantly the solubility of the heavy-metals. The pH dropped at value of 7-9 for the 5 % CEM I treated soil samples, while decrease to 9-10 in the 10 % and 20 % CEM I treated samples. Percentage of stabilization is steady with the decreasing of pH, so high percentage of stabilization has been reached in both the curing conditions. Copper and lead slightly increased their solubility under accelerated carbonation curing condition.

Based on the dispersion of the data soil samples treated with 10 % of CEM I showed a better efficiency of stabilization.

The pH shows the same behaviour in the soil samples S2, whereas stabilized samples had higher value of percentage of stabilization. Copper and lead reached percentage of stabilization between 65% and 80% for the three cement concentrations and for both the curing conditions.

5.3 AGGREGATE PRODUCTION BY ENHANCED STABILIZATION/SOLIDIFICATION

5.3.1 Introduction

Stabilisation/solidification (S/S) is a treatment for wastes and soils which normally uses cementitious or pozzolanic binders, to form a solid monolith that incorporates the contaminants (Bone et al., 2004; Dermatas and Al-Tabbaa, 2007; ITRC, 2011). The application of S/S is particularly effective for the treatment of heavy metal-contaminated soils (Chen et al., 2009). Stabilization/solidification can also utilise other additives/fillers in a pre-treatment phase to amend adverse chemical and physical characteristics e.g. high moisture content (Bone et al., 2004, ITRC, 2011). Alternative methods to solidify soil have been used, however the application of a carbonation -based cementation was successfully carried out in the UK in 2000 (Antemir et al., 2010a).

This part reported here examines the use of stabilisation/solidification to valorise soil washing residues, and produce a lightweight recycled aggregate. Additional batches of aggregate were prepared using synthetic flue gas (20% CO_2), to induce carbonation of the aggregate. This was to attempt to produce an aggregate with imbibed carbon, and hence a lower CO_2 footprint. The effect of carbonation was evaluated by XRD and SEM analysis. Carbon uptake was calculated for the carbonated pellets.

5.3.2 Materials characterization

The soil washing residues (SW1, SW2, SW3 and SW4) were in the form of cohesive silt with high moisture content. Table 5.6 shows their main physical chemical characteristics. Samples SW2 and SW3 were characterized by high organic contents, with SW2 being a hazardous waste, and SW3 being a stable non-reactive hazardous waste, according to landfill waste acceptance criteria (WAC). Dissolved organic carbon (DOC) was found also in the leachate of both SW2 and SW3 residues.

Table 5.6 Physical-chemical characteristics of the soil washing residues

	Texture	LL [%]	PL [%]	PI -	MC [%]	TC [%]	TOC [%]	IC [g/kg]	DOC* [mg/kg]	pH -
SW1	Sandy-loam	23.5	16.8	6.63	14.2	4.4	3.2	1.3	ND	9.0
SW2	Silt	40.9	30.2	10.6	36.9	12.9	**12.0**	0.9	**213**	7.9
SW3	Silt-loam	43.1	21.7	21.3	42.8	8.5	**5.3**	3.2	**76.2**	8.9
SW4	Silt-loam	49.3	24.3	24.9	45.3	6.4	3.2	3.2	ND	8.8

Bold type indicates hazardous properties according to the Hazardous Waste Regulation, **ND – not detected.**
*DOC measured from leaching test BS EN 12457 with liquid to solid ratio of 10

XRD pattern showed that the residues were mainly formed by the crystalline phases of quartz (SiO_2), Iron Oxide (Fe_2O_3) and clay minerals illite, kaolinite and montmorillonite. Heavy metals, including lead, zinc and chromium were detected by XRF in the soil washing residues in the forms of PbO, ZnO and Cr_2O_3. PA and CEM I were principally composed of calcium oxide (CaO), while SSA of quartz (SiO_2). LOI at 980°C were higher for SW2 and SW3 and related to the TOC content (Table 5.7).

Table 5.7 Elemental chemistry of the raw materials and binder CEM I (values in % by weight)

	SiO₂	CaO	Fe₂O₃	Al₂O₃	SO₃	K₂O	MgO	TiO₂	P₂O₅	Na₂O	Cl	LOI
SW1	22.5	8.5	4.7	4.2	0.97	1.4	0.51	0.60	0.18	0.11	0.14	2.96
SW2	26.7	10.4	6.4	5.8	3.6	1.6	0.6	0.60	0.2	0.15	-	7.26
SW3	28.1	17.7	6.0	6.5	1.0	1.6	0.8	0.59	0.23	0.27	0.15	7.50
SW4	30.9	10.5	7.5	8.3	1.2	2.0	1.0	0.69	-	0.30	0.35	6.17
PA	10.9	55.2	0.6	5.38	0.57	-	1.9	0.22	0.12	-	0.07	7.01
SSA	24.5	18.5	6.0	8.5	1.8	2.1	2.1	1.2	12.2	0.33	<0.02	1.06
CEM1	13.3	57.4	2.2	3.0	4.1	0.74	0.65	0.17	0.14	0.21	-	1.01

Carbon dioxide uptake behaviour of materials is related to the elemental content of calcium, potassium, sodium and sulphur through the Steinour Formula (Fernández Bertos et al., 2004). The maximum CO_2 uptake measured by carbonation was 25.86 ± 4.5 % for CEM I and 30.43 ± 1.5 % for the Paper Ashes, while no carbonation was measured for Sewage Sludge Ashes. Calcium oxide was present as varying amount of calcite ($CaCO_3$), lime (CaO), and Portlandite ($Ca(OH)_2$) as identified by XRD for phase composition in the un-carbonated and carbonated Paper Ashes. XRD of fully carbonated CEM I and Paper Ashes identified the conversion of reactive lime and Portlandite to calcium carbonate.

Table 5.8 reports the total concentration of regulated heavy metals, while the results of the leaching test are showed in the Table 5.9. The metals in

the leachates are compared to the limits of the WAC regulation for inert, non-hazardous and hazardous waste.

Table 5.8 Trace metals in the raw materials (values in mg/kg)

	Pb	Cu	Ba	Cd	As	Sb	Mo	Hg	Zn	Cr	Ni	Se
SW1	276	130	225	<655	15.3	3.1	2.7	<259	216	42.2	22.0	
SW2	262	89.8	276	<665	18.7	5.1	2.9	<259	249	50.7	25.6	
SW3	262	106	238	<665	16.4	3.9	2.5	<259	226	45.5	23.4	
SW4	465	159	381	<665	27.2	1.8	0.9	<259	353	65.1	40.3	
PA	9.8	289	92	<665	<144	<217	<152	<259	36.8	38.6	9.47	
SSA	319	1091	655	2.92	33.3	2.1	28.1	<260	1897	105	66.5	

All the metals in the leachates were below the limits for inert waste with the exception of antimony (Sb) for all residues, and Molybdenum (Mo) for SW1 and SW4, only. The leaching of Mo and Sb from all the soil washing residues was one order of magnitude below their total concentrations, indicating that they were highly soluble. Molybdenum (Mo) in the leachate from the PA and SSA was above the prescribed 'stable non-reactive' limit.

Table 5.9 Untreated wastes leachate concentrations of WAC regulated contaminants (values in mg/kg)

	Pb	Cu	Ba	Cd	As	Sb	Mo	Hg	Zn	Cr	Ni	Se
SW1	0.15	0.36	0.58	<0.03	<0.18	0.21	0.55	<0.2	0.34	0.09	0.09	<0.16
SW2	0.16	0.32	0.45	<0.03	<0.18	0.16	0.38	<0.2	0.16	0.08	0.06	<0.16
SW3	0.18	0.27	0.31	<0.03	<0.18	0.11	0.20	<0.2	0.11	0.08	0.04	<0.16
SW4	<0.1	0.31	0.42	<0.03	<0.18	0.11	0.45	<0.2	<0.2	<0.1	<0.14	<0.16
PA	0.64	0.53	3.90	<0.03	0.38	0.43	0.68	<0.2	<0.2	1.59	0.34	<0.16
SSA	<0.13	<0.04	0.95	<0.02	0.20	0.16	16.1	<0.2	<0.2	0.02	<0.14	<0.16
Inert	0.50	2.0	20	0.04	0.50	0.06	0.50	0.01	4.0	0.50	0.40	0.10
Stable non-reactive	10	50	100	1.0	2.0	0.70	10	0.20	50	10	10	0.50
Hazardous	50	100	300	5.0	25	5.0	30	2.0	200	70	40	7.0

Bold type indicates hazardous properties according to WAC regulation.

5.3.3 Pelletising trials

5.3.3.1 *Aggregates from soil washing residues and PA*

In the first part of the experimental procedure the four soil washing residues (S1, S2, S3, S4) were each mixed with the required amount of PA to regulate water content, and then with CEM I.

All residues were mixed with the required amount of paper ash to regulate water content, and then with CEM 1. Each residue required a

series of trials to achieve their optimum formulation as the addition of the ash was necessary to regulate free moisture to aid agglomeration.

The mixtures containing soil residues SW3 and SW4 became very hot during mixing and pelletising, resulting in similar textures and plastic indices. The high organic content of SW3 was found not to have an effect upon the mixing. However, SW2 exhibited a hydrophobic tendency due to the high organic content, resulting in difficulty in obtaining a uniform product.

The free lime present in the PA reacted with the free water in a highly exothermic reaction, raising soil temperature and driving off some of the pore water as vapour (Bone et al., 2004). Among all the materials treated just SW1 required the adding of water to enhance the granulation, due to high percentage of sand. Example of aggregates produced is shown in the Figure 5.3.

Figure 5.3 Aggregate produced from SW residues and PA

5.3.3.2   Aggregates from SW4 and SSA

The second part of the experimental procedure focused on the recovery of the SW4 residue using SSA. This was due to the necessity of the Company, which provided them, to find a method of recovering.

Another combined process of pelletising and carbonation was used to produce the aggregates, as described in the section 4.3.2. Not reactive waste silt SW4 and SSA were blended with CEM I, which is reactive to CO_2. A series of trials to achieve the optimum formulation was required. As described in the section 4.3.2, the aggregate were first carbonated during the pelletising stage. In a second step if the experimental procedure they were cured in a carbonation dynamic chamber. The ashes

reduced the moisture of the silt enhancing the pelletising of the residue as an aggregate. The trials were conducted until the product with the required characteristics was reached. Aggregates typical formed are showed in the Figure 5.4.

Figure 5.4 Aggregates produced from SW4 and SSA

5.3.4 Leaching

5.3.4.1 Aggregates from soil washing residues and PA

The leaching of the aggregated produced from the four soil washing residues and PA are shown in Table 5.10 for the normal hydrated aggregate and in Table 5.11 for the carbonated. Whilst no measurable levels of lead, zinc, chromium and nickel were found in the leachates of the untreated residues, they were given from both the not-carbonated and carbonated aggregates. The leaching of copper, barium and molybdenum were below the inert landfill limit for all aggregates. The presence of leachable barium in the untreated residues may have arisen from the paper ash and CEM I (it markedly increased with cement content).

Copper was found to decrease with increasing cement content, indicating increasing stabilisation. Carbonation also reduced the mobility of copper and barium in all the residues treated. Molybdenum, which was found in the SW1 and SW3 residues, was unaffected by carbonation in accordance with other research. Carbonation did not change significantly the pH of the not-carbonated material. DOC was not found in the leachates of all the soil washing residues treated.

Table 5.10 Manufactured hydrated aggregates leachate concentrations of detected regulated contaminants.

	CEM I	Cu	Ba	Cd	As	Sb	Mo	Hg	Zn	Cr	Pb	Se
	5%	0.34	8.76	<0.02	<0.02	<0.08	<0.02	<0.2	<0.2	<0.1	<0.13	<0.16
SW1	10%	0.31	10.75	<0.02	<0.02	<0.08	<0.02	<0.2	<0.2	<0.1	<0.13	<0.16
	20%	0.14	7.04	<0.02	<0.02	<0.08	<0.02	<0.2	<0.2	<0.1	<0.13	<0.16
	5%	1.91	8.29	<0.02	<0.02	<0.08	0.28	<0.2	<0.2	<0.1	<0.13	<0.16
SW3	10%	1.57	9.16	<0.02	<0.02	<0.08	0.29	<0.2	<0.2	<0.1	<0.13	<0.16
	20%	1.35	10.48	<0.02	<0.02	<0.08	0.30	<0.2	<0.2	<0.1	<0.13	<0.16
	5%	2.31	7.19	<0.02	<0.02	<0.08	<0.02	<0.2	<0.2	<0.1	<0.13	<0.16
SW2	10%	1.96	9.33	<0.02	<0.02	<0.08	<0.02	<0.2	<0.2	<0.1	<0.13	<0.16
	20%	1.25	6.75	<0.02	<0.02	<0.08	<0.02	<0.2	<0.2	<0.1	<0.13	<0.16
	5%	0.81	4.34	<0.02	<0.02	<0.08	<0.02	<0.2	<0.2	<0.1	<0.13	<0.16
SW4	10%	1.31	11.04	<0.02	<0.02	<0.08	<0.02	<0.2	<0.2	<0.1	<0.13	<0.16
	20%	0.87	10.88	<0.02	<0.02	<0.08	<0.02	<0.2	<0.2	<0.1	<0.13	<0.16

Table 5.11 Manufactured carbonated aggregates leachate concentrations of detected regulated contaminants.

	CEM I	Cu	Ba	Cd	As	Sb	Mo	Hg	Zn	Cr	Pb	Se
	5%	0.25	5.55	<0.02	<0.02	<0.08	0.08	<0.2	<0.2	<0.1	<0.13	<0.16
SW1	10%	0.17	2.66	<0.02	<0.02	<0.08	0.06	<0.2	<0.2	<0.1	<0.13	<0.16
	20%	0.12	6.31	<0.02	<0.02	<0.08	0.06	<0.2	<0.2	<0.1	<0.13	<0.16
	5%	1.84	0.85	<0.02	<0.02	<0.08	0.49	<0.2	<0.2	<0.1	<0.13	<0.16
SW3	10%	0.94	2.34	<0.02	<0.02	<0.08	0.32	<0.2	<0.2	<0.1	<0.13	<0.16
	20%	0.75	4.55	<0.02	<0.02	<0.08	0.29	<0.2	<0.2	<0.1	<0.13	<0.16
	5%	1.43	6.70	<0.02	<0.02	<0.08	<0.02	<0.2	<0.2	<0.1	<0.13	<0.16
SW2	10%	1.82	6.05	<0.02	<0.02	<0.08	<0.02	<0.2	<0.2	<0.1	<0.13	<0.16
	20%	1.10	8.36	<0.02	<0.02	<0.08	<0.02	<0.2	<0.2	<0.1	<0.13	<0.16
	5%	1.18	7.96	<0.02	<0.02	<0.08	<0.02	<0.2	<0.2	<0.1	<0.13	<0.16
SW4	10%	0.90	7.41	<0.02	<0.02	<0.08	<0.02	<0.2	<0.2	<0.1	<0.13	<0.16
	20%	0.72	7.29	<0.02	<0.02	<0.08	<0.02	<0.2	<0.2	<0.1	<0.13	<0.16

5.3.4.2 Aggregates from SW4 and SSA

The leaching of the control and carbonated aggregates with the different cement cement contents are shown respectively in Table 5.12 and

Table 5.13. The release of cadmium, arsenic, mercury, zinc and lead, in the untreated waste were below detection limits in all cases. All the other heavy metals were found to be below the 'inert' limit for all the pelletized products. Molybdenum, present in the SSA above non-hazardous stable reactive waste levels, was leached and met the lower regulated limit, was unaffected by carbonation. Leachable copper and chromium was below detection limits from the carbonated aggregates, but met 'inert' limits for the control aggregate. Barium and selenium leaching was unaffected by the amount of CEM I or by curing conditions. The pH was reduced by carbonation, giving a value slightly over then 8, suggesting that the product was significantly carbonated, whereas it was approximately 12 for the control.

Table 5.12 SW4 and SSA hydrated aggregate leachate concentrations (values in mg/kg)

CEM I	Cu	Ba	Cd	As	Sb	Mo	Hg	Zn	Cr	Pb	Se	pH
10 %	0.70	2.14	<0.02	<0.18	<0.08	3.23	<0.2	<0.2	0.55	<0.13	<0.16	11.82
20 %	0.65	2.08	<0.02	<0.18	<0.08	1.66	<0.2	<0.2	0.52	<0.13	<0.16	12.29

Table 5.13 SW4 and SSA carbonated aggregate leachate concentrations (values in mg/kg)

CEM I	Cu	Ba	Cd	As	Sb	Mo	Hg	Zn	Cr	Pb	Se	pH
10 %	<0.04	0.48	<0.02	<0.18	<0.08	3.71	<0.2	<0.2	<0.1	<0.13	<0.16	8.46
20 %	<0.04	0.43	<0.02	<0.18	<0.08	3.12	<0.2	<0.2	<0.1	<0.13	<0.16	8.39

5.3.5 Strength

5.3.5.1 *Aggregates from soil washing residues and PA*

Pellet strength was measured for the normal-hydrated stabilized/solidified and carbonated manufactured pellets. The strength was compared with the pellet strength measured for commercial pellet and the value of 0.1 MPa had been chosen ad threshold value. SW1, SW3 and SW4 reached the value of 0.1 MPa at 5 % of CEM I. Strength increased with the amount of cement in each mix. Carbonation had a positive effect on the strength of the manufactured pellet increasing more than 10 % till the 60 % of the un-carbonated values. Strength was found to steadily increase with cement content. SW2 produced aggregates with comparatively lower strengths, and may be ascribed to the higher organic content of the raw material, that bound the particles of cement inhibiting the hydration reaction. The threshold value was reached with 20 % of CEM I. High organic content in SW2 had a detrimental effect on the strength of the manufactured pellets.

Figure 5.5 shows the strength of the manufactured pellets at 6 days of curing time at increasing amount of cement.
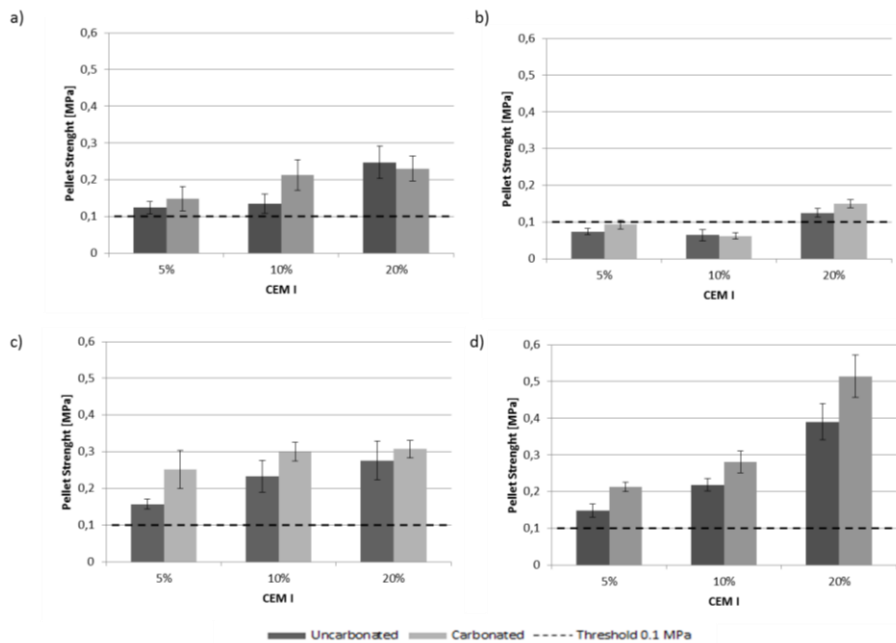
Figure 5.5 Manufactured aggregate strength treated with PA and different percentage of CEM I for hydrated (atm) and carbonated (20 % CO2) pellets of a) SW1 b) SW2 c) SW3 and d) SW4.

5.3.5.2   Aggregates from SW4 and SSA

The strength of pellets determined using the single pellet test is given in Figure 2. A target of 0.1 MPa was used as a measure of successful strength development, and the value of 0.30 was achieved after 3 days curing in CO2 for 10% CEM1, and a value of 0.22 for the control sample. At the higher cement content under CO2, 0.42 MPa was achieved at 3 days, whereas the strength of the control was 0.25 MPa.
The significant discrepancy in the strengths between aggregates containing 10 and 20% CEM I at 3 days (with the latter giving approximately 50% higher values) was observed for the CO_2-cured aggregates.
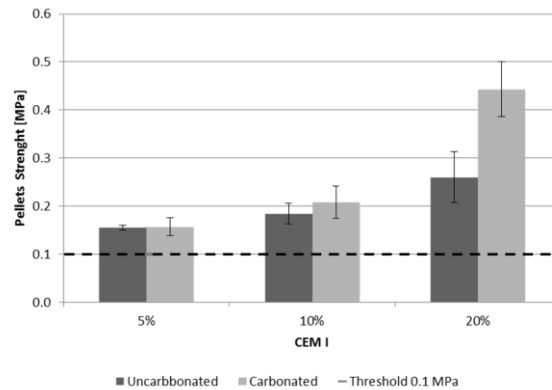
Figure 5.6 Strenght of the pellets produced by SW4 and SSA at 3 days curing time

5.3.6 Phase composition

5.3.6.1 Aggregates from soil washing residues and PA

Figure 5.7 shows the crystalline phase composition identified by XRD of the pellets at 10 % of cement for all the materials investigated. The graphs are compared for hydrated and accelerated carbonated pellets. Calcium is present in all the normal-hydrated pellets as reactive Portlandite. Other crystalline phases identified by XRD were quartz and iron with other phases present in the raw soil residues. Portlandite in the pellets was attributed to cement and paper ashes, since XRD applied to the raw residues did not detect the presence of any CO_2 reactive phases. The effect of carbonation upon the phase composition of the material treated was identified by the conversion of Portlandite to calcium carbonate. The presence of calcium carbonate in the carbonated pellets is less evident for the SW2 residue, where the effect of carbon dioxide was inhibited by the high organic substances in the raw soil residue.

a)
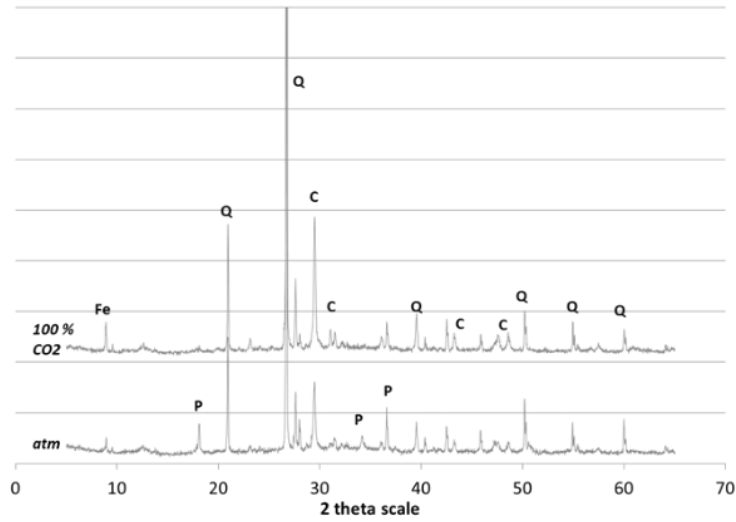
Phase compositions labels: Q: quartz, C: calcite, P: portlandite, Fe: iron.

b)
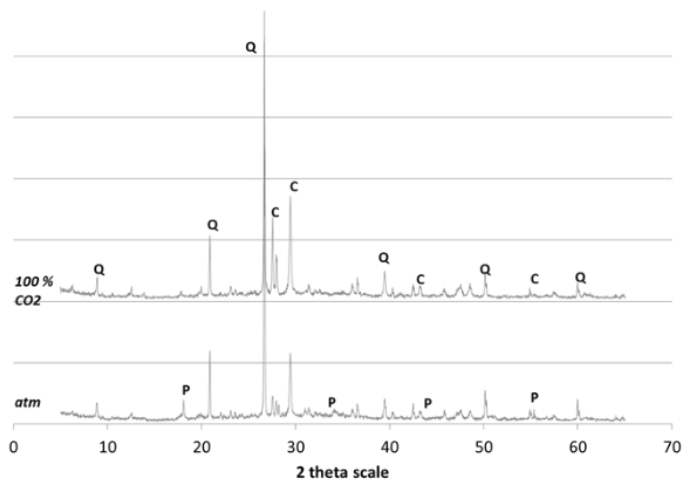
Phase compositions labels: Q: quartz, C: calcite, P: portlandite, Fe: iron.
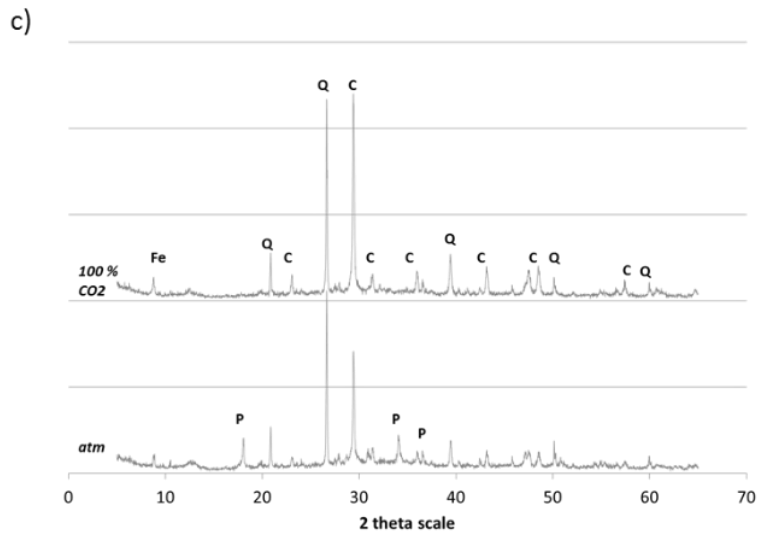
Phase compositions labels: Q: quartz, C: calcite, P: portlandite, Fe: iron.
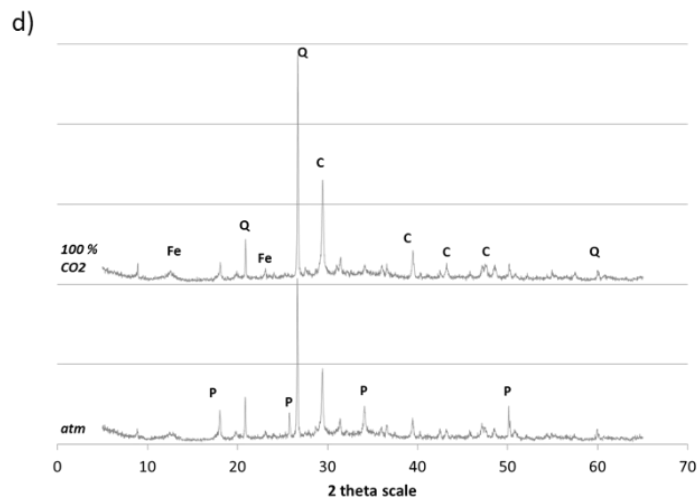
Phase compositions labels: Q: quartz, C: calcite, P: portlandite, Fe: iron.

Figure 5.7 Key crystalline phase composition identified by XRD for hydrated (atm) and carbonated (100 % CO2) pellets of (a) SW1 (b) SW2 (c) SW3 and (d) SW4.

5.3.7 Microstructure

Carbonation altered the microstructure of pellets. Precipitation of calcite occurred within the time of pelletising stage within 10 minutes. This means that the precipitation of calcite, resulting in a significant microstructure change, was due to the conversion of the free lime present in the paper ashes, which is more significant than the alteration of a calcium-silicate based material as cement (Gunning et al., 2010a). The structure precipitation of calcite in the pore spaces gave higher density to the structure improving its integrity (Malviya and Chaudhary, 2006).

Back-scattered electron micrographs of the non-carbonated and carbonated aggregates are shown in Figure 5.8, Figure 5.9, Figure 5.10 and Figure 5.11. The Figure 5.12 shows the SEM micrograph of the pellets made with the silt SW4 residue and SSA cured under carbon dioxide. The precipitation of calcite in the pore spaces due to carbonation resulted in a denser structure. The carbonated matrix was observed to infill the spaces between larger grains and produces a uniform, 'polymerised' structure. Aggregates made from SW2 showed less alteration as a result of carbonation, and may be due to the high organic content, hindering both the 'normal' hydration and accelerated carbonation of cement. This was also reflected by the lower strength of the SW2 aggregates. Microstructural changes upon carbonation can be related to the calcium-bearing phases present in the pellets. The pellets which are predominantly composed by lime, for the presence of the Paper Ashes showed a massive change of the structure due to the formation of calcite. Calcium silicate did not seem affected by carbonation.
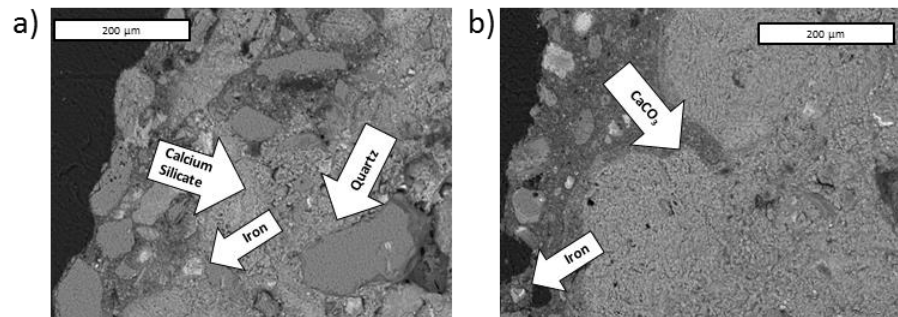
Figure 5.8 BSE micrographs of (a) hydrated and (b) carbonated aggregate of SW1
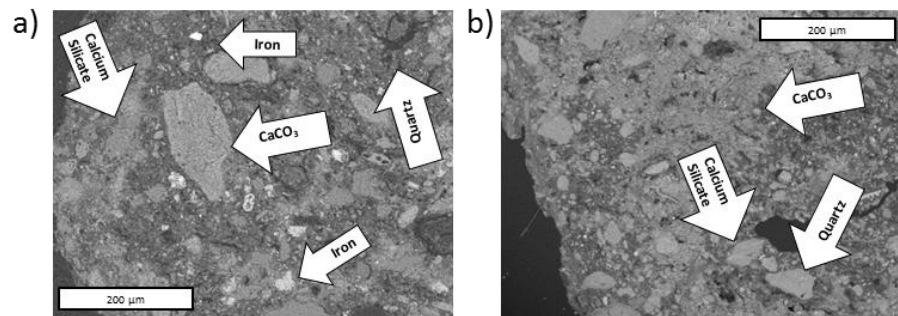
Figure 5.9 BSE micrographs of (a) hydrated and (b) carbonated aggregate of SW2
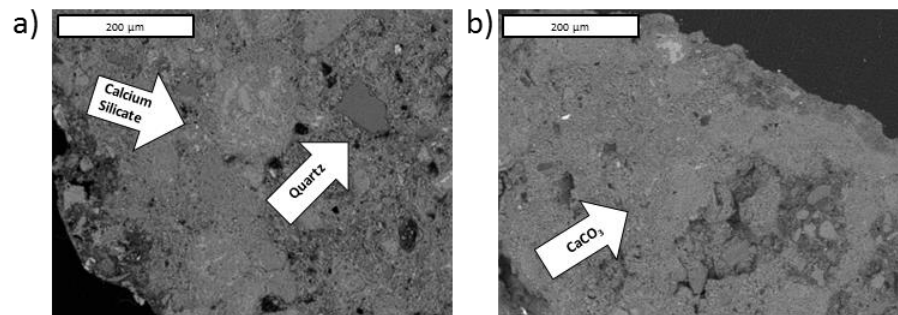
Figure 5.10 BSE micrographs of (a) hydrated and (b) carbonated aggregate of SW3
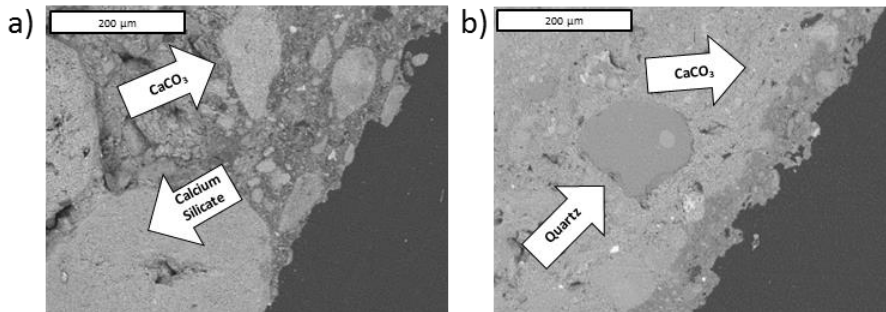
Figure 5.11 BSE micrographs of (a) hydrated and (b) carbonated aggregate of SW4
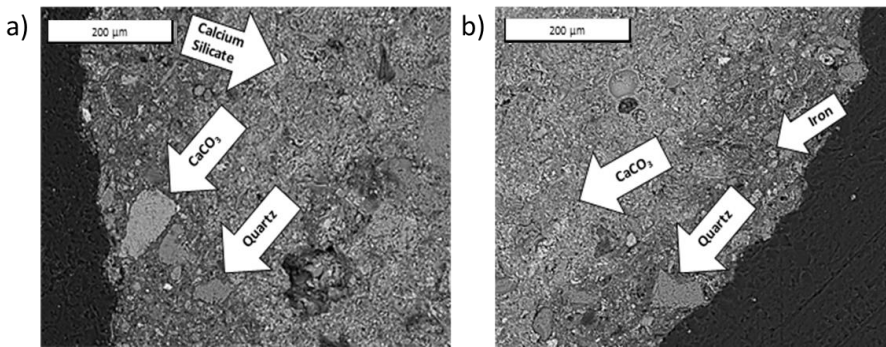
Figure 5.12 BSE micrographs of (a) hydrated and (b) carbonated aggregate of SW4 and SSA

5.3.8 Carbon uptake

During the pelletising process under CO_2, the gas chemically reacted with the pellet mixture, capturing it. The reactivity of the pellets depends upon the chemistry and the mineral composition of the mixes. As the CO_2 reacted within 10 minutes, during the granulation, the material did not reach the maximum uptake measured for PA and CEM I. The amount of gas captured varied among the finished pelletised product (Table 5.14).

Table 5.14 Carbon uptake for the SW residues and PA manufactured aggregates at 10 % CEM I

Soil residue	CO_2 uptake
SW1	2.95 %
SW2	1.72 %
SW3	4.45 %
SW4	3.07 %

The manufactured pellets with SW4 silt and SSA and 10 % CEM I, cured under 20 % synthetic flue gas reached an uptake of 9.10 ± 1.12 by weight at 6 days. In this process the carbon dioxide is permanently bound into the aggregates and laboratory tests of CO_2 uptake (through the Total Carbon analytical technique) (indicate the aggregates are carbon negative. And so there is potential to realize further carbon savings, which will make the aggregates substantially carbon negative.

5.4 AGGREGATES END OF USE CHARACTERIZATION

5.4.1 Introduction

Lightweight aggregate has been produced from construction and demolition soil washing residues and sewage sludge ash using a cement-based stabilisation step. During curing, a simulated flue gas at 20 % CO2 v/v was used to investigate the enhancement of aggregate properties by carbonation. The aggregate manufactured was evaluated for key engineering properties, including crushing strength, water absorption and particle size distribution showing conformance to the requirements for lightweight aggregates, as specified by European and British Standard. The risks associated with the leaching of contaminants in the solid wastes were managed by aggregation. Cast concrete cubes containing the CO_2-cured aggregates gave compressive strengths comparable to commercially available lightweight aggregates, indicating their re-use potential, for example, in concrete construction blocks or as a green roof substrate.

5.4.1 End use characterization

The optimised aggregate was subjected to further investigation (see Table 5.15). The manufactured carbonated aggregate had a bulk density below 1200kg/m3 and can be classified as a lightweight aggregate (BS EN 13055: 2002).

Table 5.15 Silt and SSA manufactured aggregates testing results.

	10 % CEM I	20 % CEM I	Lytag®	LECA®
Apparent density	2.9	2.6	1.7	1.0
Saturated density	1.8	1.8	NT	NT
Oven dry particle density	1.2	1.3	NT	NT
Maximum water capacity (g/cm³)	38.8	34.0	18	30.3
Bulk density (kg/m3)	974	832	697	328
Freeze–thaw (% disintegration)	82.8 %	41.7 %	3.8 %	4.3 %
pH	8.46	8.39	9.2	-
Crushing resistance (N/mm²)	0.6	2	8	2
Water permeability kf (cm/s)	1.4	1.4	1.3	NT

(*Test at 7 days cured in 20 % CO_2) NT = not tested

Aggregates properties have been analysed for green roof applications. A green roofing installation can be provided for drainage and growing layers to allow planting. Aggregates for green roofing can also improve aesthetic and building insulation properties. To support plant growth an absorbent medium aggregate is required without placing excessive load on the roof structure. Green roofs can be classified as either intensive or extensive. The layers can have different functions. Based on the properties of the aggregates: drainage course media, vegetation substrate at intensive green sites or at extensive greening sites in single-course or multicourse construction (FFL guidelines, 2002).

The high water absorption capacity indicated the pellets had suitability for green roof application and as horticultural medium.

In the former, the water permeability of the pellets at 1.4, more than the required minimal value of 0.3 cm/s, permits free draining and as such use in the drainage course layer would appear suitable. Furthermore, the relatively high water absorption of the pellets >40 %, would also be beneficial in delaying roof runoff and a maximum water capacity > 20 % make them suitable for vegetation substrate at extensive greening sites in single-course construction (see Table 5.16). However, the high freeze-thaw resistance may limit the application of the aggregate under extreme weather conditions, and this will be the subject of further investigation.

Although exposure of the aggregate to CO_2-containing synthesised flue gas did not significantly change the strength values recorded, it did have a significant effect on pH. A pH of 8 is a much more suitable value than 12 (recorded for the hydrated samples) for both horticultural and green-roofing application, where the desired pH is 5.5-8. It should be noted that a pH of up to 9.5 can permitted in specific circumstances, such as

for a single-course construction, but is dependent on the choice of vegetation.

Table 5.16 Required properties of aggregate to use in green roof application

Properties		Reference Value			
	unit	drainage courses	Vegetation substrates at intensive greening sites	Vegetation substrates at extensive greening sites in multi-course construction	Vegetation substrates at extensive greening sites in single-course construction
Granulometric Distribution -proportion of slurry-forming components (d<0.063 mm)	Mass %	≤7	≤20	≤15	≤7
-proportion of gravel (d<4 mm)	Mass %	-	-	-	≥25
Maximum water capacity	Vol.-%	-	≥45	≥10	≥20
Water permeability mod. Kf	cm/s mm/min	≥0.3 ≥180	≥0.0005 ≥0.3	≥0.001 ≥0.6	≥0.1 ≥60
pH value -at intensive greening sites -at extensive greening sites	- -	5.5 – 8 6.5 - 8	5.5 – 8	6.5 - 8	6.5 – 9.5

Table 5.17 Upflow percolation test leachate concentrations per fraction (values in mg/kg).

	Metals concentrations in the eluates						
Fraction	1	2	3	4	5	6	7
w/s ratio	0.1	0.1	0.3	0.5	1	3	5
Antimony	0.005	0.003	0.008	0.013	0.024	0.069	0.114
Arsenic	<0.002	<0.002	<0.006	<0.01	<0.02	<0.06	<0.1
Barium	0.020	0.010	0.017	0.015	0.025	0.060	0.068
Cadmium	<0.0003	<0.0003	<0.0009	<0.0015	<0.003	<0.009	<0.015
Chromium	0.002	0.008	0.020	0.020	0.026	0.030	<0.03
Copper	0.002	0.002	0.006	0.009	0.015	0.035	0.040
Lead	<0.002	<0.002	<0.006	<0.01	<0.02	<0.06	<0.1
Mercury	<0.002	<0.002	<0.006	<0.01	<0.02	<0.06	<0.1
Molybdenum	0.072	0.131	0.355	0.454	0.045	0.978	0.426
Nickel	0.010	0.007	<0.0042	<0.007	<0.014	<0.042	<0.07
Selenium	<0.001	<0.001	<0.003	<0.005	<0.01	<0.03	<0.05
Zinc	0.080	0.011	0.002	<0.01	<0.02	<0.06	<0.1
Chloride	36	59	177	161	<200	<600	<1000

Table 5.17 reports the metals concentration in the seven fractions of the upflow percolation test. Concentrations are mostly below the inert limits for each of the fraction. Chloride was found at very low concentrations in each fraction.

The bulk density and crushing resistant for the 20 % CEM I carbonated aggregates indicates that they can be considered lightweight aggregates for using in concrete blocks. The higher water absorption, typical of manufactured aggregates, is accommodated by soaking prior to use, and this would compensate for the greater adsorption recorded for the aggregate made from construction waste. The crushing resistance recorded was similar to LECA, whereas the strength and density of concrete cubes containing the carbonated aggregate were comparable with concrete containing commercial LWA (Table 5.18). Manufactured aggregates bound with 20% CEM I gave concrete cube strengths comparable to LECA and C8agg.

Table 5.18 Density and compressive strength of concrete cubes.

	10% CEM1	20% CEM1	Lytag	LECA	C8Agg
7 days strength (Mpa)	10.8	21.4	32.0	18.6	19.9
Density (kg/m³)	1960	2020	1910	1482	2150

The satisfactory mode of fracture as specified in BS EN 12390 has been observed in the concrete cubes after the crushing test (Figure 5.13).

Figure 5.13 Concrete test cube with the failure mode due to compression

It should be noted that the commercially available aggregates used in comparison with those manufactured during this work are all

successfully used in concrete. Thus, although there appear to be some significant differences for some tests between these and the aggregates being investigated here, there is general agreement that the SSA silt-product has potential for use in construction application. There are also some surprising results requiring further investigation/development if the range of applications for this new product is not to be unduly limited.

5.4.1 Proposed process

The wastes used in this study were disposed to a landfill site that also contained sanitary waste, generating landfill gas which is flared prior to emission to the atmosphere. The flue gas represented a resource of CO_2 which can be used for the carbonation of aggregates made from the incoming solid wastes, using a cement-based aggregation step.

The occurrence of these 3 wastes at one site is fortuitous; as they can be combined at one location to produce the aggregate, with re-use potential. In doing this, it is possible to demonstrate how the needs of the circular economy can be met and how useful materials normally disposed to landfill can be reclaimed and returned to the building materials supply chain.

A design for the scaling-up of the process is proposed (Figure 5.14), which comprises a mixing unit, pelletiser and curing system in one functional production process.

Silt/sludge is stored and dewatered prior to delivery to the process. Ash and cement are dry-stored in adjacent silos. Sludge and cement are weigh-batched and pre-mixer, prior to the addition of SSA, which is added as required to adjust the moisture content and rheology of the mixture for pelletising. The formed product is then transferred to a series of curing vessels, each receiving a feed of CO_2-rich flue gas. The product remains in the curing vessel and is monitored until it achieves the required strength.

This would facilitate their diversion from land-based disposal and provide a potential supply of much needed aggregate for the south east of the UK. Co-incidentally, the landfill concerned had been previously been previously used for the disposal of domestic waste, and has a gas collection and flaring system installed. Thus, a readily available source of

carbon dioxide gas for use in an aggregate production process was of great interest.
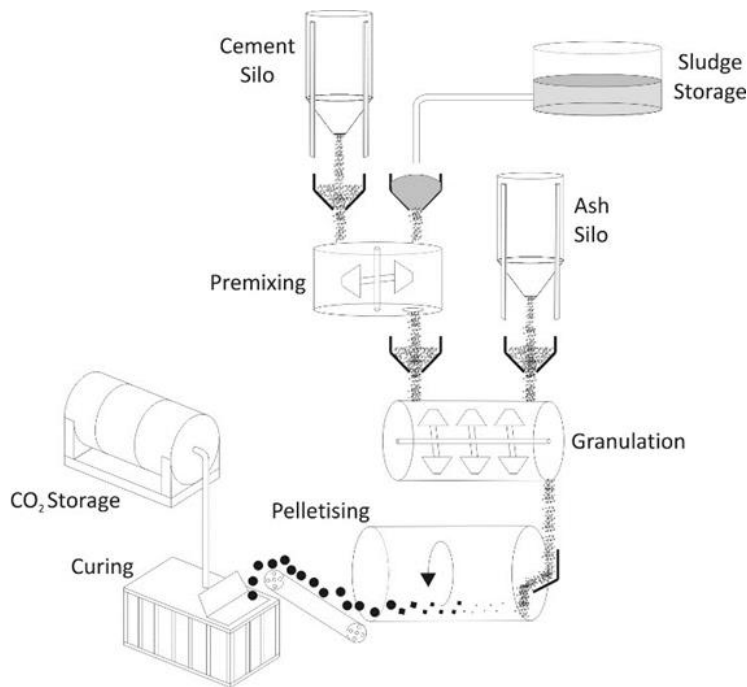
Figure 5.14 Proposed pilot-scheme process for LWA production from waste

5.5   CONCLUSION

In the first part of the research two artificial contaminated soils spiked with cadmium, copper and lead have been treated by a cement-based stabilization/solidification process. The effect of accelerated carbonation on the cement-based stabilization/solidification process has been analysed comparing two curing conditions: standard and under a 20 % carbon dioxide. Heavy metals were well stabilized at 5 % CEM I at 7 days in all the soil samples and it was not related to the contaminants initial concentrations. The concentration levels of cadmium and copper in the soil sample without organic matter were under the detection limit of the instrument for both the curing conditions. Lead concentration in the eluate was below the limit for all the soil samples, while copper and cadmium in the sample S2 were over the concentrations of the sample

S1. Organic matter had a detrimental effect on the stabilization of the heavy-metals. Stabilization was independent by the initial concentrations of contaminants.

Accelerated carbonation decreased the pH of the soil samples treated from 12 to values till 7 at 5 % CEM I. Stabilization of heavy metals was not significantly influenced by the variation of pH for the three heavy-metals investigated. Copper and lead slightly increased their solubility under accelerated carbonation curing condition. The pH shows the same behaviour in the soil samples S2, whereas stabilized samples had higher value of percentage of stabilization.

In the second part of the experimentation four soil-washing residues collected from different soil washing plants, classified as hazardous or stable non-reactive wastes, have been examined for to be treated by a carbonation-based stabilisation/solidification step to produce a recycled aggregate. The soil washing residues were classified as a sandy/silty loam and classified as stable non-reactive hazardous waste based on the heavy metals leaching concentration or as hazardous waste for the high organic content. Treatment using Paper Ashes and Portland cement was tailored for each waste to produce a pelletised product suitable for re-use in construction.

The carbonated aggregates produced had comparable strength to commercially available lightweight aggregates. Carbonation increased the strength of the pellets compared to the hydrated one. High organic content in one of the residues showed the ineffective of both hydration of cement and carbonation. Contaminants present in the soil washing residues were largely stabilized by the treatment process. Some heavy metals leaching were unaffected by carbonation, while copper and barium showed a changing of solubility between the not-carbonated and carbonated pellets. Analysis by SEM and XRD showed that carbonation was responsible for a reduction in porosity and a consequent increases density of the carbonated aggregate. Further experiments were made producing pellets from one of the silty soil washing residue and sewage sludge ash. Upon combination with SSA, cement and exposure to flue gas during curing the residue properties was enhanced enough for use a light weight aggregate. During processing, the regulated contaminants were stabilized. These pellets were further tested for physical and chemical characteristics. The aggregates had bulk densities consistent

with lightweight aggregates and had comparable properties to commercially available manufactured light-weight aggregates, with applications in concrete, or as a green roofing substrate due to the low pH of the carbonated products and the high water absorption.

The manufactured aggregates imbibed up to 20 % by weight of carbon dioxide during manufacture, ensuring that this greenhouse gas was permanently captured and not emitted to atmosphere. A simple scheme for manufactured aggregates using two solid and one gaseous waste streams, using non-bespoke processing equipment, was proposed.

6 CONCLUSION

Recovering waste, such as industrial waste or excavated contaminated soil against landfilling, is a key aim in waste management. Industrial waste and contaminated soil can be managed to reduce their hazardousness. Innovative methods to treat and to recover them are of interest in sanitary engineering. Cement-based stabilisation/solidification (S/S) employs cementitious binders to mix contaminated soils and waste to produce a chemical and physical stable product. Accelerated carbonation (ACT) is an accelerated process of natural carbonation reaction at which cement-based materials are affected. It induces a rapid reaction between carbon dioxide and reactive waste materials. ACT has been used to treat contaminated soils and waste using hydraulic binders and granulation to produce a recycled lightweight aggregate.

Combining ACT and cement-based S/S has been here investigated as a solution for the recovery of contaminated materials in the form of aggregates. The research aimed at the evaluation of enhanced S/S processes to treat and recover heavy-metals contaminated soils and waste. Preliminary tests explored the effect of accelerated carbonation on heavy-metals contaminated soil treated by cement-based S/S. Stabilization/solidification using cement was effective to stabilize cadmium, copper and lead spiked in artificially contaminated soils. The process was not influenced by the initial concentrations of the contaminants, cement content and curing time. Copper and cadmium showed a slightly higher solubility in presence of organic matter in the soil. Accelerated carbonation decreased the pH up to 7.5 of the soil samples treated. It had not a significant effect on the solubility of the three heavy metals investigated compared to the conventional cement-based S/S.

Further investigations focused on the treatment of soil washing residues for the production of innovative lightweight recycled aggregate blended with thermal ashes and cement. Prior to the treatment the raw materials were classified mostly as hazardous or stable non-reactive waste based

on the leaching test and the amount of organic carbon, requiring the disposal in the appropriate landfill class. Moreover the soil residues were in the form of fine materials with high moisture content. A correct amount of ashes in the process was required to reduce the moisture and improve the formation of the pellets.

Cement S/S reduced the leachates of all the regulated metals at values within inert limits of waste acceptance criteria. The application of accelerated carbonation reduced the concentration of copper and barium and had negligible effect upon the solubility of the other contaminants. High organic content in the raw residues influenced the strength of both the normal hydrated and carbonated aggregates. Nevertheless, the leaching of the dissolved organic carbon was reduced by the treatment allowing the reclassification of the material from hazardous to inert waste. An additive, such as an adsorbent to enhance the hydration mechanisms of the cement, should be considered to treat high organic content residues.

Accelerated carbonated aggregates showed an improvement in the strength compared to the normal-hydrated product. They also had more dense microstructure due to the precipitation of calcium carbonate from the reaction between the carbon dioxide and the calcium oxide.

The results at laboratory scale showed comparable strength and properties to commercially available manufactured light-weight aggregate. Aggregate also had bulk densities consistent with the application in concrete block production. The application of accelerated carbonation made them suitable as green roofing substrates due to the low pH of the carbonated product.

The technology described here can be proposed as a novel treatment for recovering contaminated soil residues and waste for the production of lightweight aggregate using waste and a cold-bonding process. The process designed needs to be tailored for each of the residues/waste to be treated. Variability of the waste/residues has to be considered since they can differ on the particle size distribution, the moisture content, and the level of contaminants. In the case ashes are used as filler replacements the product may have highly variable strength and durability, requiring stringent monitoring of incoming raw materials and product quality control.

Accelerated carbonation may be applied to stabilization/solidification process to reach specific characteristics of the products in term of leaching, strength and pH. Its efficacy depends also on the reactivity of the material used in the process. Properties as final strength, together with the levels of contaminants present are chosen upon the specification of the final end-use of the product.

Depending on the incoming waste/residues and on the reactivity of ashes and cement, the use of accelerated carbonation may be applied during the pelletising stage or during the curing of the product. Curing the pellets up to three days in carbon dioxide atmosphere rather than filling the pelletiser can lead to fully carbonation of the product.

A simple final scheme for manufactured aggregates using two solid and one gaseous waste streams and non-bespoke processing equipment was then proposed. Since the aggregates reacted with 20 % carbon dioxide, the use of a flue gas recovered from an emission to imbibe the pellets is preferred to a pure 100% carbon dioxide gas. This ensure that during the process this greenhouse gas may be permanently captured and not emitted to atmosphere.

Further researches are needed and can be summarize in the following points:

1. Conduct further trials with alternative CO_2 reactive fillers e.g. steel slag, biomass ash etc
2. Look at a broader range of residues or filter cakes to enhance understanding of the patterns between raw material properties and aggregate properties.
3. Conduct pilot scale demonstrations to produce sufficient material for end-use evaluation.
4. Consider other applications e.g. engineering fill, filtration medium etc
5. Conduct further testing to construct a portfolio that will facilitate licensing of the product by regulatory authorities for commercial sale
6. Explore further the use of flue gas as an economical source of CO_2

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