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# Innovative technology trains for treating excavated material in the framework of Brownfield regeneration

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# ABSTRACT

The modification of land use and the subsequent dismantling of several industrial activities has led to the formation of a number of Brownfields all across Europe. Currently, the revitalization of Brownfield sites is hindered by the need to address contamination issues, which may arise from the past land activities as well as from the interim uses of the site. The traditional approach in Brownfield regeneration in most European countries is a bottom-up approach, which consists essentially in the selection of one or more best available technologies that can respond to the site-specific needs. The environmental issues associated with a Brownfield site could be turned into opportunities to provide products or services for the site itself and the surrounding area. To this aim, the traditional bottom-up approach should be rather combined with a top-down one, starting from the identification of needs/opportunities to select the technologies capable of delivering the required services. Specifically, the clean-up of the site should be fulfilled by (re)using material and exploiting resources already present at the site and/or produced as a result of the regeneration activities themselves. To this aim, a proper combination of technologies, i.e. a technology train, may potentially fill the gap between available resources and required services at Brownfield sites.

The main objective of this doctoral thesis was to investigate two specific technology trains for the treatment of contaminated soil and alkaline industrial soil, respectively, in order to assess their applicability in a Brownfield regeneration context.

The first technology train was based on stabilization/solidification (S/S) and granulation of a metal contaminated Brownfield soil and was aimed at producing aggregates for construction applications. Preliminary tests were performed on a non contaminated natural soil in order to assess the effects of the treatment on the physical and mechanical properties of the obtained aggregates as a function of the applied operating conditions. The results obtained from the preliminary tests highlighted that the type and amount of cement employed were the factors that most influenced the particle size and mechanical strength (measured in terms of Aggregate Crushing Value, ACV) of the aggregates, while the type and amount of additives (superplasticizers) proved to be less relevant. Specifically, the use of 25% wt. of a high – resistance Portland cement led to the production of aggregates with an ACV comparable to that of a natural gravel (20%). With reference to the aggregates obtained from the S/S - granulation of the metal contaminated industrial soil, their resistance to compression was found to be similar to that of argillaceous limestone (ACV ~ 29%). With regard to the leaching behaviour of the obtained granules, the increase in the release of critical metals, especially Cu, was mainly ascribed to the characteristics of the cement used as binder, which showed to release significant concentrations of metals, as well as to the increased eluates pH (> 12), which may have an adverse effect on the immobilization of amphoteric elements.

The second technology train relied on a process based on the coupling of accelerated carbonation of alkaline industrial soil with other techniques aimed at the remediation of groundwater contaminated by volatile organic contaminants (VOCs) that may result in CO<sub>2</sub> release. The process was investigated at lab-scale performing column carbonation experiments on different particle size fractions of a stainless steel (SS) slag and applying conditions expected at Brownfield sites (100%  $CO_2$ ,  $P_{CO2} = 1$  bar; ambient temperature). In a second stage of the study, the carbonation process applied to SS slag was coupled with a new method aimed at improving the technical properties of subsoil, the Ecogrout process, developed by the Deltares institute (The Netherlands), which results in CO<sub>2</sub> release. The results showed that, even at the mild operating conditions tested, significant  $CO_2$  uptakes could be achieved for all the size fractions investigated, up to 11% for the finest size class (d < 0.84 mm) after 24 h. Besides, significant CO<sub>2</sub> uptakes (around 7%) may be potentially achieved after a relatively short timeframe (90 min) also when the CO<sub>2</sub> flow is generated by the Ecogrout process. As for the effects on the leaching behaviour of the studied stainless steel slag, carbonation showed to exert a relevant immobilization effect on Cr and Ba leaching, already after 2 h of treatment. However, the reduction of eluate pH led to an increased leaching of V and Mo.

# ABSTRACT

I cambiamenti nell'uso del suolo e il conseguente smantellamento di numerose attività industriali e produttive ha di recente portato alla formazione di un certo numero di siti Brownfield. La riconversione di tali siti è in genere ostacolata dalla necessità di affrontare i problemi di contaminazione, che possono derivare dalle attività industriali pregresse così come dagli usi provvisori del sito. L' approccio tradizionale nella bonifica e rigenerazione di un Brownfield è un approccio di tipo bottom-up, che essenzialmente consiste nell' individuare gli obiettivi di bonifica che meglio rispondono a bisogni sitospecifici. Tuttavia, i problemi ambientali associati ad un Brownfield possono diventare un'opportunità per fornire servizi/prodotti per il sito stesso ed eventualmente per le aree limitrofe. Diventa, quindi, necessario combinare l'approccio tradizionale con uno di tipo top-down, che miri ad identificare i bisogni/opportunità, per poi selezionare le tecnologie adatte a fornire i servizi richiesti. In particolare, la bonifica del sito dovrebbe essere attuata sfruttando risorse e riutilizzando materiali già presenti nel sito e/o prodotti come risultato delle stesse attività di rigenerazione. Per raggiungere questo scopo, una singola tecnologia può non essere sufficiente e si prospetta la necessità di utilizzare una opportuna combinazione di tecnologie, ovvero un treno di tecnologie, in grado di "creare un ponte" tra risorse disponibili e servizi richiesti nel sito.

Il principale obiettivo di questa tesi di dottorato è stato quello di studiare sperimentalmente due specifici treni di tecnologie per il trattamento rispettivamente di suoli contaminati e residui alcalini, così da valutare la loro applicabilità in un contesto di rigenerazione di un *Brownfield*.

Il primo treno è consistito in un trattamento di stabilizzazione/solidificazione (S/S) e granulazione di un suolo *Brownfield* contaminato da metalli finalizzato alla produzione di aggregati riutilizzabili in applicazioni dell'ingegneria civile. Un suolo naturale non contaminato è stato, inoltre, sottoposto a prove combinate di S/S - granulazione preliminari al fine di valutare gli effetti del trattamento sulle proprietà fisiche e meccaniche degli aggregati ottenuti al variare delle condizioni operative utilizzate. Dai

test condotti sul suolo naturale è emerso che il tipo e la quantità di cemento impiegato hanno influenzato, più di altri parametri, sia la granulometria che la resistenza meccanica (misurata in termini di *Aggregate Crushing Value*, ACV) degli aggregati. In particolare, l'impiego di cemento ad alta resistenza (R 52.5) in percentuale pari al 25% ha portato alla produzione di granuli con un ACV paragonabile a quello di una ghiaia naturale (20%). Con riferimento al suolo da *Brownfield*, gli aggregati ottenuti dal trattamento hanno mostrato un ACV medio paragonabile a quello di un calcare argilloso (29% circa). Per quanto riguarda il comportamento alla lisciviazione dei granuli ottenuti dal trattamento, l'aumento del rilascio di alcuni metalli, in particolare del Cu, è stato attribuito sia alle caratteristiche del cemento utilizzato come legante, che ha mostrato di rilasciare concentrazioni significative di alcuni metalli, sia all'aumento del pH (> 12), che potrebbe aver avuto un effetto negativo sulla immobilizzazione degli elementi anfoteri.

Il secondo treno di tecnologie è basato sulla combinazione di un processo di carbonatazione accelerata con altre tecniche finalizzate alla bonifica di acque di falda contaminate da composti organici volatili e che rilasciano CO<sub>2</sub> quale prodotto secondario. Il processo è stato indagato in scala di laboratorio effettuando test di carbonatazione in colonna su scorie della produzione di acciaio inossidabile e applicando condizioni operative potenzialmente presenti in un *Brownfield* (100% CO<sub>2</sub>, P<sub>CO2</sub> = 1 bar; temperatura ambiente). In una seconda fase dello studio, il processo di carbonatazione è stato accoppiato con un nuovo metodo per migliorare le proprietà tecniche del sottosuolo, messo a punto dal Deltares (Paesi Bassi). I risultati hanno mostrato che, anche alle blande condizioni operative testate, è possibile raggiungere un grado significativo di carbonatazione per tutte le classi granulometriche considerate, fino a un CO<sub>2</sub> uptake medio dell'11% per la frazione più fine (d < 0.84 mm) dopo 24 h. Inoltre, significativi CO<sub>2</sub> uptake (circa 7%) possono essere potenzialmente raggiunti dopo un lasso di tempo relativamente breve (90 min), anche quando il flusso di CO<sub>2</sub> è prodotto dal processo Ecogrout. Per quanto concerne gli effetti sul comportamento alla lisciviazione delle scorie testate, il processo di carbonatazione ha mostrato di esercitare un rilevante effetto di immobilizzazione nei confronti di Cr e Ba, già dopo 2 h di trattamento. Tuttavia, la riduzione del pH verificatasi a seguito della carbonatazione ha portato ad un aumento della lisciviazione di V e Mo.

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# BACKGROUND

Rapid technological and economic changes lead to the continuous modification of the industrial landscape. Specifically, in the past decades, modification of land use has lead to the formation of several Brownfields, i.e. "sites that have been affected by the former uses of the site and surrounding land, are derelict and underused, may have real or perceived contamination problems, are mainly located in developed urban areas and require intervention to bring them back to beneficial use" (Ferber et al, 2006). At the mean time, Greenfields are still being consumed for new construction projects and industrial developments, since the costs and timeframes required for Brownfield regeneration are generally not competitive. Furthermore, Brownfields are often characterized by soil contamination that must be dealt with. Together with soil, in these sites it is often possible to find a mixture of soil and industrial residues, commonly referred to as industrial soil, whose characteristics mainly depend on the former industrial activities. Due to their characteristics, usually different from native soil, these soils may potentially have an impact on groundwater, as they may potentially release toxic metals. Due to the lack of explicit regulations in most European countries linking Brownfield remediation and redevelopment, the latter is typically postponed after the conclusion of clean-up activities. Partly also as a consequence of the lack of a clear regualification pathway, reuse options for contaminated soils and industrial soils cannot be identified, often obliging to the landfilling of the excavated materials. The poor acceptance of landfilling and the environmental impact of this disposal practice, together with the excessive costs in the case of a large volume of soil to be disposed of, lead to the need to identify alternative solutions for the management of contaminated soil/industrial soil at Brownfield sites. From a different viewpoint, the environmental problems associated to a Brownfield site and the issues related to the management of potentially large volumes of contaminated material may turn into an occasion to supply products or services at the Brownfield itself and/or in the neighbourhood. This concept has been recently proposed

within the FP-7 European project HoMBRe (Holistic Management of Brownfield Regeneration), funded by the European Commission under the Seventh Framework Programme THEME FP7 ENV.2010.3.1.5-2: Environmental technologies for Brownfield regeneration, whose final ambition is to achieve "Zero Brownfields development". The HoMBRe strategy is based on the concept of Circular Land Management, according to which a particular site passes through different stages during its life, from planning, to the use phase (e.g. industrial use), ending with the cessation of use. This last stage may lead to the formation of a Brownfield and, consequently, to the exit of the site from the Land Cycle. Alternatively, the reintroduction of the site within the Land Cycle could be possibly met by applying a holistic approach, i.e. by addressing the overall aspects that influence Brownfield management and regeneration, i.e. social, economic, environmental and spatial planning factors. Concerning Brownfield contamination issues, the HoMBRe strategy is mainly based on the application of "Technology trains", i.e. combinations of technologies, as a tool to shift from short term and local oriented problem solving to an approach aimed at achieving sustainability in a wider perspective. Specifically, the cleanup of the site, which is mandatory for the reintroduction of a Brownfield within the Land Cycle, should be fulfilled by (re)using material and exploiting resources already present at the site and/or produced as a result of the regeneration activities themselves. According to this concept, a bottom-up approach, which is only aimed at preparing the site for a specific use or for complying with the current environmental legislation, turns out to be insufficient. Hence, it should be rather combined with a top-down approach, starting from identifying the needs/opportunities of the site so to select the technologies able to provide the desired products/services. To this aim, technology trains can provide the link between the resources available at the site (inputs) and the products or services needed for the regeneration phase (outputs).

This doctoral thesis reports about a new framework for the management of excavated soils and alkaline industrial soil within a Brownfield regeneration process developed as a part of the HoMBRe project. Specifically, two technology trains for the treatment of the above mentioned materials were evaluated, with the final aim to maximize their reuse at Brownfield sites as well as to provide a first attempt towards the assessment of the conditions of applicability, i.e. operating windows, of the proposed technology trains.

The first technology train consisted in a grain size screening step in which a metal contaminated soil sampled from an Italian Brownfield site was separated into two size fractions, followed by the treatment of the fine fraction by a combined stabilization/solidification and granulation process. The aim was to obtain aggregates with a grain size above 2 mm, characterized by physical, mechanical and environmental properties which render them suitable to be reused in construction applications. A first insight on the applicability of this process was gained by applying the treatment to a non contaminated natural soil and evaluating the effects of changing the operating conditions and mixture formulations on the final characteristics of the obtained aggregates.

The second technology train relied on a process based on the coupling of accelerated carbonation of alkaline industrial soil with a new method developed by Deltares for improving the technical properties of subsoil called Ecogrout. Specifically, the upward CO<sub>2</sub> flow evolved from the Ecogrout process may stimulate the carbonation of an overlying layer of alkaline material. Preliminary tests were performed on selected alkaline material (stainless steel slag) by means of a column carbonation experimental method and applying the conditions expected at a Brownfield site (100%  $CO_2$ ,  $P_{CO2} = 1$  bar, ambient temperature) in order to assess the effects exerted on the environmental behaviour of the treated material as well as on the achieved CO<sub>2</sub> uptakes. The potential of the coupled process was evaluated during a six months research period carried out at the Deltares institute in Utrecht (The Netherlands). Namely, batch Ecogrout tests and further column carbonation tests allowed to estimate the CO<sub>2</sub> flow evolved during the Ecogrout reaction as a function of the injection regime and stirring conditions as well as to evaluate the degree of carbonation of the stainless steel slag as a function of reaction time and particle size. Hence, a laboratory scale and a larger scale set ups were implemented by coupling Ecogrout and accelerated carbonation in order to close the loop of the whole process and replicate the real scale conditions which could be possibly found in Brownfield sites.

The present thesis is structured as follows: Chapter 1 reports a general overview on the main materials available in a Brownfield site and their potential reuse options, as well as a discussion on the available individual technologies and possible technology trains based on their combination to convert the existing inputs into the desired outputs. In particular, the conditions of applicability of each technology and the main criticalities related to the

reuse of the considered materials are highlighted. In Chapter 2 the study of the stabilization/solidification - granulation treatment applied to the metal contaminated Brownfield soil is presented and the main results are reported. In Chapter 3 the main results obtained from the carbonation as well as the combined Ecogrout - carbonation experiments are presented and discussed. Finally, Chapter 4 summarizes the most relevant results of this doctoral work, highlighting the potential of the proposed technology trains as well as their critical issues. Hence, a perspective for the further investigation of the proposed treatments is provided.

1

# TECHNOLOGY TRAINS FOR REUSING EXCAVATED MATERIALS IN A BROWNFIELD REGENERATION CONTEXT

\* This chapter discusses the potential of Technology Trains with specific reference to the issue of maximizing the reuse of materials resulting from excavation activities within Brownfield regeneration projects, so to help to close the cycles of soil and other excavated materials, making the use of resources more sustainable and reducing the consumption of virgin raw materials. Based on a review of the most recent studies, this section reports about the main characteristics of materials typically available in a Brownfield site after excavation and their potential reuse options. In addition, the individual technologies available for producing materials that can be employed in construction applications are discussed. However, individual technologies may be effective when dealing with a bottom-up approach, but they may become insufficient in view of a top-down approach. Hence, proper combination(s) of technologies, i.e. technology train(s), are proposed in order to find links between inputs and outputs and to help reintroducing the Brownfield site into the Land use Cycle.

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HoMBRe public report, 2012. Deliverable 4.1: In Depth Analysis and Feasibility of the<br/>Technology Trains. Available online at:<br/><<a href="http://www.zerobrownfields.eu/HombreTrainingGallery/HomePage/HOMBRE\_D4.1\_final\_TechnologyTrains.pdf">http://www.zerobrownfields.eu/HombreTrainingGallery/HomePage/HOMBRE\_D4.1\_final\_TechnologyTrains.pdf</a>

#### Oriana Capobianco

# 1.1 Introduction

Brownfields regeneration activities lead to the production of soils and other excavated materials that must be managed. Indeed, the regeneration of Brownfields usually requires the demolition of existing structures and the excavation of soils, which may have a functional or environmental purpose. The management options for these materials depend on the quantity and quality of material flows produced, i.e. the inputs, and on the quantity and quality of materials required by the regeneration strategy chosen for the specific Brownfield case, i.e. the outputs. Along with construction and demolition (C&D) waste, whose potential for reuse in construction application has been widely studied and assessed, and contaminated soil, Brownfield sites are commonly characterised by the presence of waste material arising from the historical use of the site. For instance, industrial by-products may be heterogeneously mixed with native soil, becoming part of the soil matrix (Renforth et al., 2009) or presented as layers or heaps, e.g. in area previously devoted to stacking raw materials (Adamo et al., 2002).

A lot of industrial activities may be potentially responsible for the presence of industrial by-products in a Brownfield site, e.g. mining, smelter operation and incineration, but only some of these activities produce solid (waste) materials which are more attractive from the point of view of their reuse, in terms of quality and quantity. For instance, blast furnace slag and coal fly ash are examples of industrial by-products with such characteristics that render them suitable to be reused in a variety of applications.

The main reuse options for blast furnace slag in Europe are reported in Figure 1.1. It has been estimated that, up to 2004, 32.6% of the reused blast furnace slag, mainly air-cooled blast furnace slag, was employed for road construction purposes. Specifically, the production of slag aggregates or slag mixtures for unbound layers was the dominant practice. 64% of the reused blast furnace slag, most of it granulated or pelletized, was employed instead for cement production. Within the European Union (EU), the utilisation of coal fly ash in the construction industry was recently found to be around 48% (Feuerborn, 2010). Furthermore, the utilization of coal fly ash is different in each European Country and is mainly based on national tradition and experience.



Figure 1.1. Use of blast furnace slag in Europe, 2004 (EUROSLAG, 2006).

In 2008, about 18 million tonnes of fly ash were utilised in the construction industry and in underground mining. Most of the coal fly ash produced was used as a concrete additive, in road construction and as a raw material for cement clinker production. Fly ash was also utilised in blended cements, in concrete blocks and for infill, i.e. for filling voids, mine shafts and subsurface mine workings. A graph on the utilization of coal fly ash in the construction industry and in underground mining in 2007 is given in Figure 1.2.

Along with blast furnace slag and coal fly ash, slags form steel production processes and residues from the incineration of municipal solid wastes may play an important role in the requalification of a Brownfield site. In fact, these materials may be present in a Brownfield as a result of the former uses of the site (Adamo et al., 2002; Renforth et al., 2009) or they may be produced in metallurgical and incineration plants nearby the site. Furthermore, the reuse of steel slag and, especially, of incinerator residues is still limited and these materials are hence still undervalued.



Figure 1.2: Utilization of coal fly ash in the construction industry and underground mining in Europe in 2007 (Feuerborn, 2010).

Steel slag is a by-product of either the conversion process of iron to steel in a basic oxygen furnace (BOF), or the melting of metallic scraps for steel manufacturing in an electric arc furnace (EAF). In 2002, about 50 million tons of steel slag were produced worldwide (Altun and Yilmaz, 2002), while in 2009 more than 40% of the global steel production was manufactured in EAF plants (Pellegrino and Gaddo, 2009). Main field of application for steel slags concern their use as aggregates for road construction (Xie et al., 2012) or concrete production (Manso et al., 2006). However, it has been estimated that in the EU at least 13% of steel slag is still dumped (EUROSLAG, 2010).

Incineration of municipal solid waste is advantageous because energy may be recovered from wastes whose volume and mass can be significantly reduced. Nevertheless, several types of solid residues with different degrees of hazardousness, generally termed Municipal Solid Waste Incinerator (MSWI) residues, are generated in these plants. They can be broadly divided into fly ashes (FA) and bottom ashes (BA), and amount to about 5% and 25% in weight of the incinerated municipal solid waste, respectively (Sabbas et al., 2003; Sorlini et al., 2011). Although some treatments aimed at the valorization of these materials can be found in the recent scientific literature (e.g.: Becquart et al., 2009; Siddique, 2010), the most applied strategy for the management of MSWI residues is

landfill disposal, preceded by cement stabilization in the case of fly ash (Pan et al., 2008; del Valle-Zermeño, 2013).

As already mentioned, in order to identify new strategies for the management of excavated material in a Brownfield regeneration context, there is a need of developing technology trains, i.e. a combination of technologies that can provide the link between these materials (inputs) and the products or services needed for the regeneration phase (outputs).

This section discusses this integrated approach with specific reference to the issue of maximizing the reuse of materials resulting from excavation activities within Brownfield regeneration projects, so to help close the cycles of soil and other excavated materials, making the use of resources more sustainable and reducing the consumption of virgin raw materials. Paragraph 1.2 reports about the main materials typically available in a Brownfield site, with specific reference to contaminated soils, slag produced as a result of steel making processes and MSWI residues. The individual technologies available for treating these materials and producing a reusable material are discussed in Paragraph 1.3. The potential output options where these products may be used are then presented and discussed in Paragraph 1.4, based on the most recent scientific works dealing with waste material reuse. In the last section, proper combination(s) of technologies, i.e. technology train(s), are proposed in order to find links between inputs and outputs and to help reintroducing the Brownfield site into the land use cycle.

# 1.2 Main characteristics of excavated materials

## 1.2.1 Physical properties

The material texture should be the primary property to be investigated, since the particle dimensions can strongly affect not only the techniques to be used for Brownfield regeneration but also the possible pre-treatment(s) to be carried out.

While soil texture may strongly vary from place to place and may show different characteristics depending on several factors, for industrial residues, such as those produced as a result of steel making and incineration processes, specific physical properties may be possibly identified. Regarding physical characteristics of steel slags and MSWI residues, Figure 1.3 shows examples of the typical grading curves for BOF and EAF slags as well as for MSWI bottom and fly ash. For comparative purposes, the optimum particle size distribution as depicted by the Fuller curve is reported too.



Figure 1.3. Example of Particle Size Distribution of (A) Steel slag and (B) MSWI residues.

Fuller curves are grading curves that provide the minimum void space and closest packing for sands and mineral aggregates with different particle sizes (Ginés et al., 2009) and they

are commonly employed as a reference for the formulation of concrete mixtures (Fuller and Thompson, 1907). As can be seen from Figure 1.3a, BOF and EAF slag generally show a well-graded particle size distribution, similar to the optimum Fuller distribution and this characteristic makes them suitable for the reuse as coarse aggregates for construction purposes, e.g. in concrete production. Figure 1.3b reports the particle size distribution of MSWI residues. However, it should be noted that the physical as well as the chemical characteristics of MSWI residues mainly depend on the type of waste that is incinerated but especially on the type of thermal process and flue gas treatments employed. Regarding bottom ash, the results shown in the figure suggest that they usually require a pre-treatment step in order to approximate the Fuller curve. However, a different particle size distribution from that proposed in Figure 1.3 showing a good match with the Fuller curve may be found for MSWI bottom ash (Ginés et al., 2009; del Valle Zermeño et al. 2013).

## 1.2.2 Chemical properties

Table 1.1 reports selected chemical properties of some Brownfield soils. Specifically, the table reports the pH value and the fraction of total organic carbon as well as the content of inorganic carbon of soils collected at sites which hosted different types of industrial activities and are now dismissed or under used. As highlighted in the table, the characteristics of a Brownfield soil are strongly affected by the former use of the site and may vary largely even in the same site (Hartely et al., 2009). For instance, the pH can reach very acidic values in the case of a former mining site (Bertocchi et al., 2006) while the Total Organic Carbon (TOC) content is usually higher than that commonly found for natural soil.

As stated in the Background of this thesis, Brownfield sites may be contaminated by inorganic and organic compounds which may hinder their requalification pathway. With special reference to the contamination by inorganic contaminants, an idea of the heavy metals content of soils in Brownfield sites could be gained from the data reported in Table 1.2. Similarly to the chemical properties reported in Table 1.1, the heavy metals content which can be found in Brownfield soils ranges between very wide intervals, depending

on the former uses of the sites. As an example, the concentration of Zn in soil coming from a former Zn smelter is generally significant, up to about 50 times higher than the limits imposed by the Italian regulation for commercial and industrial sites (Legislative Decree 152/06).

Site	рН	Total carbon (%)	Organic carbon (%)	Inorganic carbon (%)	References
А	6.8	-	8.7	-	van Herwijnen et al., 2007
А	7	-	3.8	-	van Herwijnen et al., 2007
В	8.49	5.87	5.13	0.74	Hartley et al., 2009
С	6.98	10.22	9.56	0.66	Hartley et al., 2009
D	7.06	8.87	8.16	0.71	Hartley et al., 2009
Е	2.83	1.27	-	-	Bertocchi et al., 2006
F	4.7	3.03	-	-	Gray et al., 2006
G	8.3	1.2	1.2	negligible	Capobianco et al., 2014a

Table 1.1. Selected chemical properties of a few Brownfield soils.

A: Former Zn smelter (UK)

B: Clay pits where coal fly ash and other industrial wastes have been disposed of (UK)

C: Canal embankment augmented with dregded sediments (UK)

D: Previous alkali industry (Le Blanc process) (UK)

E: Former mining site (Italy)

F: Zn/Pb smelter (UK)

G: Former wool production plant (Italy)

Table 1.3 and Table 1.4 exhibit, respectively, the chemical composition and the heavy metal content reported for MSWI residues. Considering that the composition of these residues mainly depends on the type of waste, the content of heavy metals may vary significantly from one country to another and from one city to another. Therefore, for comparative purposes data from different sources are proposed, both for the chemical composition and heavy metal content. As shown in Table 1.3, the main components of BA are amorphous silica (usually more than 50%), alumina, iron oxide and calcium oxide. Fly ash is generally characterized by the same main components but in different concentrations, Ca being by far the main constituent. The composition of these materials suggests that they could present pozzolanic or hydraulic behaviour (Bertolini et al., 2004).

Site	Cu	Zn	Pb	As	Cd	Hg	Ni	Cr	References
А	46.7	1074	315	19.7	10.9	0.43	27	36.7	van Herwijnen et al., 2007
А	218	9580	1688	30.6	128	1.28	31.5	41.1	van Herwijnen et al., 2007
В	32.5	68.7	-	78	0.83	-	25.7	-	Hartley et al., 2009
С	508.3	114.1	-	59.5	36.2	-	44.3	-	Hartley et al., 2009
D	101.7	117.9	-	71.9	1.65	-	29.9	-	Hartley et al., 2009
Е	999.6	1376	101712	58952	1827	0.624	25.8	120	Bertocchi et al., 2006
F	311	3970	4210	-	79	-	36	46	Gray et al., 2006
G	475	129	105	8.69	0.48	1.02	43.6	34.4	Capobianco et al., 2014a
Н	708	23014	8650	37	289	-	49	-	Voglar and Leštan, 2010
Н	175	77980	59460	227	90	-	63	-	Voglar and Leštan, 2010

Table 1.2. Heavy metals content of Brownfield soils (concentrations expressed in mg/kg dry matter).

A: Former Zn smelter (UK)

B: Clay pits where coal fly ash and other industrial wastes have been disposed of (UK)

C: Canal embankment augmented with dregded sediments (UK)

D: Previous alkali industry (Le Blanc process) (UK)

E: Former mining site (Italy)

F: Zn/Pb smelter (UK)

G: Former wool production plant (Italy)

H: Former Zn smelter. Production of Zn, Pb oxides and Ba salts (Slovenia)

Referecens	Cl	SO <sub>3</sub>	K <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	CaO	SiO <sub>2</sub>	
del Valle-	-	0.4	1.3	2.02	7.79	6.5	12.2	15.6	47.8	Weathered
Zermeño et al.,										BA
2013										
Gines et al.,	-	0.6	1.41	2.32	6.58	7.8	8.4	14.68	49.4	Weathered
2009										BA
Cioffi et al.,	-	0.5	0.8	1.8	28	0.5	5	8.1	52	BA
2011										
Pera et al., 1997	-	-	1.3	1.5	8	12.8	8.5	11.1	54.6	BA
Filipponi et al.,	-	-	0.6	2.7	10.7	-	1.9	12.2	59.6	BA
2004										
Saikia et al.,	1.8	-	0.9	1.3	8.3	1.36	4.9	10	60.6	BA
2008										
Gao et al., 2008	10.2	8.7	6.2	3.8	6.9	6.68	4	23.6	19.8	FA
Shi and Kan,	10	12	4.6	2.7	7.4	4	4	23.4	24.5	FA
2009										
Wang et al.,	18.9	5.2	5.5	1.4	0.9	5.71	1.7	53	4.36	FA
2010										
Pan et al., 2008	9.7	6.3	3.8	3.2	0.9	4.16	3.8	45.4	13.6	FA

Table 1.3. Chemical composition of MSWI residues (% wt.).

Moreover, MSWI bottom ash are normally characterized by a relevant amount of metallic alluminum (see Table 1.4), which may hinder the reuse of this type of residues in the presence of Portland cement. In fact, in the alkaline environment resulting from the presence of cement, bottom ash may be responsible of swelling and delayed expansion due to the oxidation of metallic alluminum (Bertolini et al., 2004; Cioffi et al., 2011). Conversely, MSWI fly ashes are normally characterized by the presence of high concentrations of leachable toxic metals and soluble salts; hence, it is generally classified as a hazardous waste in most countries.

Table 1.4. Heavy metals content of MSWI residues (concentrations expressed in mg/kg dry matter).

	Al	As	Cd	Crtot	Cu	Ni	Pb	V	Zn	References
BA	59691	2.1	25.2	478	6278	110	3064	_	2194	Onori et al., 2011
(> 0.425 mm)										
BA	44051	1.2	14	517	6790	152	4235	-	1964	Onori et al., 2011
(<0.425 mm)										
BA	18400	3.4	3	169	850	35	683	16	1173	Sorlini et al., 2011
(< 10 mm)										
BA	5600	1.4	0.5	150	153	34	145	2.3	936	Sorlini et al., 2011
(10-20 mm)						• •				
BA	7460	1.3	0.4	80	114	23	93	2.2	433	Sorlini et al., 2011
(20-30 mm)										
BA	8393	-	<8	168	1084	332	$<\!\!80$	-	201	Filipponi et al., 2004
BA	-	-	-	1790	1892	-	974	-	1547	Cioffi et al., 2011
FA	26140	26.4	36.7	157	563.2	70.6	1515	33.3	3269	Shi and Kan, 2009
FA	-	-	96.9	103.2	1426	-	2251	-	5278	Wang et al., 2010
FA	-	21	270	450	670	50	4000	32	11000	Remond et al., 2002
FA	-	-	410	240	370	100	5.4	-	22720	Gao et al., 2008

Table 1.5 and Table 1.6 report the typical chemical composition and the heavy metal content of BOF and EAF slag. These type of materials are primarily comprised of fluxing agents added during steel manufacturing (mainly lime and silica). Specifically, the presence of free calcium oxide is mainly responsible for both hydration and expansion phenomena typical of such slag. Once in contact with water, calcium oxide hydrates very fast causing a rapid volumetric expansion (Pellegrino and Gaddo, 2006). It was shown (Manso et al., 2006) that a proper treatment aimed at stabilize slag by exposing them to

outdoor weather and regular spraying for at least 90 days, may eliminate any subsequent expansive phenomenon, allowing a safe use of such slag in construction applications.

	SiO <sub>2</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	MnO	<b>SO</b> <sub>3</sub>	Referecens
BOF	18	37	14.1	2.6	14.1	7.5	0.36	Altun and Yilmaz, 2002
BOF	10.8	45	32.0	1.9	4.5	-	0.4	Belhadj et al., 2012
BOF	12.5	41.3	31.2	2.4	4.3	6.1	-	Chaurand et al., 2007
BOF	18.9	40	8.8	2.9	5.4	-	0.35	Li et al., 2011
EAF	22.9	53.3	-	2.1	7.8	-	0.44	Li et al., 2011
EAF	15.3	24.4	-	12.2	2.9	5.6	-	Luxan et al., 2000
EAF	15.3	23.9	-	7.4	5.1	4.5	0.1	Manso et al., 2006
EAF	23.3	30.8	-	6.1	12	-	-	Muhmood et al., 2012
EAF	33.5	46.9	0.4	2.3	6.2	2.6	-	Shen et al., 2004

Table 1.5. Chemical composition of steel slag (% wt.).

Regarding the heavy metal content of steel slags, Table 1.6 reports some examples of the typical heavy metal content of BOF and EAF slags. It can be noticed that most of these elements are found in trace concentrations, while chromium and vanadium are usually present in significantly higher concentrations.

Table 1.6. Heavy metals content in steel slag (concentrations expressed in mg/kg dry matter).

	As	Cd	Crtot	Cu	Ni	Pb	V	Zn	References
BOF	-	2.5	1271	30	4.9	50	992	46	Proctor et al., 2000
BOF	-	-	506	8	25	-	14800	37	Tossavainen et al., 2007
EAF	1.9	7.6	3046	178	30	27.5	513	165	Proctor et al., 2000
EAF	-	0.3	37330	170	480	90	970	260	Baciocchi et al., 2010a
EAF	5.3	0.45	7760	166	45	21.5	1210	244	Fallman, 2000
EAF	-	-	32700	140	3180	-	310	130	Tossavainen et al., 2007

### **1.2.3** Environmental properties

Regardless of the chemical composition, the potential reuse of excavated material produced during Brownfield regeneration activities is severely dependent of the

environmental behaviour of the materials themselves. Indeed, hazardous substances may be released from the solid matrix under the effect of water and may produce detrimental environmental effects on groundwater, even in a long-term scenario. Table 1.7 reports the leaching concentrations found for some Brownfields soils. As depicted in Table 1.7, Brownfield excavated material may release variable amounts of metals, depending on several factors, among others type and extent of contamination and physical and chemical characteristics of the soil. For instance, the release of Cd, Cu, As, Pb and Zn from highly aggressive mining waste may be relevant (Bertocchi et al., 2006).

	Site E	Site G	Site H
Standard test	Not reported	EN 12457-2	EN 12457-4
Leaching conditions	Ø< 5 mm; L/S =10 l/kg	Ø < 2mm; L/S=10 l/kg	Ø< 2mm; L/S=10 l/kg
pH	2.79	8.3	-
Ba	-	0.009	-
Zn	8.112	0.009	1.26
Cu	1.33	0.09	0.021
Pb	4.755	< 0.0015	0.118
Cd	0.072	< 0.0015	0.029
As	2.376	< 0.04	0.005
Ni	-	-	0.025
References	Bertocchi et al., 2006	Capobianco et al., 2014a	Voglar and Leštan, 2010

Table 1.7. Leaching behaviour of Brownfield soil (Concentrations expressed in mg/l).

E: Former mining site (Italy)

G: Former wool production plant (Italy)

H: Former Zn smelter. Production of Zn, Pb oxides and Ba salts (Slovenia)

Regarding the leaching behaviour of MSWI residues, some data are reported in Table 1.8 together with the type of leaching test employed. As shown in the table, usually the main critical species are Pb and Zn. Besides, the release of soluble salts, such as chlorides and sulphates, may be of concern, in particular in the case of fly ashes. Due to these features, fly ashes usually undergo a washing treatment to reduce the chloride content and heavy metal content prior to disposal or reuse (Bertolini et al., 2004; Aubert et al., 2006; Gao et al., 2008).

Table 1.9 provides an idea about the typical leaching behavior of BOF and EAF slags. In spite of the fact that EAF and BOF slag contain heavy metals in higher concentrations than in most soils (see Table 1.6), these metals are tightly bound to the slag matrix and not readily leached (Proctor et al., 2000).

	Cd	Crtot	Cu	Ni	Pb	Zn	Standard	References
							test	
BA	-	1.61	1.4	-	1.29	3.12	UNI 10802	Cioffi et al., 2011
Weathered BA	< 0.004	0.124	0.208	0.055	0.128	0.059	EN 12457-4	Gori et al., 2011
Weathered BA	0.004	0.039	0.099	0.006	0.008	0.082	EN 12457-4	del Valle-Zermeño et al., 2013
W BA	0.001	0.031	0.261	0.01	0.01	0.051	EN 12457-2	Gines et al., 2009
FA	0.017	0.18	0.014	0.035	0.026	0.08	EN 12457-1	Saika et al., 2010
FA	0.004	0.364	0.499	0.129	13.82	3.508	EN 12457-4	del Valle-Zermeño et al., 2013
FA	0.005	0.363	0.271	0.184	21.1	10	EN 12457-2	Gines et al., 2009

Table 1.8. Leaching behaviour of MSWI residues (Concentrations expressed in mg/l).

However, the release of Cr from steel slag may be of concern for both BOF and EAF slag, with leaching concentrations that are often higher than the limits imposed by the European legislation for disposal in Inert Waste Landfill (0.05 mg/l). Besides, Cr leaching usually exhibits an amphoteric behavior, hence explaining the lower leaching concentrations obtained as a result of the TCLP test.

Table 1.9. Leaching behaviour of steel slag (Concentrations expressed in mg/l).

	Crtot	Ni	Pb	Zn	V	Standard test	References
BOF	0.01	0.012	0.004	0.07	-	TCLP	Proctor et al., 2000
BOF	0.003	-	-	-	0.03	EN 12457-2	Tossavainen et al., 2007
EAF	0.04	0.07	0.004	0.11	-	TCLP	Proctor et al., 2000
EAF	0.13	0.008	< 0.002	0.45	-	EN 12457-2	Baciocchi et al., 2010a
EAF	0.58	-	-	-	0.03	EN 12457-2	Tossavainen et al., 2007
EAF	0.07	0.0008	-	-	-	Not reported	Shen et al., 2004

## 1.3 Individual technologies aimed at reuse

This section provides an overview of the main techniques which could be possibly employed for soils and other excavated materials in the context of Brownfield regeneration. Stabilization/solidification, accelerated carbonation and granulation were considered as they may allow to reduce the mobility of several types of contaminants and also to obtain a product meeting given engineering requirements.

### 1.3.1 Stabilization/solidification

### 1.3.1.1 Introduction

Stabilization/Solidification (S/S) is a relatively simple civil engineering-based remediation technique that relies on the reaction between a binder and a contaminated solid matrix to form a new solid material, either in a granular or a monolithic form (Angel et al., 2004). Specifically, solidification refers to processes that encapsulate a waste to form a solid material and to restrict contaminant migration by decreasing the surface area exposed to leaching and/or by coating the waste with low-permeability materials; stabilization refers to processes that involve chemical reactions that allow to reduce the solubility of the contaminants when exposed to leaching fluids (Environment Agency UK, 2004). As a result of the S/S process, contaminants become virtually non-leachable and are prevented from being available to the environment, although they are not removed or destroyed.

## 1.3.1.2 Binders

Binders are used during S/S to enable disposal, or reuse in a beneficial way. Binders can impart both chemical stability and physical solidity to the treated product. The high pH induced by the addition of the most common binders, such as lime and Portland cement, results in the precipitation of many contaminant species and a corresponding reduction in mobility. Secondly, the ability of the binder to set into a solid mass encapsulating the contaminant results in a physical immobilization process (solidification).

It is possible to distinguish between hydraulic, latent hydraulic and pozzolanic materials.

The reactivity of hydraulic, latent hydraulic and pozzolanic materials depends among other things on the ratio of lime to silica, CaO:SiO<sub>2</sub>. The larger this ratio is, the more hydraulic is the material, as shown in Table 1.10.

Hydraulic materials, such as Portland cement, yield high-strength reaction products immediately upon reaction with water. Latent hydraulic materials contain lime but require activation before they can react with water. The most common latent hydraulic binder is ground granulated blast furnace slag, which is a processed residual product from iron smelting. Pozzolanic materials contain practically no lime but have a high silica content. They therefore require lime from an external source before they can react.

Material	Grain size [µm]	Structure	CaO/SiO <sub>2</sub>	SiO2 content [%]	Specific surface [m <sup>2</sup> /kg]
Portland cement (hydraulic)	1-100	Crystalline	~3	~20	300-500
Ground granulated blast furnace slag (latent hydraulic)	1-100	Vitreous (amorphous)	~1	~35	300-500
Fly ash (pozzolanic)	1-100	Vitreous (amorphous)	~0	50-60	300-500
Silica fume (pozzolanic)	0.01.1	Vitreous (amorphous)	~0	85-95	20000

Table 1.10. Properties of hydraulic, latent hydraulic and pozzolanic materials (Janz and Johansson, 2002).

Two commonly used pozzolanic materials are fly ash, a residue from pulverized coal fuelled power plants and heating plants, and silica fume, a residue from the manufacture of metallic silicon or ferrosilicon. The essential difference between silica fume and fly ash is their size: silica fume is extremely fine with a specific surface of ~20000 m<sup>2</sup>/kg, while fly ash has a specific surface of ~300-500 m<sup>2</sup>/kg. On the other hand, lime alone reacts with water to form calcium hydroxide, which has no bearing capacity itself but which develops mechanical strength in a secondary reaction with certain pozzolanic additives. Table 1.11 summarizes the strength-enhancing reactions of the most common binders used for S/S treatments.

Binder	Reaction	<b>Co-reagents</b>	Time scale
Cement	Hydraulic	Water	Days
Lime	Pozzolanic	Water+ Pozzolanic additives	Months
Ground granulated blast furnace slag	Latent hydraulic	Water+ Ca(OH) <sub>2</sub> form e.g. cement or lime	Weeks
Pulverized fly ash	Pozzolanic	Water+ Ca(OH) <sub>2</sub> form e.g. cement or lime	Months

Table 1.11. Strength enhancing reactions (Janz and Johansson, 2002).

The main characteristics of the most common binders used in S/S techniques and reported in Table 1.11 are briefly described in the following sections.

#### Cement

Cement is a finely ground inorganic material which, when mixed with water, forms a paste that sets and hardens by means of hydration reactions and which, after hardening, retains its strength and stability even under water. Cement is the most adaptable binder currently available for the immobilization of heavy metals since immobilization of contaminants can be achieved by reaction between the contaminants and the compounds formed during the hydration of the cement and/or by physical entrapment within the cement paste matrix.

Portland cement is a hydraulic binding agent, i.e. it reacts with water forming a hard mass. The usual raw materials for the manufacture of Portland cement are clay and limestone. Portland cement is manufactured by mixing Portland clinker with approximately 5% of gypsum and grinding it to a particle size of approximately 1-100  $\mu$ m and a specific surface of ~300-550 m<sup>2</sup>/kg.

A typical chemical composition of Portland cement is reported in Table 1.12.

Table 1.12. Typ	pical composition	of Portland ceme	nt (Janz and Johansson,	2002).
-----------------	-------------------	------------------	-------------------------	--------

Component	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O
Content [%]	60-70	17-25	2-8	0-6	0-6	1-4	0.2-1.5	0.2-1.5

While the chemical composition is expressed in terms of oxides, the substances are actually present in the form of compounds known as clinker minerals, as shown in Table 1.13.

Compound name	Compound	Shorthand	%
Tricalcium silicate	3CaO·SiO <sub>2</sub>	C <sub>3</sub> S	54
Dicalcium silicate	$2CaO \cdot SiO_2$	$C_2S$	17
Tricalcium aluminate	$3CaO \cdot Al_2O_3$	C <sub>3</sub> A	11
Tetracalcium aluminoferrite	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	$C_4AF$	9

Table 1.13. Compound composition of Portland cement (Angel et al., 2004).

The following properties are associated with the four primary cement compounds reported in Table 1.13:

- Tricalcium Silicate, C<sub>3</sub>S, hydrates and hardens rapidly and is largely responsible for initial set and early strength. In general, the early strength of Portland cement concrete is higher with increased percentages of C<sub>3</sub>S.
- Dicalcium Silicate, C<sub>2</sub>S, hydrates and hardens slowly and contributes largely to strength increase at ages beyond one week.
- Tricalcium Aluminate, C<sub>3</sub>A, liberates a large amount of heat during the first few days of hydration and hardening. It contributes to early strength development. Gypsum, added during final cement grinding, slows down the hydration rate of C<sub>3</sub>A. Without gypsum, a cement with C<sub>3</sub>A present would set rapidly. Cements with low percentages of C<sub>3</sub>A are especially resistant to sulphates contained in wastes or soils.
- Tetracalcium aluminoferrite, C<sub>4</sub>AF, reduces the clinkering temperature, thereby assisting in the manufacture of cement. It hydrates rather rapidly but contributes very little to strength.

## <u>Lime</u>

The lime used for stabilization is made from limestone, which mainly consists of calcium carbonate (CaCO<sub>3</sub>). The limestone is crushed and heated at somewhat over 700°C, which

drives off carbon dioxide. The product is mainly calcium oxide (CaO), known as burnt lime or quicklime. The calcination reaction is described in Eq. 1.1, while a typical quicklime composition is reported in Table 1.14.

$$CaCO_3 + heat \rightarrow CaO + CO_2$$
 Eq. 1.1

Table 1.14.Example of the composition of quicklime (Janz and Johansson, 2002).

Component	Total CaO	CaO active	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	K <sub>2</sub> O	Na <sub>2</sub> O
Content [%]	94	90	1.5	0.8	0.4	1.7	0.1	0.05

When quicklime is mixed with water hydrated lime, Ca(OH)<sub>2</sub>, is formed (Eq. 1.2):

$$CaO + H_2O \rightarrow Ca(OH)_2$$
 Eq. 1.2

The hydration of lime generates a great deal of heat; the reaction also results in the pH increasing to  $\sim$ 12.5, which is a condition for the secondary pozzolanic reactions to occur. During soil stabilization, hydration dewaters the material, so it is very effective as a drying agent and is used to reduce the moisture content of materials.

Hydrated lime does not set and hence gives no strength gain. The gain in strength from soil stabilization with lime is dependent on secondary pozzolanic reactions with additives or with the surrounding soil (Eq. 1.3):

$$Ca(OH)_2 + pozzolan + H_2O \rightarrow C - S - H$$
 Eq. 1.3

The increased pH promotes precipitation of metals as their metal hydroxides and this, combined with cementitious reactions, can result in the effective S/S of contaminants. However, if Ca(OH)<sub>2</sub> comes in contact with air it reacts with carbon dioxide and calcium carbonate reforms, as shown in Eq. 1.4 below.

 $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$  Eq. 1.4

#### Ground granulated blast furnace slag (GGBS)

Ground granulated blast furnace slag (GGBS) is widely in use in a variety of cement mixtures, and also its use as type II addition in the production of concrete is under regulation of EN 15167-1. GGBS is used to make durable concrete structures in combination with ordinary Portland cement and/or other pozzolanic materials.

Blast furnace slag is a by-product from the manufacture of iron, which is tapped from the blast-furnace as a molten liquid. If allowed to cool slowly, it forms a crystalline material with virtually no cementitious properties but if rapidly quenched in water (granulated), it remains in a glassy, non-crystalline state and is a latent hydraulic binder (Taylor, 1997). For use as a binder, the granulated blast furnace slag is ground to a fine powder. Table 1.15 gives an example of its mineral content.

 Table 1.15. Example of composition of granulated blast furnace slag (Janz and Johansson, 2002).

Component	CaO	SiO <sub>2</sub>	$Al_2O_3$	MgO	S	FeO	K <sub>2</sub> O	Na <sub>2</sub> O
Content [%]	36	36	10	13	1	0.4	0.4	0.6

Before granulated blast furnace slag will react it must be activated, e.g. with Ca(OH)<sub>2</sub>. The reaction products of lime and Portland cement contain Ca(OH)<sub>2</sub>, making these products excellent activators for slag. Activation by Ca(OH)<sub>2</sub> from lime or cement gives a latent hydraulic reaction. After the slag is activated the reaction takes place largely spontaneously with its own lime content. The main strength-enhancing reaction product is a Calcium Silicate Hydrate (CSH) gel of the same type as that formed by Portland cement, but its CaO/SiO<sub>2</sub> ratio is lower and the gel contains more aluminium oxide and magnesium oxide.

#### Pulverized fuel ash (PFA)

Pulverized fuel ash (PFA) is a fine powder of mainly spherical, glassy particles, derived from the burning of pulverized coal. It has pozzolanic properties and consists mainly of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. It is obtained by electrostatic or mechanical precipitation of dust-like particles from the flue gases or furnaces fired with pulverized anthracite or bituminous coal. For the chemical composition of the fly ash see Table 1.16.

Table 1.16. Example of composition of a fly ash (Janz and Johansson, 2002).

Component	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	$SO_3$	K <sub>2</sub> O	Na <sub>2</sub> O
Content [%]	3-7	40-55	20-30	5-10	1-4	0.4-2	2	1

High-lime fly ash can have significant self-cementing properties, which can, when used on its own, be very rapid and presenting a considerable heat evolution. Used on its own low-lime PFA has little or no cementitious value. However, in the presence of moisture and lime or cement, it will react to form compounds with cementitious properties.

### 1.3.1.3 Water content

The strength of the cement paste depends largely on its porosity. Wide separations between the particles result in higher porosity and lower strength. A measure of the cement content, and hence of the separation between the particles, is given by the water: cement ratio (W/C). A high W/C ratio implies wide separations between the cement particles, which means high porosity and low strength. The W/C ratio is one of the most important quality parameters of cement when used as a binding agent. An example of the relation between quality and W/C ratio may be seen in Figure 1.4 which shows how the strength of a concrete increases as W/C ratio decreases. The curve refers to concrete (cube specimens), but similar relations apply in S/S processes.

Water is essential to initiate the hydration reactions but a broad range of water/cement ratios can be sustained. Generally, if flowable mixes are required, W/C ratios usually lie in the range 0.4-1.0 (Glasser, 1997). Water in excess of the minimum required for hydration increases fluidity but also increases the porosity and ultimately, the
permeability of the hardened product. Thus, since in a S/S process low permeability materials are required, W/C ratios need to be kept as low as possible. On the other hand, it may be desirable to maximize the material to be treated to cement ratio.



Figure 1.4. Relation between the w/c ratio and the compressive strength of concrete cube specimens (Janz and Johansson, 2002).

Table 1.17 reports some examples of the water/solid ratio used by different researchers in stabilization/solidification experimental works. As shown in the table, lime requires a considerable amount of water to hydrate when compared to other types of binder. Moreover, already wet materials, e.g. sludge, require a lower amount of water to start and complete the hydration reaction (Karamalidis and Voudrias, 2007).

Matrix	W/S	<b>Binder/Additives</b>	References
EAF slag	0.4	Portland Cement	Salihoglu and Pinarli, 2008
	0.6	Lime	
Matal as a tanging tail Cail	0.22.0.28	De stless il Como est	Martin and Latter 2010
Metal contaminated Soli	0.22-0.38	Portland Cement	Voglar and Lestan, 2010
MSWI bottom ash	0.28-0.33	Portland Cement	Cioffi et al., 2011
	0.29	Portland Cement+ lime	
	0.31-0.35	lime + Coal Fly Ash	
MCW/I flag only	0.4	Doutlou d Comont	Manaialandi 2002
MIS WI HY ash	0.4	Portland Cement	Manglalardi, 2003

Table 1.17. Some examples of W/S ratio used in various works.

## 1.3.1.4 Applications of the S/S process

S/S treatment methodologies have been widely used over the past three decades, particularly in the United States where it already was an established treatment methodology more than ten years ago (EPA, 2000). S/S has been used to treat hazardous waste, residues from treatment processes and for the remediation of contaminated land. Nowadays, S/S is also an increasingly technology for Brownfield regeneration since treated materials can be also reused within the site or in the surrounding area, improving site conditions and eliminating the need for virgin raw materials (EPA, 2009). Figure 1.5a shows the type of contaminants for which S/S has been used in the USA until 2005 (EPA, 2007). The data show that S/S has been used predominantly for the treatment of metals and metalloids, with other uses being relatively minor. Figure 1.5b provides a detail of the metals treated by S/S at Superfund remedial sites until 2000. As shown in the graph, the top four metals treated by S/S were lead, chromium, arsenic and cadmium.



Figure 1.5. a) Contaminant types treated by S/S (EPA, 2007); b) Percentage of S/S projects treating specific metals (EPA, 2000).

Figure 1.6 shows the types of sites treated by S/S projects (EPA, 2000). Waste management/disposal areas, organic chemical manufacturing, petroleum refining, and metal ore mining, smelting and recycling facilities have been the most common site types addressed by S/S until 2000.



Figure 1.6.Superfund remedial actions: site types for S/S (EPA, 2000).

### 1.3.1.5 Factors affecting the process

As depicted in Paragraph 1.3.1.4, Solidification/Stabilization is a widely applied and well established technology for the immobilization of inorganic hazardous constituents. However, its application to organic compounds has always been controversial. It was reported that organic compounds tend to have a detrimental effect on the properties of cementitious materials and they may be leached out after the curing process (Sora et al., 2002; Karamalidis and Voudrias, 2007; Antemir et al., 2010a). However, the efficiency of S/S treatment of organic contaminants may be improved using adsorbents for the organic components. These adsorbents can be incorporated as additives in the cement mix, or they can be used in a pre-treatment phase. Several materials have been

investigated for use as adsorbents for organics in Solidification/Stabilization treatments, some of which are reported in Table 1.18.

Organic compound	Modifying agent	Reference
2- chloroaniline	Organophilic clay	Sora et al., 2005
BTEX	Bentonite clay	Gitipour et al., 1997
Phenol	Activated carbon	Hebatpuria et al., 1999
2-chlorophenol, 1- chloronapthalene	Organophilic bentonite	Cioffi et al., 2001
Phenol, 2-chlorophenol	Activated carbon, H <sub>2</sub> O <sub>2</sub>	Rho et al., 2001
2-chloroaniline	Organophilic clay	Botta et al., 2004
PAHs	Organophilic clay, activated carbon	Mulder et al., 2001

Table 1.18. Use of adsorbents in the Stabilization/Solidification of organic compounds.

Regarding the immobilization of inorganic contaminants by S/S processes, in most cases, the dominant fixation mechanism for heavy metals is through the chemical precipitation of low solubility species (Chen et al ., 2009). Furthermore, the solubility of contaminants in S/S products tends to be a function of matrix pH other than metals speciation. Moreover, the highly alkaline conditions produced as a result of S/S treatments may have an adverse effect on the immobilization of amphoteric metals, e.g. Cu (Voglar and Leštan, 2010). Indeed, soluble Cu compounds can form at pH > 12, thus increasing Cu mobility (Kumpiene et al., 2008). Other factors which influence Stabilization/Solidification processes are briefly listed and commented in Table 1.19.

Variables	Considerations	References
Acid	Will consume costly binders in acid/base reactions	Stegemann and Zhou, 2009
Heavy metals (e.g., Zn)	May cause inhibition of hydration	Stegemann and Zhou, 2009
Aluminium and sulphate	May results in delayed formation of expansive ettringite, and ultimately destroy the matrix	Stegemann and Zhou, 2009
Soluble salts	May cause deterioration of the matrix	Stegemann and Zhou, 2009
Organic compounds	Tend to be incompatible with the binder, interfering with hydration and leading to detrimental effects on the final compressive strength;	Paria and Yuet, 2006; Stegemann and Zhou, 2009
	Hydrophilic organic contaminants leach readily;	
	Hydrophobic contaminants may form a problematic separate phase	
Specific material to be treated	MSWI fly ash cause inhibition in Portland cement hydration	Alba et al., 2001
Chloride	Chloride are only partially immobilized and can limit the stabilization/solidification efficiency	Alba et al., 2001
Additives	Durability may decrease with a certain addition of additives, e.g. as silica fume or coal fly ash	Paria and Yuet, 2006

Fable 1.1	<b>9. Factors</b>	affecting	S/S	processes.
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## 1.3.2 Granulation

## 1.3.2.1 Introduction

Granulation is the process of agglomerating particles together into larger, semi-permanent aggregates. In wet granulation processes, this is performed by spraying a liquid binder onto the particles as they are agitated in a tumbling drum, fluidized bed, high shear mixer or similar device (Iveson, 1996).

The liquid binds the particles together by a combination of capillary pressure, surface tension and viscous forces until solid bonds are formed by subsequent drying. Some advantages of agglomerated materials include improved flow properties, reduced dustiness and increased bulk density. Because of these features, granulation unit operations occur in a wide range of industries including agricultural products, pharmaceuticals, detergents and food stuffs. (Iveson et al., 2001)

Three principal mechanisms need to be considered in granulation processes (Iveson et al., 2001). These are:

- wetting and nucleation: where the liquid binder is brought into contact with a dry powder bed, and is distributed through the bed to give a distribution of nuclei granules;
- consolidation and growth: where collisions between two granules, granules and feed powder, or a granule and the equipment lead to granule compaction and growth;
- breakage and attrition: where wet or dried granules break due to impact, wear or compaction in the granulator or during subsequent product handling.



Figure 1.7. Schematic of the granulation process (Iveson et al., 2001).

# 1.3.2.2 Binders

Different binders can be used to produce aggregates by means of granulation depending essentially on their final destination. Water is the more adaptable and less expensive binder and it has been widely used in the past, especially by the food industry. However, when particular properties are required, more viscous binders can be employed (e.g., glycerol) in order to get more strength granules. Regarding this aspect, also cement seems to be a promising binder since it is able to improve the mechanical properties of the granules allowing their safe reuse in concrete production or road pavement as aggregates. Furthermore, it has been reported that some additives can be used in conjunction with granulation. The addition of a superplasticizer to the mixture when using cement as binder, for example, may allow the water/cement ratio to be reduced to lower values, increase density and prolong granules life in severe conditions (Scanferla et al., 2009). On the other hand, the presence of the additives such as formaldehyde and phenol supports the carbonation of lime, thus accelerating and enhancing the development of short-term compressive strength of the granules (Medici et al., 2000).

Binders	Considerations	References
Water	$\mu$ = 0.00089 Pa sec (25°C)	Iveson et al., 2002
Glycerol	μ= 0.70 Pa sec (25°C)	Iveson et al., 2002
Cement , lime	To improve mechanical properties and eventually stabilized contaminated matrix.	Cioffi et al.,2011; Scanferla et al., 2009; Medici et al., 2000

## 1.3.2.3 Applications of the granulation process

As already said, granulation finds application in many different industries such as pharmaceuticals, fertilizers, detergents and food processing. In these processes, granulation is desirable in many cases to improve powder attributes such as flowability, bulk density and dusting behaviour.

In the last few years, granulation processes have been applied to waste materials treatment in order to obtain granules with suitable properties which could allow to reuse them for construction purposes. For this kind of application a combination of technologies is often required in order to obtain suitable physical, mechanical and environmental characteristics. The "technology trains" recently investigated will be presented and discussed in Paragraph 1.5.

# 1.3.2.4 Factors affecting the granulation process

The main factors influencing the granulation process generally rely on binder characteristics and binder distribution systems.

Binder viscosity influences three of the key rate limiting steps involved in granulation process, i.e. binder dispersion, consolidation and growth (Iveson et al., 2001). Increasing binder viscosity generally inhibits binder atomization and dispersion. Hence, a viscous binder will often form larger initial nuclei and may take longer to disperse uniformly through the powder. This will delay the onset of uniform growth. However, increasing binder viscosity generally reduces the granule consolidation rate and increases granule strength (Iveson et al., 1996; Iveson et al., 2001).

The granulation rate and the mean size of the granule products increase with increasing binder content up to a certain extent. In addition, it has been shown (Salman et al., 2006) that the porosity increases with increasing binder content, due to pores being filled with binder. Typically, a reduction in porosity leads to an increase in granule strength, and hence a higher resistance to breakage (Iveson et al., 2001).

The degree of binder dispersion indicates the quality of the mixing between the powder and the binder fluid, and is strongly affected by the binder delivery method (Iveson et al., 2001; Ramachandran et al., 2008). The degree of dispersion of the binder is reflected in the product size distribution (Tardos et al., 1997). If all particles contain an equal amount of binder, their physical properties should be the same and produce a narrow size distribution. If the binder is unevenly distributed, some nuclei will be more saturated than others and their growth will be preferential.

Further considerations on the effects of binder properties as well as of reaction times on the granulation process are reported in Table 1.21.

Variables	Considerations
Binder viscosity	Retarding effect on granulation.
	Viscous binder are more difficult to distribute.
	Drop penetration time higher with viscous binders.
	Low-viscosity binder reduces the strength of the granules.
	A critical minimum binder viscosity is required for a given size of constituent particles to form granules and this critical value increases with increasing primary particle size.
	Increasing binder viscosity reduces granules deformability.
	Lower binder viscosity lead to more spherical granules.
Binder content	The granulation rate and the mean size of the granules increases with increasing binder content up to a certain extent.
	The porosity decreases with increasing binder content.
	The critical strain before failure generally increases with increasing binder content.
	Increasing the amount of low viscosity binders (e.g. water) has generally been found to increase both the initial rate and the final extent of granule consolidation.
Binder	Pouring: granules are larger, less porous and with a faster growth kinetics.
delivery/distribution	Binder atomization improves binder distribution.
	Pre-wetting by kneading distributes the binder evenly and produce a narrow size distribution.
	Spraying: a wide range distribution is produced; can cause segregation due to the unevenly distribution of the binder.
Granulation time	Granules strength increases with increasing granulation time.
	Granules porosity is reduced with granulation time.
	The critical impact velocity required for breakage increases, approximately, linearly with increasing granulation time.
	In spite of the addition method used, binder distribution is granule size dependent initially, but tends toward a uniform distribution with increasing granulation time.

# Table 1.21: Factors affecting the granulation process (Iveson et al., 1996; Iveson et al., 2001; Salman et al., 2006).

### 1.3.3 Accelerated carbonation

### 1.3.3.1 Introduction

Carbonation is a natural occurring process which involves the reaction between gaseous CO<sub>2</sub> and alkaline materials.

When CO<sub>2</sub> reacts with metal oxides (indicated here as MO, where M is a divalent metal, e.g., calcium, magnesium, or iron) the corresponding carbonate is formed and heat is released according to the chemical reaction reported in Eq. 1.5 (IPCC, 2005):

$$MO + CO_2 \rightarrow MCO_3 + heat$$
 Eq. 1.5

Natural carbonation reactions are generally quite slow and became significant in the long term. This reaction can be accelerated by contacting the alkaline material with a gas stream concentrated in CO<sub>2</sub> at specific operating conditions (e.g.: temperature, CO<sub>2</sub> partial pressure and liquid to solid ratio).

Apart from accelerated carbonation of primary alkaline earth minerals (in particular Mg and Ca silicates, such as olivine and serpentine), which is especially investigated as a CO<sub>2</sub> capture and storage (CCS) option, the accelerated carbonation of alkaline waste residues has been taken into consideration in recent years for several reasons. These materials are often associated with CO<sub>2</sub> point source emissions and tend to be chemically more unstable than geologically derived minerals and therefore require a lower degree of pre-treatment and less energy intensive operating conditions. Furthermore, carbonation processes have significant effects on alkaline materials, which include specifically: CO<sub>2</sub> uptake in a solid and thermodynamically stable form, pH decrease and modifications of the leaching behaviour of the material, besides variations of some of the physical, mineralogical and mechanical properties of the treated material.

Many waste materials are reactive with carbon dioxide, particularly those derived from industrial thermal processes, such as incineration ashes (Arickx et al., 2006; Baciocchi et al., 2006, 2010b) and steel slags (Baciocchi et al., 2010a). Other materials investigated include biomass ash, cement kiln dusts, paper wastewater sludge incineration ash,

pulverized fuel ash, sewage sludge ash, wood ash (Gunning et al., 2009; Gunning et al., 2010) and in general waste containing cementitious phases (Fernandez Bertos et al., 2004a).

# 1.3.3.2 Application of the carbonation process

In the last years, accelerated carbonation of alkaline industrial residues has been proposed for different purposes, including sequestration of CO<sub>2</sub> emitted from industrial point sources as well as improvement of the environmental behaviour of different types of alkaline residues. In fact, accelerated carbonation can be regarded as a stabilization technique and/or as a possible CO<sub>2</sub> capture and storage (CCS) technology, the former combining the use of cementitious materials with the addition of gaseous carbon dioxide to treat soils and wastes, the latter involving the absorption of CO<sub>2</sub> by an initially alkaline material, which causes the pH to decrease and calcite to precipitate. As already mentioned, the technology is suitable in the case of residues with high free Ca oxides and hydroxides content such as MSWI air pollution control residues and fly ash, cement kiln dust, deinking ash and paper mill waste, due to the typically high reactivity of these materials with CO<sub>2</sub> even at mild operating conditions. Table 1.22 lists some experimental works regarding accelerated carbonation, together with the operating conditions adopted.

Material	CO <sub>2</sub> conc.	Pressure	Temperature	Water content	References
MSWI bottom ash	100% vol.	3 bar	Ambient	0-60 %	Fernandez Bertos et al., 2004b
MSWI bottom ash	10% vol. 20% vol.	Not specified	30 °C, 37 °C, 50°C	2.3%, 6%, 13%, 25%, 37%, 50%	van Gerven et al., 2005
MSWI bottom ash	10% vol.	atmospheric	50 °C	natural moisture content	Arickx et al., 2006
MSWI fly ash	100% vol.	atmospheric	300 °C, 400 °C, 450 °C, 500 °C	0%	Baciocchi et al., 2006
Steel slag (EAF, AOD)	100 %vol.	1-10 bar	30 - 50 °C	0-60 %	Baciocchi et al., 2010a

Table 1.22: Some examples of experimental works regarding Accelerated Carbonation.

# 1.3.3.3 Factors affecting the carbonation process

The main factors affecting the accelerated carbonation process are briefly listed and commented in Table 1.23.

Table 1.23.Main	factors affecting	the carbonation	process (F	Fernandez F	Bertos et al	2004a).
I abie 1.20 milain	inclus anecong	the car bonation	process (1	t el manacz L	<i>i i i i i i i i i i</i>	200 iu).

Variables	Considerations
Particle size	The fine fractions are often enriched in Ca.
	More specific surface area is available for reaction
Solid composition	Materials must be inorganic in nature, containing calcium and /or silicon salts.
Ca content	Carbonation is known to occur in materials which have available Ca. the higher the concentration of Ca in the material, the better the results of carbonation
Water content	Some water is necessary for the reaction, but an excess of water limits the rate of carbonation. Materials with high initial free water contents have increased gas permeability, letting more $CO_2$ enter the solid. However, as the pores are filled with water, the penetration of $CO_2$ is hindered as the rate of diffusion of $CO_2$ is reduced
Temperature	The uptake of $CO_2$ increases with increasing temperature up to 60 °C (at atmospheric pressure). Higher temperatures decrease the solubility of $CO_2$ in water, therefore decreasing the rate of carbonation.
CO <sub>2</sub> partial pressure	The higher the amount of $CO_2$ in the gas phase, the higher is the rate of carbonation.

# 1.4 Reuse options for excavated materials

Excavated soils are potentially suitable for a variety of construction applications, ranging from hydraulically bound mixtures and aggregates to filling material to be used in place of imported virgin material.

Table 1.24 lists some selected experimental studies which deal with the (re)use of contaminated and non contaminated soil as "alternative" construction materials. Often, soils originating from abandoned industrial sites are contaminated by metals and/or other substances, so that their potential reuse is linked to a preliminary proper treatment which

should reduce the mobility of the contaminants. Often, this goal is achieved through a stabilization/solidification process (Dermatas and Meng, 2003; Voglar and Leštan, 2010). Conversely, non-contaminated soils originated from a Brownfield site often require stabilization in terms of mechanical characteristics, with the main purpose of meeting the requirements of specific engineering projects (Kolias et al., 2005). A hydraulically bound mixture is the result of both of these processes, being a combination between the material to be treated and a hydraulic binder. As expected, specific treatments are generally required in order to obtain a product with suitable mechanical and environmental characteristics for reuse, i.e. with enough mechanical strength (which depends on the intended use of the product itself) and a leaching behavior complying with the current legislation regarding material reuse. Some examples of soil reuse options are reported in Table 1.24.

Mixture composition	Proposed reuse	References
Cement Contaminated soil Aggregates	Road base or subbase	Hassan et al., 2005
Lime Cement Contaminated drilling wastes Coal fly ash	Road subbase	Tuncan et al., 2000
Cement Contaminated soil	Aggregates	Scanferla et al., 2009
Lime Coal fly ash Contaminated soil	Engineering fill, road pavement	Dermatas and Meng, 2003
Cement Coal fly ash Soil	Pavement structure	Kolias et al., 2005
Cement Contaminated soil	Construction material on site	Voglar and Leštan, 2010

Table 1.24. Examples of reuse options for soils after treatment with hydraulic binders.

As mentioned in Paragraph 1.2, there are many possibilities for (re)using steel slag and MSWI residues in construction applications, such as for the building of transportation infrastructures or concrete production. Some examples of steel slag and MSWI residues reused as aggregates in construction applications are reported in Table 1.25.

As shown in Table 1.25, BOF and EAF slags can be reused as artificial aggregates in road construction and concrete production. It should be pointed out that some of the characteristics of steel slags make them particularly suitable for reuse without treatment. For example, it was reported (Xue et al., 2006; Shen et al., 2009) that BOF slags have a proper particle size distribution and are characterized by a good compressive strength, which make these slags similar to natural aggregates, as also mentioned in Paragraph 1.2. In other cases only a physical pre-treatment is needed in order to adjust the particle size distribution (Manso et al., 2006). The main problem when using steel slag is the stability of the material (Motz and Geiseler, 2001; Wang et al., 2010): the presence of free calcium and magnesium oxides is mainly responsible for both hydration and expansion phenomena typical of such slag. Once in contact with water, calcium oxides hydrates very fast causing a rapid volumetric expansion, whereas magnesium oxides hydrate more slowly causing an expansion over a longer time. A proper treatment aimed at stabilize slag by exposing them to outdoor weather and regular spraying for 90 days or more (Manso et al., 2006; Shen et al., 2009; Pellegrino and Gaddo, 2009) may eliminate any subsequent expansive phenomenon.

MSWI bottom ashes as well have some characteristics that make them suitable for reuse as aggregates for concrete production or road construction (Cheeseman et al., 2005; Sorlini et al., 2011) as shown in Table 1.25. However, these materials usually require a more important preliminary treatment than steel slags: a screening step is often needed to discard particles above a certain size or a crushing procedure is applied in order to achieve the desired particle size distribution. In addition to the mentioned physical pre-treatments, these residues often need further treatment, such as washing (Sorlini et al., 2011), vitrification (Cheeseman et al., 2005) or stabilization with a hydraulic binder coupled with granulation (Cioffi et al., 2011).

Matrix	<b>Pre-treatments</b>	Aggregates D <sub>max</sub> [mm]	<b>Proposed reuse</b>	References
BOF slag	Crushing, screening, weathering for 3 years	19	Aggregates in porous asphalt	Shen et al., 2009
BOF slag	-	16	Road construction	Xue et al., 2006
EAF slag	-	22.4	Aggregates for concrete	Pellegrino and Gaddo, 2009
EAF slag	Crushing, weathering for 90 days	20	Aggregates for concrete	Manso et al., 2006
EAF slag	-	15	Road construction	Pasetto and Baldo, 2010
EAF slag	Weathering for 9 months	12	Aggregates for concrete	Papayianni and Anastasiou, 2010
MSWI BA	Sieving, sintering (1000-1050 °C)	10	Lightweight aggregate for concrete	Cheeseman et al., 2005
MSWI BA	Sieving	50	Road construction	Forteza et al., 2004
MSWI BA	Sieving	20	Aggregates for concrete	Pera et al., 1997
MSWI BA	Grounding, sieving, sintering (1450 °C)	20	Aggregates for concrete	Ferraris et al., 2009
MSWI BA	Sieving, iron removal, washing	31.5	Aggregates for concrete	Sorlini et al., 2011

<b>Table 1.25.</b>	Examples	of steel	slags	and	MSWI	residues	reused	as	aggregates	in	different
constructio	n applicatio	ons.									

Table 1.26 reports some recent studies which deal with the reuse of MSWI residues as partial substitutes of cement in clinker production. The recycling of industrial wastes in concrete manufacturing is of increasing interest worldwide, due to the high environmental impact of the cement and concrete industries and to the rising demand of infrastructures. Blended cements are normally produced by adding to Portland cement clinker different quantities of coal fly ash (CFA) or ground granulated blast furnace slag (GGBS). These mineral additions, that have been initially simply used to recycle wastes, turned out to be

beneficial with regard to the properties of concrete, especially in relation to its resistance to aggressive species.

Matrix	Pre-treatments	Proposed reuse	References
MSWI BA	Grinding	Cement production	Bertolini et al., 2004
MSWI BA	Milling	Cement production	Filipponi et al., 2004
MSWI BA	Sieving, self-grinding, magnet separation processes	Cement production	Juric et al., 2006
MSWI BA and MSWI FA	Grinding, washing	Cement production	Pan et al., 2008
MSWI FA	Washing, phosphatation, calcination	Cement production	Aubert et al., 2006
MSWI FA	Washing	Cement production	Bertolini et al., 2004

Table 1.26. Examples of MSWI residues reused as a substitute for cement in concrete production.

This practise is so well established all over the world that dedicated standards exist (EN 450-1, EN 15167-1) which provide specify requirements for the chemical and physical properties as well as quality control procedures for these kinds of materials.

Several authors have studied the possibility of recycling other types of industrial byproducts in cement manufacturing, since these materials have some analogies with the above mentioned traditional mineral additions. Specifically, MSWI residues have a great potential in this field of application since both bottom and fly ash show pozzolanic behaviour and their addition to the concrete mix could have a beneficial role in the development of the microstructure of the hydrated cement paste. Regarding bottom ashes, a preliminary grinding step is often required in order to achieve a suitable particle size distribution, comparable to that of cement (Bertolini et al., 2004). On the other hand, fly ashes are normally characterized by a high content of chlorides and significant amounts of dangerous substances, therefore they must undergo a washing treatment to reduce the content of chlorides and heavy metals (Bertolini et al., 2004, Pan et al., 2008).

# 1.5 Technology trains

As previously mentioned, the link between available soil/residues and required products/services can be provided by matching the individual technologies, i.e. by assembling a technology train. Figure 1.8 shows the general scheme of a technology train in a Brownfield regeneration context, which can be seen as the bridge between input and output materials. It can be noticed that the individual techniques discussed in Paragraph 1.3 represent just one step (wagon) of the train, as some pre-treatment steps may be required to make the materials(s) suitable to be treated in order to produce a specific output. Specifically, when dealing with the treatment of soil/waste materials in order to reuse them as useful products, a physical/mechanical pre-treatment is often required.



Figure 1.8. General scheme of potential technology trains in a Brownfield regeneration context.

This pre-treatment may consist in a simple sieving step to "adjust" the grain size distribution of the starting material, that may be useful if the next treatment step requires a material with a given particle size, but also to separate the coarse fractions, usually less polluted, from the finer more contaminated ones. When the starting material is not suitable to be directly reused on site or directly treated, because it is too coarse to allow for material mixing and handling, a crushing step may be added in order to reduce its particle size. As an example, Table 1.27 lists some methods of pre-treatment used to modify the physical properties of a material before being processed by a granulation treatment.

Pre-treatments	Considerations	References
Tre-treatments	Consider ations	Kelerences
Milling	To reduce the particle size dimension in	Cheeseman and Virdi, 2005;
	order to get a powder.	Cioffi et al., 2011
Washing with distilled water	To remove the water-soluble compounds in order to improve the chemical characteristics of final products.	Mangialardi, 2001
Screening	When using soil, enables granulation treatment and allows the reuse of the coarse fraction directly, without processing (the coarse fraction is the cleanest one).	Scanferla et al., 2009
Pre-wetting by kneading	To distribute the binder evenly and produce a narrow agglomerate size distribution.	Iveson et al., 2001

Table 1.27:	<b>Pre-treatment</b>	method in	granulation	process.
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Furthermore, it should be pointed out that the optimal coupling of technologies and the choice of the best train can occur once that the limit of applicability of the individual technologies are known, i.e. once that their operating windows are defined. Since the applicability of the individual technologies to soils and waste materials depends on several variables, site-specific data and results of treatability tests are needed. Nevertheless, some "applicability indication" can be extrapolated from lab-scale experimental data and data collected from field-scale case studies. As an example, a list of the main properties of the materials to be treated, affecting the applicability and the expected performance of Stabilization/Solidification, are reported in Table 1.28. Preliminary values of these properties allowing for applicability of S/S treatment are also proposed in the same table, although it should be noted that other works have reported the effectiveness of this type of treatment for different conditions than those discussed in Table 1.28 (Dermatas and Meng, 2003; Garcia et al., 2004; Mater et al., 2006).

Table 1.29 reports some examples found in the recent scientific literature concerning the application of selected combinations of technologies to different types of contaminated material with the final aim of obtaining aggregates with proper characteristics to be reused in construction applications. This possibility is of particular interest in a Brownfield regeneration framework.

Main properties	Applicability conditions	Reference
Organic contaminants	PCB < 500 ppm	EPA, 2009;
concentration	PCP < 200 ppm	Environment Agency UK, 2004
	PAH < 30 ppm	
	Dioxins < 50 ppm	
Particle size	$\Phi > 74 \ \mu m.$	Chen et al., 2009;
	$\Phi < 4 \text{ mm}$	Scanferla et al., 2009
Carbon content	TOC < 1%	Stegemann and Zhou, 2009
		G/ 1.71 0000
pH	pH > /;	Stegemann and Zhou, 2009
	pH < 12	
Chloride concentration	< 5%	Stegemann and Zhou 2009.
		Leonard and Stegemann, 2010

Table 1	.28.	Preliminary	operating	windows	for the	S/S	process.
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In fact, in this type of context, there is generally a request of construction materials such as aggregates and/or fillers; therefore, the possibility of replacing virgin raw materials with site-excavated material presenting specific properties could be an interesting asset, both from an economical and environmental point of view.

As can be noted from Table 1.29, the production of recycled aggregates essentially relies on the application of technology trains based on two different processes: granulation and vitrification. As described in Paragraph 1.3.2, granulation involves the addition of a binder to a powder material to allow an enlargement size through mechanical mixing, while vitrification implies a high temperature treatment without the addition of any liquid binder, in which the material is converted into a glass or glassy substance, which results substantially inert towards most chemical and biological agents. Although vitrification is a well established technology in the treatment of different types of contaminated materials, among others MSWI bottom ash (Haugsten and Gustavson, 2000; Park and Heo, 2002), it is energy intensive and highly expensive. Due to these features, vitrification is not properly suitable to be applied in Brownfield site, where the regeneration costs and the availability of energy sources is of great concern.

The recently investigated technology trains based on granulation processes mainly rely on its coupling with stabilization/solidification techniques (Medici et al. 2000; Rossetti et al. 2006; Scanferla et al., 2009; Cioffi et al., 2011) or both stabilization/solidification and carbonation treatments (Melton et al., 2008; Gunning et al., 2009).

With specific reference to excavated soil in a Brownfield scenario, a potentially interesting management strategy is that proposed by Scanferla et al. (2009) that entails the screening of the material into two fractions (coarse and fine). The coarse fraction (the cleaner one), generally composed of glass, brick and stone debris is directly reused on site as filling material in place of virgin materials after passing through a washing treatment section, whereas the fine fraction, generally more contaminated, is treated by a cement-based granulation process. The cementitious material obtained is relocated in situ in the form of aggregates, after a specific curing time in on-site storage areas to allow for binder hydration (Scanferla et al., 2009).

Matrix	Process	Pre-treatments	References
MSWI fly ash	Granulation-S/S	-	Medici et al.,2000
Shredder residues	Granulation-S/S	-	Rossetti et al., 2006
Soil	Granulation/SS	Screening	Scanferla et al., 2009
MSWI bottom ash	Granulation/SS	Milling	Cioffi et al., 2011
Quarry fine	Carbonation- S/S- granulation	-	Gunning et al., 2009
Sediments	Carbonation- S/S- granulation	Screening, crushing	Melton et al., 2008
MSWI bottom ash	Granulation-Vitrification	Milling	Cheesemann et al.,
			2005
Sewage sludge ash	Granulation-Vitrification	-	Cheesemann and Virdi,
			2005

 Table 1.29: Examples of Technology trains applied to different matrices to obtain aggregates for construction purposes.

# 2 CEMENT-BASED GRANULATION OF BROWNFIELD SOIL FOR AGGREGATE PRODUCTION

\*This section reports the results of a lab-scale investigation carried out to assess the performance of a treatment for excavated soil from a Brownfield site based on stabilization/solidification (S/S) and granulation aimed at producing aggregates for construction applications. Preliminary tests were performed on a natural soil to investigate the effects of the operating conditions and mixture formulations on the physical and mechanical properties of the product. In a second phase, the process was tested on three samples of industrial soil, collected in a Brownfield site located in Central Italy, applying the operating conditions and binder type that provided the best results in the preliminary tests. Making reference to the industrial soil, an average mechanical strength approaching that of argillaceous limestone was obtained as a result of the S/Sgranulation treatment. With regard to metals leaching, an increase in the release of Ba, Cr and Cu was noted compared to the untreated soil, in particular for the aggregates obtained with the highest contents of cement (30%). This result was related to the alkaline pH of the leachates (> 12) as well as to the composition of the cement employed as binder. In spite of this, the proposed technology train proved to be an effective way for recycling the excavated soil, once that the appropriate type and amount of binder were selected.

### \*Part of this chapter was published as

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# 2.1 Introduction

As mentioned in Paragraph 1.5, a potentially interesting management strategy for industrial soil in a Brownfield regeneration context consists in its treatment to produce aggregates for construction purposes, e.g. in concrete production, since this practice may allow to avoid landfilling as well as to reduce the consumption of virgin raw material. In addition, industrial soils originating from abandoned industrial sites may cause detrimental environmental effects related to the release of toxic metals and metalloids into the environment (Voglar and Leštan, 2010). Therefore, the proposed treatment should also reduce the mobility of potential contaminants. Often, this goal is achieved through a stabilization/solidification (S/S) process, which involves the controlled addition and mixing of hydraulic binders with contaminated soils to form a monolith showing an improved environmental behaviour and high mechanical resistance (Dermatas and Meng, 2003; Voglar and Leštan, 2010). In spite of this, the application of S/S treatments does not allow to obtain a product with a suitable particle size to be reused in substitution of natural aggregates in civil applications. Granulation processes may be applied to obtain a significant particle size enlargement, which is achieved by mixing a liquid binder with a fine particle size material in a rotary drum or similar device (Iveson et al., 1996; Iveson et al., 2001). Recently, a number of studies have focused on the coupling of the two above mentioned techniques in order to obtain aggregates from the treatment of several waste materials, such as contaminated soil (Scanferla et al., 2009), municipal solid waste incinerator bottom (Cioffi et al., 2011) and fly ash (Medici et al., 2000; Marruzzo et al., 2001) and automotive shredder residues (Rossetti et al., 2006). It was proved that such a treatment may be effective in obtaining pellets with sufficient mechanical strength to be reused in civil engineering applications and exhibiting a decreased release of toxic elements, such as As, Pb, Cd and Hg (Scanferla et al., 2009).

This work is the first step towards the assessment of the conditions of applicability, i.e. operating windows, of a technology train employing the above mentioned combined techniques and aiming at producing aggregates to use in construction applications from industrial soil. The proposed approach appears to be particularly relevant in a Brownfield

regeneration context, since it may potentially allow to decrease landfilling, save natural resources and make Brownfield redevelopment more viable and sustainable.

In particular, the selected technology train consists in a grain size screening step in which the material is separated into two size fractions, followed by the treatment of the fine fraction by the combination of stabilization/solidification with granulation. The aim of this treatment is to obtain a product with a grain size above 2 mm, characterized by both mechanical and environmental properties suitable to be used as an aggregate in construction applications. In order to gain a first insight on the operating windows of this process, a lab-scale investigation was first performed on a natural soil, by varying the operating conditions and the type and amount of binder and additive. In a subsequent phase, a second set of experiments was carried out on an industrial soil sampled from a Brownfield site, selecting the operating conditions and binder type that provided the best results in terms of mechanical strength in the preliminary tests.

# 2.2 Materials and methods

## 2.2.1 Materials

The industrial soil used in this study was sampled from an Italian Brownfield site located in central Italy that hosted a cotton and wool manufacturing plant up to the early 30's. Specifically, three samples of industrial soil, hereafter termed Q1, Q2 and Q3, were collected at approximately 1 m of depth and 2 m of mutual distance. A non contaminated natural soil was also tested in order to assess the influence of the composition of the mixture on the mechanical strength of the final product. The particle size distribution of the materials was evaluated by applying the standard procedure ASTM D422, whose results are reported in Figure 2.1. The finer fractions of the investigated soil (d < 2 mm) corresponded to 63, 49, 48 and 94 % of the natural soil, Q1, Q2 and Q3, respectively. The coarser fraction (d > 2 mm) was discarded, while the finer fraction was characterized in terms of its main chemical constituents, by acid digestion of air dried soil samples, following the standard procedure EPA 3050b, and analysing the obtained solutions by inductively coupled plasma optical emission spectrometry (ICP-OES). Total organic carbon (TOC) was assessed by using a Shimadzu TOC VCPH analyser equipped with a solid sample module by applying the standard procedure EN 13137.



Figure 2.1. Initial particle size distribution of the non-contaminated natural soil and of the three samples of industrial soil (Q1, Q2, and Q3) collected at an Italian Brownfield site.

The elemental composition of the industrial soil is reported in Figure 2.2 together with the regulatory limits set by the Italian legislation for residential use that is foreseen for the new destination of the site. As shown in Figure 2.2, the major constituents of Q1, Q2 and Q3 included Fe, Al, Ca, Mg and Na. Regarding the regulated elements, appreciable concentrations of As, Cu, Hg, Pb, Sn and Zn were observed. Specifically, Cu, Pb, Hg and Sn concentrations in sample Q1 exceeded the respective Italian threshold values for residential use. The natural soil was mainly constituted by Al (20 wt.%), Na (4.4 wt.%), Ca (3.4 wt.%) and Fe (2.9 wt.%) and its concentration of regulated elements proved to be lower, as expected, than that of the industrial soil. The TOC content of the industrial soil was around 1.2 wt. % for sample Q1, while the natural soil as well as samples Q2 and Q3 seemed to be free of organic matter, exhibiting a TOC content below the instrumental quantification limit.



Figure 2.2. Main composition of the fine fraction (d< 2 mm) of the three samples of the industrial soil (mg/kg dry wt.). The respective regulatory limits for residential use are shown as black lines (Italian Legislative Decree 152/06).

# 2.2.2 Methods

The S/S-granulation experiments were performed in a laboratory scale granulator with a diameter of 0.3 m and a height of 0.23 m, equipped with a blade to promote granules formation, operated at 24 rpm for 5-10 minutes, with a tilt of 66° (see Figure 2.3). The rotation speed, the granulator inclination, as well as the duration of the tests were selected by performing preliminary optimization experiments on the natural soil, the results of which are not reported in this work.

A high resistance Portland cement (CEM I 52.5R) and a Portland composite cement (CEM II/A-LL 42.5 R) were tested as binders, while sulfonate-based (A1) or acrylic-based (A2) superplasticizers were employed as additives, in order to decrease the amount of required water and possibly improve the mechanical performance of the product.



Figure 2.3. Laboratory scale device used to perform the S/S-granulation tests.

For each S/S-granulation experiment, approximately 500 g of air dried soil and cement were preliminarily mixed with the deionized water, or with a solution containing water and additive, in a plastic bag before being inserted into the granulator. The preliminary screening tests on the natural soil were carried out by varying the water/solid ratio (W/S), cement/solid ratio (C/S) and additive/cement ratio (A/C), in order to gain a first insight on the operating windows of the process and study the influence of the different parameters on the process performance. Based on the results of these tests, S/S-granulation experiments were performed on the industrial soil, employing the mixture formulations that provided the best results in terms of the achieved particle size distribution and mechanical resistance.

The obtained granules were cured for 28 days at room temperature and 100% relative humidity and subsequently tested for assessing their suitability to be reused in construction applications through the analysis of the particle size distribution, mechanical strength and inorganic contaminant leaching.

The mechanical strength of the granules was evaluated by performing the Aggregate Crushing Value (ACV) test, applying the British standard BS 812-110. The leaching behaviour of the untreated industrial soil and cured granules was determined by performing the standard compliance leaching test EN 12457-2, followed by ICP-OES

analysis of eluate concentrations. Specifically, the test was performed both on crushed granules (d < 4 mm) in order to comply with standard specifications, as well as on uncrushed ones, in order to evaluate the effective release of contaminants from the granules obtained as a result of the S/S - granulation treatment.

A control sample of cement R 52.5 was prepared by following the standard procedure EN 196-1 and applying a liquid to cement ratio of 0.5 l/kg. After a period of curing under water for 28 days, the obtained specimen was crushed and subjected to the standard compliance leaching EN 12457-2 in order to assess the potential release of metals from cement R 52.5.

## 2.3 Results and discussion

### 2.3.1 Initial tests on natural soil to assess the optimum mixture formulation

The main results obtained from the S/S - granulation treatment carried out on the natural soil are shown in Figure 2.4 and Figure 2.5.

Figure 2.4 reports the particle size distribution curves of the granules as a function of the different mixture formulations tested. The obtained granules showed a particle size mostly comprised between 2.36 and 25 mm and an average d<sub>50</sub> between 6 and 10 mm, one order of magnitude greater than that of the untreated natural soil (about 0.5 mm). In Figure 2.4a, the influence of the employed W/S ratio on granule size is reported. As can be noted, the average particle size increased with increasing water content, confirming the results of previous studies on granulation processes, which report that the granulation rate and the mean size of the granules product increases with increasing water content (Iveson et al., 1996; Salman et al., 2006). In Figure 2.4b, the particle size distribution of the manufactured granules is shown as a function of the cement content. For both cements, the average diameter of the granules varied proportionally with the binder content, this effect being more pronounced for cement R 52.5. As shown in Figure 2.4c, the use of the additives allowed to obtain finer aggregates, especially when using the sulfonate-based superplasticizer in combination with cement R 42.5. This behaviour is

consistent with the results of previous studies indicating that a more viscous binder generally leads to the reduction of the granules consolidation rate and subsequently of the compaction and growth of the granules (Iveson et al., 1996). In order to possibly evaluate the influence of the additive content on the particle size distribution of the final granules, S/S - granulation tests were carried out varying the amount of acrylic-based superplasticizer. Results showed that an increase of the acrylic-based additive amount from 1 to 2 % by weight did not imply any appreciable modification of the particle size distribution of the obtained granules, regardless of the type of cement used as a binder.

The main results in terms of the mechanical resistance of the final product are reported in Figure 2.5. By comparing Figure 2.4 and Figure 2.5, it can be noted that larger particles generally showed a poorer mechanical strength when subjected to the ACV test.

The influence of the water content on the ACV is reported in Figure 2.5a. For cement R 42.5 the lowest ACV, corresponding to a higher resistance to compression, was achieved at a W/S ratio value of 0.175 l/kg and was found to be 28 %, this value being comparable to that obtained with cement R 52.5 employing the same W/S ratio. In spite of this, while for cement R 42.5, 0.175 l/kg was found to be the optimum W/S, for cement R 52.5 a linearly increasing trend of ACV with the water content was noted. With regard to the influence of the binder content on the final mechanical resistance of the granules, a different behaviour of the granules was noted, depending on the type of cement used as binder in the S/S - granulation tests. Regarding cement R 52.5, the best ACV results were obtained at a C/S ratio equal to 25% and 30% by weight. At these binder contents, an average ACV of about 21% wt. was achieved, this value being comparable to that of a natural gravel. Conversely, the granules manufactured with cement R 42.5 showed an increasing ACV for a higher binder content, allowing to attain the best mechanical performance at a C/S ratio equal to 20%. The use of either type of additive did not imply any relevant improvement of the mechanical performance of the granules manufactured with both cements. In particular, for cement R 42.5 the sulfonate-based superplasticizer seemed to influence negatively the resistance to compression of the granules, with an ACV value being about five percentage points greater than that obtained with cement only.



Figure 2.4. Comparison of the particle size distribution curves of the as received natural soil and of the granules obtained after the S/S-granulation treatment for cement R 52.5 and cement R 42.5 as a function of: a) water content (C/S=30% wt.); b) cement content at optimum water content; c) additive type at optimum water content (C/S=30% wt.); d) additive content at optimum water content (C/S=30% wt.).

A similar behaviour was observed also increasing the content of the acrylic-based additive, as reported in Figure 2.5d, i.e. no relevant effects for cement R 52.5 as well as for cement 42.5R. Anyhow, it should be pointed out that for both types of cement the use of the additives allowed to reduce the W/S ratio down to 0.14 l/kg, this value also being the minimum value for which appreciable increases of the granules resistance were achieved.



Figure 2.5. Results of the Aggregate Crushing Value (ACV) test for cement R 52.5 and cement R 42.5 as a function of: a) water content (C/S=30% wt.); b) cement content at optimum water content; c) additive type at optimum water content (C/S=30% wt.); d) additive content at optimum water content (C/S=30% wt.).

### 2.3.2 Tests on industrial soil

A few of the mixture formulations for which aggregates with a suitable mechanical performance for use in construction were obtained from the natural soil were selected to test the S/S - granulation treatment on the three samples of industrial soil. Specifically, cement R 52.5 was used and two concentrations C/S were tested: 25 and 30%. In addition for each cement concentration, the effect of the addition of the acrylic-based superplasticizer (A2) at a A2/C concentration of 2% was also investigated.

The results obtained are reported in the following paragraphs, discussing separately the performance in terms of the physical and mechanical properties and of the environmental behavior of the obtained granules.

### 2.3.2.1 Effects of the treatment on particle size of the obtained granules

The results in terms of the particle size distribution of the produced granules are reported in Figure 2.6a. As for the natural soil, the cement-based granulation treatment applied to the industrial soil allowed to obtain aggregates with an average diameter one order of magnitude greater than that of the untreated soil. As expected, the minimum water to solid ratio which allowed the soil particles to grow and nucleate was found to be strictly particle size-dependent, i.e. a higher W/S ratio was needed to granulate finer particles. In fact, granules are formed and increase in size due to the presence of liquid bridges between particles; hence, more liquid is generally required to wet finer particles due to the higher specific surface area (Salman et al., 2006). For instance, an optimum W/S ratio of 0.17, 0.185 and 0.22 l/kg was found for sample Q1, Q2 and Q3, respectively, when employing a C/S ratio of 30%. In addition, similarly to the natural soil, the use of a more viscous liquid obtained by adding the acrylic-based superplasticizer, generally allowed to produce slightly finer pellets, in agreement with the findings of Iveson et al. (1996). Differently from the natural soil, no increase of the average diameter of the granules with increasing binder content was noted.

## 2.3.2.2 Effects of the treatment on the mechanical strength of the obtained granules

The results in terms of the ACV of the produced granules are reported in Figure 2.6b.

Regarding the mechanical resistance of the resulting granules, an average resistance to compression approaching that of argillaceous limestone was obtained as a result of the S/S - granulation treatment. As expected, the ACV resulted strongly influenced by the size of the obtained granules. Indeed, granules with a similar particle size distribution showed a similar resistance to compression, this behaviour being particularly evident for sample Q3. Besides, the treatment of sample Q3 also provided relatively high ACV, i.e. a lower strength. This result was probably related to the finesses of this soil; indeed it is commonly recognized that coarser particles generally yield a particles - cement paste product characterized by a higher mechanical performance (Meddah et al., 2010). Similarly to the natural soil, the use of the acrylic-based superplasticizer generally did not provide any appreciable improvement of the strength of the granules, expect for sample Q1. In fact, an optimum ACV value of about 20%, which is between that of carboniferous limestone and mixed gravel, was obtained for this sample employing the following mixture formulation: C/S = 30%, W/S = 0.14 l/kg, A2/C = 2%. Hence, differently from the natural soil and samples Q2 and Q3, for sample Q1 the use of the acrylic additive and especially of a higher cement content appeared to yield a noteworthy improvement on the mechanical properties of the product. The differences noted on the effects of the binder composition may be tentatively related to the higher TOC content of sample Q1 compared to that of the other tested soils. In fact, previous works regarding the Stabilization/Solidification of waste materials have reported that a TOC greater than 1% can interfere with the solidification of the cementitious binder as well as with the mechanical resistance of the final product (Stagemann and Zhou, 2009).

## 2.3.2.3 Effects of the treatment on the leaching behaviour of the obtained granules

The granules obtained as a result of the S/S - granulation treatment of sample Q1, which showed the best mechanical performance in terms of ACV (Cement R 52.5 with a C/S = 30%, W/S = 0.14 l/kg and A2/C = 2%), were subjected to the compliance leaching test EN 12457-2. As mentioned in Paragraph 2.2.2, the test was performed both on crushed granules (d < 4 mm) in order to comply with standard specifications, as well as on uncrushed ones, in order to evaluate the effective release of contaminants from the granules obtained as a result of the S/S - granulation treatment.



Figure 2.6. Effects of the S/S-granulation treatment on the properties of the three samples of the industrial soil for four mixture conditions in terms of: a) Particle Size Distribution and b) Aggregate Crushing Value (ACV). The first number after the term mix indicates the percentage of cement R 52.5 over the solid sample employed (25 or 30%), while the second the content of superplasticizer A2 with respect to cement (0 or 2%).

The main results are reported in Figure 2.7. In the same figure, the results of the compliance leaching test performed on cement R 52.5 are reported for comparison, together with the limits imposed by the Italian regulation for groundwater quality (It. LD 152/06) and material reuse (It. DM 186/06).

Despite the presence of relevant concentrations of Sn, Pb and Hg in the as received sample Q1, the concentrations of these elements in the eluates obtained applying the standard leaching compliance test to both untreated and treated soil resulted to be negligible, lower than instrumental quantification limits. The S/S - granulation treatment yielded a pH increase from a value of 8.3 to alkaline values of 11.6 and 11.9 for uncrushed and crushed samples, respectively, due to the addition of the cement (pH=13). From Figure 2.7 it can be observed that the concentrations of Ba in the eluates of the treated soil were significantly higher than in the leachates of the untreated soil. This result was attributed to the cement employed as binder in the S/S - granulation experiments. Indeed, remarkable concentrations of Ba were released from cement R 52.5, even exceeding the regulatory limit established by the Italian legislation for reuse in simplified procedure, which is set at 1 mg/l (It. MD 186/06). Furthermore, the treatment appeared to exert a mobilizing effect also for Cr and Cu, which, besides the addition of the cement, was correlated to the increase in eluate pH. Indeed, some works reported that the highly alkaline conditions produced as a result of cement-based treatments may have an adverse effect on immobilization of Cu (Voglar and Leštan, 2010) and may lead to the formation of more soluble phases containing these metals (Paria et al., 2006; Kumpiene et al., 2008). Moreover, Cu leaching concentrations were found to be comparable to those observed for the eluates of the untreated industrial soil, especially for uncrushed samples, but in all cases they proved lower than the limits established for groundwater quality (It. LD 152/06). Moreover, they proved higher than the limit established for material reuse, which is set at 0.05 mg/l (It. MD 186/06). For the above mentioned metals, as expected, the release increased as particle size decreased, owing to the higher specific surface area available for leaching. From this point of view, an unexpected behaviour was found for V, since its release from the crushed samples was observed to be lower than that obtained from the uncrushed ones. Moreover, V release was found to be positively affected by the
treatment, since a decrease was observed as a result of the cement-based granulation treatment, down to the instrumental quantification limit.

In order to assess the leaching behaviour of the granules produced from the different soil samples collected at the Brownfield site, a standard compliance leaching test EN 12457-2 was performed on the uncrushed aggregates obtained employing a C/S ratio equal to 30% without the use of the acrylic-based superplasticizer.



Figure 2.7. EN 12457-2 leaching test results for the as received industrial soil (sample Q1) and the granules obtained after the S/S-granulation treatment (CEM R 52.5; C/S = 30% wt.; W/S = 0.14 l/kg; A2/C = 2% wt.). Data resulting below the instrumental Limit of Quantification (LOQ) are reported as the LOQ value and marked with starred bars in the graph.

The obtained results are reported in Figure 2.8. As shown in the graphs, the concentrations of metals released from the aggregates produced as a result of the S/S - granulation treatment of sample Q1 where similar to those attained for the same sample employing 2% of the additive A2 (see Figure 2.7). However, the release of Cr and V seemed to be negatively affected by the presence of the additive, since it was noted to be higher for the granules manufactured with the mixture of the water and the acrylic-based superplasticizer in comparison to those produced with water only.



Figure 2.8. EN 12457-2 leaching test results for the as received industrial soil and the granules obtained after the S/S-granulation treatment (CEM R 52.5; C/S = 30% wt.; optimum water content; no additive). Data resulting below the instrumental Limit of Quantification (LOQ) are reported as the LOQ value and marked with starred bars in the graph.

Similarly to sample Q1, the increased leachates pH up to 12.9 for both Q2 and Q3, had an adverse influence on the release of Cu and Cr, whose leaching concentrations increased upon the S/S - granulation treatment, for the latter remaining lower than the Italian limits established for groundwater quality and material reuse (0.05 mg/l). This result suggested that the initial material composition plays a relevant role with regard to the environmental behaviour of the products of the cement-based treatment. Indeed, for the highest Cu content in the soil (475 mg/kg for sample Q1), the highest Cu release was obtained from the recycled aggregates.

In order to assess the effect of decreasing the cement content on the leaching of contaminants from the produced aggregates, a standard compliance leaching test EN 12457-2 was performed on the products attained as a result of the cement-based granulation of sample Q3. To this aim, Figure 2.9 reports the concentrations of Ba, Cu and Cr in the eluates of the aggregates produced with cement only and applying a C/S ratio of 25 and 30% by weight.



Figure 2.9. EN 12457-2 leaching test results for the granules obtained after the S/S - granulation treatment of sample Q3 for different mixture formulations (mix 30/0: CEM 52.5 R; C/S = 30% wt.; W/S = 0.22 l/kg; no additive; mix 25/0: CEM 52.5 R; C/S = 25% wt.; W/S = 0.218 l/kg; no additive).

As reported in Figure 2.9, a decreased release with decreased cement content from 30 to 25% wt. was observed for Ba, while no relevant effects were noted for Cr and Cu. Besides confirming the effect of cement on the release of metals from the recycled aggregates, especially for Ba, the obtained results highlighted the major influence of the eluate pH on the release of Cu and Cr, which was found to be around 12.9, regardless of the cement content employed.

# 3 "IN-SITU" CARBONATION OF STAINLESS STEEL SLAG

\*The main aim of this work was to assess the potential of in situ carbonation as a treatment to modify the properties of alkaline materials such as industrial soil in terms of its leaching behaviour and mineralogy and to store the CO<sub>2</sub> generated by specific treatments applied in the context of Brownfield regeneration. The process was investigated through lab-scale column carbonation experiments, in which 100% CO<sub>2</sub> was fed through humidified stainless steel slag under ambient temperature and pressure for set reaction times. The reaction kinetics and the maximum CO<sub>2</sub> uptake attained for the size fraction 0.177 - 0.84mm of the tested SS slag (5.5%) after 4 h treatment proved slightly lower than those resulting from batch tests carried out on the same particle size fraction at enhanced operating conditions. The mineralogy of the material showed to be affected by column carbonation, exhibiting a higher calcite content and the decrease of Ca hydroxide and silicate phases. As a result of carbonation, the material showed a decrease in pH and Ca release as well as an increase in Si mobility. Furthermore, a reduction of Cr and Ba leaching, up to 63% and 96% respectively, was achieved after 2 h of reaction. However, carbonation was observed to lead to an increased leaching of V and Mo.

\*Part of this chapter was published as

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# 3.1 Introduction

In a Brownfield regeneration context, soil is commonly referred to as industrial soil, since it may be characterized by the presence of material of anthropogenic origin arising from the historical use of the site that may cause detrimental environmental effects related to the release of toxic metals and metalloids (Voglar and Leštan, 2010). For instance, the profile of an industrial soil may be characterized by the stratification or the heterogeneous mixture of native soil and industrial by-products, such as demolition waste and slag from steel making processes (Renforth et al., 2009) for which the leaching of specific elements may be significant, e.g.: Cr from stainless steel slag (Shen et al., 2004). Furthermore, Renforth et al. (2009) showed that some kinds of alkaline soils present in Brownfield sites may act as carbon sinks by reacting with atmospheric carbon dioxide. Namely, they found that the 20 cm-layer of the industrial soil pertaining to a former steelmaking company was characterized by a variable CaCO<sub>3</sub> content, ranging between 0 and 38% but presenting a poor correlation with sample depth. A step forward aimed at employing this type of industrial soil as alkalinity source could be represented by the application of accelerated carbonation, using far more concentrated carbon dioxide sources than atmospheric air. So far, accelerated carbonation, has been developed as an ex-situ CO<sub>2</sub> storage option, by which a material rich in alkaline earth metal oxides and/or silicates is contacted with carbon dioxide at optimized operating conditions (i.e. temperature, pressure and pH), thus leading to the formation of the corresponding thermodynamically and chemically stable carbonate phases (Lackner et al., 1995). Several reaction routes (e.g. indirect, direct gas-solid or direct aqueous) have been investigated with the aim of maximizing the CO<sub>2</sub> uptakes achievable by ex-situ carbonation of minerals and alkaline residues such as steel slag (see e.g. Doucet, 2010; Bobicki et al., 2012).

In addition, ex-situ carbonation processes carried out in aqueous conditions, applying liquid to solid (L/S) ratios above 2 (slurry phase route) or below 1 (wet route) and generally mild operating conditions have been tested as treatment strategies to reduce the release of metals and metalloids from alkaline industrial residues, such as incineration bottom ash and steelmaking slag (e.g. van Gerven et al., 2005; Baciocchi et al., 2010b; 2010c; van Zomeren et al., 2011). Furthermore, accelerated carbonation has been tested

in combination with cement as a stabilization treatment for contaminated industrial soil (Antemir et al., 2010b) and also as a technique to increase the compressive strength of compacts formed by residues rich in Ca silicates such as steel slag (Johnson et al., 2003). Hence, the application of accelerated carbonation in a Brownfield regeneration context appears to be of particular interest since it may allow the achievement of multiple benefits. In Brownfield sites primary CO<sub>2</sub> sources, such as combustion or power plants or other industrial processes, may be no longer available; however, CO<sub>2</sub> emissions may result as a consequence of treatments aimed at the remediation of groundwater contaminated by organic compounds such as oxidation or CO<sub>2</sub> stripping (Nelson et al., 2009). Besides, CO<sub>2</sub> may evolve from innovative treatments for the improvement of the structural properties of the subsoil in view of Brownfield sites redevelopment (Hartog et al., 2013). Therefore, in these types of contexts, CO<sub>2</sub> upward flows through the subsoil may be exploited to induce in situ carbonation reactions in existing or specifically prepared layers of alkaline residues and/or industrial soil to improve the environmental and technical properties of the materials as well as to permanently store CO<sub>2</sub>. A schematic representation of the proposed in-situ carbonation process as a treatment for industrial soil in Brownfield sites coupled with in-situ stripping of volatile organic contaminants (VOCs) from groundwater is depicted in Figure 3.1. In this application the injected CO<sub>2</sub> can first serve to strip VOCs from groundwater before stimulating the carbonation of the slag material in the overlying industrial soil. As shown in Figure 3.1, the reagents are injected into the subsurface, resulting in the evolution of a CO<sub>2</sub> upward flow as well as the volatilization of organic contaminants affecting groundwater quality. Once the CO<sub>2</sub> reaches the layer of alkaline industrial soil, carbonation occurs, resulting in the improvement of the environmental properties of the carbonated material and CO<sub>2</sub> storage. Extraction wells are also foreseen in order to collect the unreacted carbon dioxide and the volatilized organic compounds to submit to proper treatment.

The main aim of this work was to assess the feasibility of the proposed in-situ carbonation process by means of a column carbonation experimental method in terms of the effects exerted on the environmental behaviour of the treated material as well as on the achieved CO<sub>2</sub> uptakes. Specifically, this work reports the results of laboratory scale column

carbonation tests performed flowing 100% CO<sub>2</sub> through stainless steel (SS) slag, and applying operating conditions expected at Brownfield sites.



Figure 3.1. Schematic overview of the in-situ carbonation process proposed as a treatment option for alkaline industrial soils at Brownfield sites coupled with in-situ stripping of volatile organic contaminants (VOCs) from groundwater.

In addition, to assess the reactivity of the material with CO<sub>2</sub>, accelerated carbonation tests were also carried out under enhanced conditions in a stainless steel batch reactor. All tests were performed on a mixture of freshly produced slags provided by a stainless steelmaking plant. Despite this sample may seem not adequately representative of aged slags typically found in Brownfield sites, it is worth pointing out that the effect of aging on the extent of carbonation is often limited to the top layer of an industrial soil. For instance, Suer et al. (2009) and Arm et al. (2011) reported upon weathering a pH shift of steel slags sampled from a pile, whereas for instance those buried beneath a road did not show remarkable changes of pH. Similarly, also Renforth et al. (2009) found the extent of carbonation of an industrial soil collected in a former steelmaking plant below a depth

of 20 cm to be negligible. Therefore, this evidence seems to suggest that the use of fresh slag samples adopted in this work may provide meaningful results also for slags present in Brownfield sites. As for the effects of carbonation on the properties of the residues, the modifications occurring in the mineralogy, acid neutralization capacity and release of major elements and trace components from the material both at its native pH and as a function of pH are analyzed.

# 3.2 Materials and methods

#### 3.2.1 Materials

The slag sample tested in this study, provided from a stainless steel production plant, is representative of the residues mix that is sent out of the plant for disposal. As the main residues produced by the plant are those generated from the Electric Arc Furnace (EAF) and from the Argon Oxygen Decarburization (AOD) converter units, the sample may be expected to be a mixture of these types of slag. After determining its particle size distribution (ASTM D422), the coarser fraction (d > 0.84 mm) was discarded as it was not considered suitable for performing reproducible lab-scale experiments. The remaining material was divided into a fine (d < 0.177mm) and an intermediate (0.177 - 0.84 mm) fraction. Both fractions were characterized in terms of their elemental composition and mineralogy.

The elemental composition was determined by alkali fusion of the slag samples with  $Li_2B_4O_7$  at 1050 °C followed by dissolution with 10% HNO<sub>3</sub> of the molten material and analysis of the solutions by inductively coupled plasma optical emission spectrometry (ICP-OES). The mineralogy of the as received and carbonated slag was evaluated by X-ray diffraction (XRD) analysis with Cu K $\alpha$  radiation using a Philips Expert Pro diffractometer (equipped with a copper tube operated at 40 kV and 40 mA) with an angular step of 0.02° held for 2 seconds with 20 spanning from 5 to 85°.

The intermediate fraction was also characterized in terms of its leaching behaviour before and after column carbonation tests, in order to evaluate the influence of this treatment on the mobility of major and trace elements. Specifically, the EN 12457-2 compliance test and the CEN/TS 14429 pH-dependence leaching test were applied both on as received and carbonated samples and the eluates were analyzed by ICP-OES. For the latter type of test, in order to span a wide pH range, acid additions were performed employing a 2 mol/l HNO<sub>3</sub> solution; while in order to increase the pH of the eluates of the carbonated samples a 2 mol/l NaOH solution was used. All chemical analyses, except the pH-dependence leaching test, were performed in triplicate.

# 3.2.2 Carbonation tests

Column carbonation experiments were performed in a glass column with a height of 16 cm and a diameter of 2 cm, packed with the intermediate particle size fraction of the slag, supported by a 3 cm layer of glass spheres to ensure homogeneous inlet gas distribution. The employed experimental set-up is shown in Figure 3.2.



Figure 3.2. Experimental set-up used to perform the column carbonation tests.

The coarser fraction of the slag was discarded as the particle size was too large with respect to the column diameter, whereas the finest one was discarded as it was assumed that the pressure drop through the column could become too high. Hence, the selection of the intermediate grain size range was aimed at obtaining a sufficient gas flow through the material as well as a significant degree of carbonation, which is reported to vary greatly with grain size (see e.g.: Baciocchi et al., 2009). Besides, the intermediate fraction corresponded to a relevant portion of the as received material.

In each experiment, 40 g of dry material and 8 ml of distilled water were mixed, following two different water addition methods. The first method (mixing) entailed the addition of the water to the slag in a glass beaker until the material was homogeneously wetted. In the second (percolation), the dry material was first packed into the column in layers and then each layer was humidified from the top with a standardized procedure so to possibly ensure uniform dispersion of the water throughout the slag. The latter approach was adopted in order to more closely reproduce the wetting of the material under a real application scenario, whereas the former one was applied to obtain a homogeneously wetted slag. In both cases, the material was placed into the column from the top and compacted in subsequent layers to avoid the presence of preferential flow pathways.

The carbonation experiments were carried out at ambient temperature (T = 22-25 °C) and pressure (P = 1 bar) flowing 100% CO<sub>2</sub> through the column for reaction times of 1, 2, 4 and 8 hours. I chose to use 100% CO<sub>2</sub> as this composition is in keeping with that employed in in-situ remediation of volatile organic contaminants from groundwater using CO<sub>2</sub>supersaturated water injection (Nelson et al, 2009). The 100% CO<sub>2</sub> flow was first humidified with a bubbler and then fed to the bottom section of the column with a flow rate of around 10 ml/min. At the end of the experiment, slag samples were collected from the top, middle and bottom level of the column with the aim of identifying potential differences in the extent of carbonation. All of the collected samples were weighted and then dried overnight at 105 °C, allowing to measure their moisture content. A fraction of each sample was subsequently milled below 0.177 mm and analyzed to determine its Inorganic Carbon (IC) content with a solid sample module for total organic carbon analysis (Shimadzu-5000A) through acidification of the sample with phosphoric acid at 200 °C and quantification of the evolved CO<sub>2</sub> by infrared analysis (EN 13137). Selected milled samples were kept for mineralogy evaluation, whereas representative unmilled samples obtained at different reaction times were collected for the leaching tests.

Accelerated batch carbonation tests were performed on both the fine and intermediate slag particle size fractions at the operating conditions (T = 50 °C, P = 10 bar, L/S = 0.4 l/kg) that showed to enhance SS slag carbonation reaction in previous investigations (Baciocchi et al., 2009). These tests were aimed at assessing the maximum reactivity with CO<sub>2</sub> of the two grain size fractions. In each test, performed in a pressurized stainless steel reactor following the procedure described in previous works (Baciocchi et al., 2010a), three 1 g samples, humidified at the set L/S ratio, were exposed to a 100% CO<sub>2</sub> flow for different reaction times, ranging from 0.25 to 24 h. Batch tests were also carried out on the intermediate fraction under similar conditions to those applied in the column experiments (T = 23 °C, P = 1 bar, L/S = 0.2 l/kg). The aim of these tests was to evaluate possible changes in the extent and kinetics of carbonation resulting from the different reaction mode adopted (batch or column). The carbonated samples obtained from the batch tests were analysed to determine their IC content and mineralogy applying the same procedures as those adopted for the column experiments.

# **3.3 Results and discussion**

# 3.3.1 Main properties of the tested slag

The stainless steel slag employed in this study was quite heterogeneous in its grain size distribution and showed a large amount (about 40% wt.) of coarse particles (d > 0.84 mm). The two classes selected for the carbonation experiments presented the following weight distribution: 23.5% wt. the fine fraction (d < 0.177 mm) and 36.8% wt. the intermediate fraction.

The elemental composition of both grain size classes is reported in Table 3.1. The major constituents of the slag included Ca, Si, Cr, Fe, Al and Mg. Appreciable concentrations of Ni (0.05 - 0.14%) and V (0.06 - 0.11%) were also observed. The Ca content (> 30% wt.) proved to be comparable to the concentrations generally reported for Electric Arc

Furnace (EAF) slags (Shen et al., 2004; Baciocchi et al., 2009; Baciocchi et al., 2010a) but were lower than those exhibited by the residues generated by steel refining processes, such as Argon Oxygen Decarburization (AOD) (Shen et al., 2004; Baciocchi et al., 2010a). Also Mg and Si contents resulted higher in the intermediate fraction, showing average concentrations of 1.9 and 10.7% wt., respectively. Significant concentrations of Fe and Cr were measured in the intermediate fraction, the Cr content being rather high and comparable to that reported for EAF slag between 3.2% (Shen et al., 2004) and 3.7% wt. (Baciocchi et al., 2009).

Table 3.1. Elemental composition of the fine (F) and intermediate (I) size fractions of the SS slag; the concentrations of major constituents are reported in % wt. while those of trace constituents in mg/kg.

	F (d < 0.177 mm)	I (0.177 < d < 0.84 mm)
Major elements (% wt.)		
Al	1.73	2.57
Ca	31.04	32.99
Cr	2.99	4.79
Fe	1.99	4.08
K	0.08	1.21
Mg	1.64	1.89
Mn	0.90	1.34
Na	0.10	0.15
Ni	0.05	0.14
Si	9.16	10.77
V	0.06	0.11
Trace elements (mg/kg)		
As	21.5	20.5
Ba	297.1	359.2
Bi	25.7	30.8
Cu	305.6	157.3
Hg	11.2	5.5
Мо	31.8	64.9
Pb	20.9	22.2
Sb	276.9	348.3
Sn	24.9	11.6
Zn	80.5	105.8

The XRD patterns resulting for the fine and intermediate fractions are reported in Figure 3.3. In both of the as received grain size classes several silicate phases were detected, in agreement with the results reported in previous studies on SS slag (Shen et al., 2004; Baciocchi et al., 2009; Baciocchi et al., 2010a). Moreover, some differences between the two fractions were observed. In the fine fraction a prevalence of dicalcium silicate (Ca<sub>2</sub>SiO<sub>4</sub>) was retrieved, while aluminum calcium silicate (Ca<sub>4</sub>L<sub>2</sub>SiO<sub>6</sub>) and melilite (Ca<sub>2</sub>(Mg<sub>0.5</sub>Al<sub>0.5</sub>)(Si<sub>1.5</sub>Al<sub>0.5</sub>O<sub>7</sub>)) appeared to be the most abundant minerals in the intermediate fraction. In both cases, some Fe phases, including iron sulfide (FeS), iron oxide (Fe<sub>2</sub>O<sub>3</sub>) and calcium oxide (CaO) were identified, together with calcite (CaCO<sub>3</sub>) and fluorite (CaF<sub>2</sub>). Despite a peak corresponding to portlandite (Ca(OH)<sub>2</sub>) was also detected in particular in the intermediate size class, the XRD results confirmed that the analyzed residues were mainly characterized by Ca-bearing reacting phases typical of EAF and AOD slags, i.e.: dicalcium silicate, calcium-aluminium silicates and calcium-magnesium silicates (see Baciocchi et al., 2010a).



Figure 3.3. XRD patterns of the as received SS slag as a function of particle size: (i) fine size fraction (d < 0.177 mm) and (ii) intermediate size fraction (0.177 < d < 0.84 mm). Legend: a) calcium aluminum silicate (CaAl<sub>2</sub>SiO<sub>6</sub>); c) calcite (CaCO<sub>3</sub>); f) fluorite (CaF<sub>2</sub>); i) iron sulfide (FeS); m) melilite (Ca<sub>2</sub>(Mg<sub>0.5</sub>Al<sub>0.5</sub>)(Si<sub>1.5</sub>Al<sub>0.5</sub>O<sub>7</sub>)); o) calcium oxide (CaO); p) portlandite (Ca(OH)<sub>2</sub>); s) dicalcium silicate (Ca<sub>2</sub>SiO<sub>4</sub>); x) iron oxide (Fe<sub>2</sub>O<sub>3</sub>).

The main results of the compliance leaching test carried out on the intermediate fraction are reported in Figure 3.4. For the elements whose concentrations resulted lower than the instrumental quantification limit, the corresponding limit of quantification (LOQ) is reported and indicated in Figure 3.4 with a star. In the same figure, the limits imposed by the Italian regulation for inert waste landfilling (It. MD 27/09/10) and material reuse (It. MD 186/06) are shown for comparison. Even though the limits for groundwater quality (It. LD 152/06) are not exhibited in this figure as well as in the following of this Chapter, similar considerations to those made hereafter for Cr with regard to material reuse and inert waste landfilling may be extended to groundwater quality, since the limit for Cr is the same (0.05 mg/l).

The natural pH of the eluates was high, about 12.4, above the limits imposed by the Italian regulation for reuse as a filling material or for similar applications (5.5 < pH < 12).



Figure 3.4. Comparison of the results of the leaching test at native pH on the intermediate fraction (0.177 < d < 0.84 mm) of SS slag before and after column carbonation (2 h and 8 h at T = 22-25 °C, P = 1 bar, L/S = 0.2 l/kg) in terms of: a) pH, b) major elements and c) regulated elements.

The composition of the leachates was characterized by relevant concentrations of Ba and Ca, 4.6 and 2.5% of the available amount based on total elemental content, respectively. Leaching of Mg, Mo and V was negligible, while Cr concentrations (0.24 mg/l) resulted higher than the values reported in previous studies for SS slag (Shen et al., 2004; Baciocchi et al., 2010a) and significantly above the limits for reuse and inert waste disposal (0.05 mg/l).

#### 3.3.2 CO<sub>2</sub> uptake kinetics

The CO<sub>2</sub> uptake achieved after carbonation was determined as a function of the CO<sub>2</sub> content after (CO<sub>2</sub> final) and before (CO<sub>2</sub> initial) the treatment by applying Eq. 3.1. The CO<sub>2</sub> contents were derived from the results of the inorganic carbon analysis; for the as received slag a CO<sub>2</sub> content of 0.62% and 2.04% by wt. were obtained for the intermediate and fine particle size fractions, respectively.

$$CO_{2uptake}(\%) = \frac{CO_{2final}(\%) - CO_{2initial}(\%) \cdot \frac{100 - CO_{2final}(\%)}{100 - CO_{2initial}(\%)} \cdot 100$$
 Eq. 3.1

On the basis of the  $CO_2$  uptake value, the corresponding calcium conversion yield achieved may be directly calculated as the ratio between the carbonated Ca, proportional to the measured  $CO_2$  uptake, and the amount of potentially reactive Ca phases, given by the difference between the total Ca content and the initial carbonate content (expressed as Ca) of the specific particle size fraction of the slag (see Eq. 3.2).

$$\eta(\%) = \frac{CO_{2uptake}(\%) \cdot \frac{40}{44}}{Ca_{tot}(\%) - CO_{2initial}(\%) \cdot \frac{40}{44}} \cdot 100$$
 Eq. 3.2

In Figure 3.5a, the CO<sub>2</sub> uptake resulting for slag samples collected at different column heights is reported as a function of reaction time. As can be observed, significant

differences in the values obtained at different heights were evident only for the 1 h test for which the upper layer presented a lower CaCO<sub>3</sub> content; for longer reaction times the material appeared to react homogeneously with CO<sub>2</sub>, with a maximum uptake of 5.5% achieved after 4 h, corresponding to a Ca conversion yield of 15.6%. As can be observed in Figure 3.5b, a very similar evolution of CO<sub>2</sub> uptake over time resulted from the carbonation tests carried out in batch mode applying the same L/S ratio and operating conditions. It should be noted that the static batch tests were carried out using a much lower amount of material so to favour CO<sub>2</sub> diffusion and assess the maximum reactivity of the material at set operating conditions.



Figure 3.5. Results of carbonation tests performed on the intermediate size fraction (0.177 < d < 0.84 mm) of the SS slag: a) column experiments at different depths (T = 23-25 °C, P = 1 bar, L/S = 0.2 l/kg, water added by mixing); b) batch experiments (T = 23 °C, P = 1 bar, L/S = 0.2 l/kg).

The main results of the batch carbonation experiments carried out at enhanced conditions with the aim of assessing the reactivity of the examined type of residues in comparison to the data reported in previous works on steel slag carbonation are reported in Figure 3.6. After a rapid increase, the carbonation kinetics resulting for the fine fraction seemed to reach completion in almost 8 hours with a CO<sub>2</sub> uptake higher than 13% by weight, implying a Ca conversion yield above 42%. These values appeared to be quite similar to those found in previous batch tests carried out at similar conditions on the fine fraction (d

< 0.15 mm) of mixed SS slag (Baciocchi et al., 2009) and on milled EAF slag (Baciocchi et al., 2010a). The intermediate fraction showed almost the same trend with time but halved CO<sub>2</sub> uptakes compared to the fine fraction, reaching a maximum value of 7.4% after 24 hours, corresponding to a Ca conversion yield of 20.8%, confirming the strong influence of particle size on the reactivity of alkaline materials with CO<sub>2</sub> (Baciocchi et al., 2009). The lower reactivity of the intermediate particle size fraction with CO<sub>2</sub> may be mainly related to the lower specific surface of the material, but also partly to the differences in the mineralogy of the two types of fractions, since the fine one was characterized by a higher content of dicalcium silicate (see Figure 3.3), a phase that has been reported to exhibit a significant reactivity with CO<sub>2</sub> at the tested operating conditions (Johnson et al., 2003; Baciocchi et al., 2010a).



Figure 3.6. Results of the accelerated batch carbonation tests performed at enhanced operating conditions (T = 50 °C, P = 10 bar, L/S = 0.4 l/kg) on the fine (d < 0.177 mm) and intermediate (0.177 < d < 0.84 mm) size fractions of the SS slag.

Comparing the results of the experiments performed at ambient conditions in either the column or batch set-up (see Figure 3.5) with those resulting for the intermediate size fraction in batch mode at enhanced conditions (see Figure 3.6), a slight decrease in the reaction rate and  $CO_2$  uptake values may be noted. This result may be ascribed mainly to the decrease in operating temperature, which is a parameter that is known to enhance the dissolution of silicate phases (Baciocchi et al., 2009; Baciocchi et al., 2010a).

The influence of the amount of water (expressed as L/S ratio) and type of water addition method adopted on the results of the carbonation column tests is reported in Figure 3.7a and Figure 3.7b, respectively. As can be observed in Figure 3.7a, CO<sub>2</sub> uptakes and reaction kinetics seemed not to be considerably affected by the applied L/S ratio in the timeframe of the experiments, during which no significant variations of the humidity of the samples was observed to occur. The L/S ratios employed in these tests proved comparable to those indicated as optimal in a previous study (Johnson et al., 2003) for SS slag with a similar composition to that used in this work. The CO<sub>2</sub> uptakes resulting at different sampling heights for the two water addition methods tested are reported in Figure 3.7b. The slightly better performance of the "mixing" method, more evident after 2 h reaction, was probably due to the more uniform distribution of water in the material. On the contrary, the water percolation method probably produced preferential water flow routes and consequently a less homogeneous reaction of the slag with CO<sub>2</sub>. Nevertheless, the results achieved with the water percolation approach are satisfactory in view of a possible future field-scale application of the process, where the wetting of the alkaline material will take place through percolation of rainwater or by artificial irrigation.



Figure 3.7. Results of the column carbonation tests (T = 22-25 °C, P = 1 bar) performed on the intermediate size fraction (0.177 < d < 0.84 mm) of the SS slag as a function of a) the L/S ratio applied (water added by mixing); b) water addition method at different column depths (L/S = 0.2 l/kg, M = water added by mixing, P = water added by percolation).

#### 3.3.3 Effects of carbonation on slag properties

#### 3.3.3.1 Effects on physical and chemical properties

The column carbonation experiments did not notably affect the physical properties of the slags. The moisture content measured at the end of the different experiments was quite in line with the initial one after water addition, with a maximum reduction of about 3.5% and 3% for the tests carried out at L/S equal to 0.1 and 0.2 l/kg, respectively. Besides, no hardening of the material was observed. Consequently, also considering that the gas flow rate was constant throughout the experiments, it seems reasonable to assume that the pressure drop through the packed column did not notably change as well over time. As far as the chemical properties are concerned, the results obtained by XRD analysis of carbonated samples of the intermediate size fraction of the slag are shown in Figure 3.8. Specifically, the diffraction patterns of the products obtained from the column tests carried out at ambient conditions are reported in Figure 3.8i, while those resulting from the batch tests performed at enhanced operating conditions are reported in Figure 3.8ii.



Figure 3.8. XRD patterns for the intermediate (0.177 < d < 0.84 mm) size fraction of the column carbonated SS slag as a function of the reaction mode: i) Column experiments at T = 23-25 °C, P = 1 bar, L/S = 0.2 l/kg, reaction time = 8 h; ii) Batch experiments at T = 50 °C, P = 10 bar, L/S = 0.4 l/kg, reaction time = 24 h. Legend: a) calcium aluminum silicate (CaAl<sub>2</sub>SiO<sub>6</sub>); c) calcite (CaCO<sub>3</sub>); f) fluorite (CaF<sub>2</sub>); i) iron sulfide (FeS); m) melilite (Ca<sub>2</sub>(Mg<sub>0.5</sub>Al<sub>0.5</sub>)(Si<sub>1.5</sub>Al<sub>0.5</sub>O<sub>7</sub>)); o) calcium oxide (CaO); p) portlandite (Ca(OH)<sub>2</sub>); s) dicalcium silicate (Ca<sub>2</sub>SiO<sub>4</sub>); x) iron oxide (Fe<sub>2</sub>O<sub>3</sub>).

The two carbonated samples showed a very similar mineralogy and indicated that the most considerable variation in slag mineralogy compared to that of the as received material reported in Figure 3.3ii, was a significant reduction of portlandite peak intensities and a slight decrease in Ca-Al silicates and melilite peaks. Apparently this could suggest that the main reacting phase is portlandite. Nevertheless, it should be noted that XRD results are qualitative and that the peak intensity is not directly correlated to the concentration of a given phase. This is also proven by the trend of the ANC curve of the as received slag reported in Figure 3.9 (discussed in Section 3.3.3.2) that shows very limited buffering capacity at pH 12 typical of portlandite (i.e. around 2 meq/g corresponding to a Ca(OH)<sub>2</sub> content of 7.4% wt.). Assuming the Ca(OH)<sub>2</sub> content deriving from the ANC analysis and considering only portlandite as the reacting phase would in fact result in Ca conversion yields higher than 100% for reaction times above 1 h, therefore confirming that Ca-containing silicates must have participated in the reaction. Besides, if the main reacting phase were portlandite, most probably the carbonation rate would have been the same both at ambient and enhanced conditions, whereas the operating temperature was shown to exert a positive effect on the carbonation rate (compare Figure 3.5 and Figure 3.6); this finding can be explained if calcium silicates were the main reacting phases, as the rate of silicate dissolution may be actually affected by the operating temperature. Therefore, the decrease of the CO<sub>2</sub> uptake rate over time observed in all the carbonation kinetics trends can be explained, rather by the depletion of fast-reacting phases such as portlandite, by the formation of a calcite and/or silica layer on the particle surface that hinders the further dissolution of Ca-containing reactive phases. The calcium carbonate content of the slag increased upon both types of treatment, indicating that Ca-minerals partly converted into calcite as a result of carbonation. Other carbonate phases besides calcite were not detected, indicating that, at least under the tested operating conditions, Mg and Fe oxides do not directly take part in the carbonation reaction, as reported also in previous studies (Johnson et al., 2003; Huijgen and Comans, 2006; Baciocchi et al., 2010a). The diffraction patterns of Fe-phases remained in fact essentially unvaried.

# 3.3.3.2 Effects on leaching

Regarding the results of the compliance leaching test performed on the carbonated samples obtained from the column experiments, the pH of the eluates compared to the as received slag showed to decrease progressively with reaction time reaching values suitable for reuse even after 2 h of treatment (see Figure 3.4a). Ca concentrations in the eluates of the carbonated slag (see Figure 3.4b) were also found to be lower than in the leachates of the as received slag, in agreement with the findings of previous studies that were ascribed to solubility control by less soluble phases caused by the changes in the mineralogy of the treated material (Huijgen and Comans, 2006; Baciocchi et al., 2010a; van Zomeren et al., 2011). Conversely, Mg and Si leaching concentrations increased upon carbonation; also these effects were reported in previous works and were related for Mg to the pH reduction (Baciocchi et al., 2009) and for Si to the conversion of the original silicate minerals into more soluble phases (Huijgen and Comans, 2006).

The effect of carbonation on the leaching of regulated elements is summarized in Figure 3.4c. Ba release showed to decrease considerably upon the reaction, as also reported in previous studies on steel slag carbonation (van Zomeren et al., 2011). Regarding Cr release, a decreasing trend with reaction time, leading to a 65% reduction after 8 hours, was observed, even though the leaching concentrations still remained above the limit values set by Italian legislation for both reuse and disposal. This result proved in good agreement with the effects on Cr mobility reported for batch carbonation tests carried out on SS slag at enhanced conditions, which were associated mainly to the decrease in pH caused by the carbonation treatment (Baciocchi et al., 2009). An opposite trend was found for Mo and V, whose concentrations were found to rise with increasing reaction times, but remained within the regulatory limits (see Figure 3.4c).

In order to better analyze the effects of the tested column carbonation treatment on the leaching behaviour of the slag and to identify the main mechanisms governing the release of major and regulated elements in a long-term scenario, especially relevant for the proposed application since the slag/industrial soil is expected to remain on site, the pH dependence test was performed. On the basis of the amount of acid or base added in each sub-test and the resulting pH of the leachate at equilibrium conditions, the acid/base

neutralization capacity of the slag before and after the carbonation treatment, reported in Figure 3.9, was evaluated.



Figure 3.9. Acid/base neutralization capacity curves for the intermediate (0.177 < d < 0.84 mm) size fraction of as received and column carbonated SS slag (T = 23-25 °C; P = 1 bar; L/S = 0.2 l/kg; reaction time = 8 h); negative x-axis values correspond to base additions.

As for the as received sample, the acid titration curve exhibited a noticeable buffering capacity at alkaline pH values (between 8 and 12), consistent with the presence of calcium hydroxide and silicate phases detected by XRD analysis. A second acid neutralization plateau was observed in the pH range between 4 and 6 that may be partly related to carbonate/bicarbonate buffering. As shown in Figure 3.9, the acid neutralization capacity of the slag was found to change substantially upon carbonation. The buffering capacity of the treated slag at pH higher than 7 was notably reduced, since a rapid drop in the pH of the eluate was observed after the addition of around 1 meq acid/g dry material. This behaviour was correlated to the partial reaction of alkaline phases such as portlandite and Ca-containing silicates with CO<sub>2</sub>. Conversely, the significant increase of the buffering plateau observed in the pH range from 4 to 6.5 was related to the higher calcite content of the carbonated slag. Besides a confirmation on the effects of the tested carbonation treatment on the mineralogy of the material, these results provide an indication on the pH value of the eluates that may be expected in a long-term perspective upon contact with

water under field conditions. From these results it appears hence that the pH of the leachate of the carbonated material may decrease to around neutral values, whereas that of the as received slag may most probably remain quite alkaline (above 11), if substantial natural weathering were not to occur.

The leaching curves of major elements as a function of pH, derived from the pHdependence test, are reported in Figure 3.10, together with the respective limits of quantification (LOQ). As can be observed in Figure 3.10, the shape of the Al leaching curve showed not to be noticeably modified upon carbonation, except at pH values above 12, for which a lower mobility was retrieved.



Figure 3.10. Leaching of major elements as a function of pH for the intermediate (0.177 < d < 0.84 mm) size fraction of as received and column carbonated SS slag (T = 23-25 °C; P = 1 bar; L/S = 0.2 l/kg; reaction time = 8 h). As a convention, data resulting below the LOQ are reported as half of the LOQ value.

Hence, the reduction observed in Al release upon the compliance leaching test may be related chiefly to the decrease in eluate pH. Regarding Mg, its solubility curve seemed to remain unvaried throughout the entire pH range, highlighting the negligible conversion of Mg into carbonate phases, as also indicated by the results of XRD analysis.

This behaviour was consistent with the results of the EN 12457-2 test and confirmed that Mg release from the carbonated slag was related to the decrease of the native pH of the slag upon carbonation rather than to a change in mineralogy and solubility-controlling phases.

Conversely, the leaching curve of Ca showed to be notably affected by carbonation, exhibiting a decrease in mobility at pH values higher than 6, proving the occurred conversion of the reactive phases into calcite as a result of the reaction with CO<sub>2</sub> and, subsequently, a change in the solubility-controlling phases compared to the as received slag (Huijgen and Comans, 2006; Baciocchi et al., 2009; van Zomeren et al., 2011). Si leaching curves for the as received and carbonated slag showed the same trend up to a pH value of around 10, from which the mobility of the as received slag showed to decrease sharply with increasing pH, while the eluate concentrations of the carbonated slag remained quite constant. This behaviour confirmed that at least part of the Ca silicate content of the material was significantly affected by the carbonation reaction. Similar results were also reported in previous studies (Huijgen and Comans, 2006; Baciocchi et al., 2010c) and explained by the fact that, during carbonation, a Ca-depleted silicate rim is formed around the slag particles, which causes the solubility of Si to be controlled by amorphous SiO<sub>2</sub> rather than Ca-silicate minerals (Huijgen and Comans, 2006).

The leaching of regulated elements as a function of pH is shown in Figure 3.11. In the same figure the limits imposed by the Italian legislation for material reuse (Ministerial Decree 186/06) and inert waste landfilling (Ministerial Decree 27/09/10) are also reported for comparison. The concentrations of Ba in the leachates dropped by several orders of magnitude upon carbonation with the most relevant changes occurring at pH higher than 7. Similar results were also found in a previous study carried out on steel slag carbonated in slurry phase under enhanced operating conditions (Huijgen and Comans, 2006) and attributed to the possible formation of a Ba-Ca carbonate solid solution, resulting in the

incorporation of Ba in a calcite structure and leading to a reduction of Ba release. The solubility curves obtained for the metalloids Cr, Mo and V appeared to be differently affected by carbonation. Cr leaching both before and after carbonation exhibited an amphoteric behaviour with a minimum solubility value between pH 6 and 10. The leaching behaviour of this element proved not to be considerably altered by carbonation, probably due to solubility control by Cr<sup>+3</sup>, as also reported in previous studies (Huijgen and Comans, 2006; Baciocchi et al., 2010c). For Mo, the leaching curves as a function of pH indicated only a negligible influence of the tested carbonation treatment on its release, with a slight decrease of leaching concentrations between pH 9 and 11. The slight mobilization effect of carbonation for Mo resulting from the batch compliance test may be also in this case most probably related to the variation in eluate pH; yet the shape of the leaching curves suggests that a minor decrease in release may be obtained if more relevant pH reductions were achieved upon carbonation. The shape of the leaching curves of V as a function of pH suggested instead that a change in solubility-controlling minerals occurred upon carbonation for a pH value above 11 and between 4.5 and 6. Specifically, in these pH ranges the as received slag exhibited an almost negligible release of V, while the mobility of this element proved significantly higher (especially at pH values above 11) in the eluates of the carbonated slag. A similar effect of carbonation on V leaching at alkaline conditions was reported also in other studies (Huijgen and Comans, 2006; van Zomeren et al., 2011) and attributed to the incorporation of this element in Ca phases such as dicalcium silicate that react during carbonation. However, observing the shape of the V leaching curve resulting for the carbonated sample, it may be expected that for long reaction times the pH of the treated sample could decrease further, approaching the leaching concentrations found for the as received slag at the same pH conditions.

Hence, it may be concluded that notwithstanding the rather mild operating conditions adopted in the carbonation column experiments and quite limited resulting CO<sub>2</sub> uptakes, the effects of the treatment on the leaching behaviour of the material proved relevant even for short reaction times and quite similar to those reported in studies carried out applying enhanced operating conditions (Huijgen and Comans, 2006; Baciocchi et al., 2010c). In addition, with regard to the behaviour of the material in the proposed in situ application, observing the trends of the acid neutralization capacity (Figure 3.9) and of the leaching

curves of the critical contaminants as a function of pH (Figure 3.11), it may be anticipated that, due to the expected decrease in pH to neutral values, the long-term release of the carbonated material in an application scenario may result significantly improved in the case of Cr, improved or at least similar to that of the as received slag (Ba and Mo), while still higher than that of the as received slag with respect to V.



Figure 3.11. Leaching of regulated elements as a function of pH for the intermediate (0.177 < d < 0.84 mm) size fraction of as received and column carbonated SS slag (T = 23-25 °C; P = 1 bar; L/S = 0.2 l/kg; reaction time = 8 h) and comparison with Italian regulatory limits. As a convention, data resulting below the LOQ are reported as half of the LOQ value.

# **3.4** Further investigation: combining the Ecogrout and carbonation processes

# 3.4.1 Introduction

The EcoGrout process is a new method for soil reinforcement and permeability reduction in development at Deltares (The Netherlands) and it is based on the overall reaction that drives the dissolution of calcite by natural shallow groundwater and precipitation of calcite in caves (Appelo and Postma, 2005). The process involves the reaction between calcium chloride (CaCl<sub>2</sub>) and dissolved sodium carbonate (NaHCO<sub>3</sub>) according to Eq. 3.3.

$$CaCl_2 + 2NaHCO_3 \rightarrow CaCO_3 + 2NaCl + CO_2$$
 Eq. 3.3

The reaction produces calcium carbonate (CaCO<sub>3</sub>) and carbon dioxide (CO<sub>2</sub>) in an equimolar ratio. The precipitation of calcite may cause an in-situ increase in stiffness and strength of the soil and a decrease in permeability while the produced CO<sub>2</sub> may potentially allow the in-situ stripping of volatile organic contaminants (VOCs) from groundwater. In addition, the upward CO<sub>2</sub> flow evolved from the Ecogrout process may stimulate the carbonation of an overlying layer of alkaline material, resulting in the improvement of its environmental properties as well as in CO<sub>2</sub> storage.

The Ecogrout process has been so far tested focusing on the improvement of the structural properties of gravel by means of calcite precipitation (Hartog et al., 2013) and on CO<sub>2</sub> stripping potential for different types of VOCs (van der Waals, 2013). However, the effects of a combined Ecogrout - carbonation process on the properties of alkaline residues had not been evaluated yet. This work was a first step towards the assessment of the applicability of the combined process in a Brownfield regeneration context and was mainly aimed at evaluating the effects exerted on the achieved CO<sub>2</sub> uptakes of the SS slag as a function of the conditions induced by the Ecogrout process.

A 3-stage sequential experimental investigation was carried out. In stage 1, column carbonation tests were carried out in order to investigate the influence of particle size on

the carbonation degree of the SS slag and evaluate the maximum CO<sub>2</sub> uptake achievable as a function of particle size, especially for longer reaction times than those considered in the previous phase of the experimental activities (24 hours). In stage 2 preliminary batch Ecogrout tests were performed in a lab-scale set-up in order to estimate the CO<sub>2</sub> flow evolved during the reaction as a function of the injection regime. In stage 3 combined tests were performed by assembling the set-ups used in the previous phases applying the operating conditions which gave the best results in the preliminary tests. Finally, to closely reproduce real scale conditions, a combined test was performed using a larger reactor with the aim of possibly estimating the differences in the carbonation degree as a function of the slag layer length and identify the possible criticalities of the coupled process in a real scale scenario.

#### 3.4.2 Materials and methods

#### 3.4.2.1 Carbonation tests

The results discussed in Paragraph 3.3.2, confirmed the strong influence of particle size on the reactivity of the alkaline material with CO<sub>2</sub> (Baciocchi et al., 2009), mainly due to the higher specific surface of the fine fraction (d < 0.177 mm) as well as differences in the mineralogy of the two size fractions analyzed (see Figure 3.3). Besides, the column carbonation experiments were mostly performed on the intermediate fraction of the SS slag (0.177 - 0.84 mm), assuming that the pressure drop through the column could become too high when employing a finer material. In order to better investigate this point, column carbonation tests were performed on the size fractions < 0.84 mm and < 2 mm, which represent about the 60% wt. and 75% wt. of the bulk material, respectively. Moreover, the slag appeared slightly hardened, suggesting that weathering reactions had occurred to a some extent. This hypothesis was confirmed by the evaluation of the carbonate content, measured by burning the samples at 600 °C to remove organic carbon and by analysing the inorganic carbon content with a carbon analyzer (Leco 3186 series) operating at 1350 °C. Indeed, the carbonate content of the intermediate fraction of the SS slag was found to be 4.7 %, more than 3 times higher than that observed during the previous experimental phase. Therefore, the column carbonation tests were performed also on the intermediate size fraction (0.177 - 0.84 mm) of the slightly weathered SS slag, in order to assess the potential differences in CO<sub>2</sub> uptakes as well as in the leaching behaviour in comparison with those obtained for the freshly produced SS slag. Finally, column carbonation tests were performed on the bulk SS slag (d < 10 mm), in order to assess the CO<sub>2</sub> uptakes potentially achievable in a real scale scenario when employing all the available material. Table 3.2 reports the CaCO<sub>3</sub> content of the tested size fractions of the slightly weathered SS slag.

The column carbonation tests were performed by following the experimental procedure described in Paragraph 3.2.2 at the operating conditions that gave the best results in the previous experimental phase (L/S ratio of 0.2 l/kg; water added by mixing). The experiments were carried out at ambient temperature (T = 22-25 °C) and pressure (Pco2 = 1 bar) for reaction times of 1, 2, 8 and 24 hours. At the end of the experiment, slag samples were collected from the top, middle and bottom level of the column and analyzed to determine their carbonate content. Selected unmilled samples obtained at different reaction times were collected for the leaching tests (EN 12457-2).

Size fraction	Particles dimensions (mm)	CaCO₃ content (% wt.)
A	0 - 0.84	6.9
В	0.177 - 0.84	4.7
C	0 - 2	6.1
D	0 - 10	6

Table 3.2. Initial characteristics of the SS slag as a function of particle size.

#### 3.4.2.2 Ecogrout tests

Batch Ecogrout tests were carried out in a plastic cylindrical reactor with a total volume of 7 L, whose steel cover was equipped with specifically designed holes for the inlet of reagents and for the outlet of the released  $CO_2$  as well as with a proper bore for the insertion of a pH sensor for continuously monitoring the pH of the Ecogrout solution.

For each test, CaCl<sub>2</sub> and NaHCO<sub>3</sub> solutions were prepared by dilution of a 2M CaCl<sub>2</sub> and a 1.19 M NaHCO<sub>3</sub> stock solutions, respectively. The headspace to total volume ratio was kept constant at a value of 0.7.

In each test, the NaHCO<sub>3</sub> solution was manually poured into the reactor whereas the CaCl<sub>2</sub> solution was injected with a peristaltic pump set at 10 ml/min, after tight closing the vessel. As preliminary Ecogrout tests performed without applying any stirring condition resulted to be not repeatable, the mixing of the CaCl<sub>2</sub> and NaHCO<sub>3</sub> reagents was maintained for the entire duration of the tests by continuously stirring the Ecogrout solution by means of a magnetic stirring bar and a magnetic plate set at 100 rpm. As soon as the injection of the CaCl<sub>2</sub> solution started, the Ecogrout reaction began leading to the precipitation of CaCO<sub>3</sub> and the release of CO<sub>2</sub> in the headspace. The released CO<sub>2</sub> flow was conveyed from the outlet hole of the reactor to a digital flowmeter (ADM Agilent 2000E) operating in the range 0.1 - 1000 ml/min and the flow rate data were recorded by hand. When the reaction reached the equilibrium, the test was interrupted and the pH and CO<sub>2</sub> flowrates were written down. The Ecogrout tests were performed at CaCl<sub>2</sub> and NaHCO<sub>3</sub> concentrations of 125, 250, 300 mM and 250, 500, 600 mM, respectively. All the tests were performed in duplicate.

# 3.4.2.3 Combined Ecogrout-carbonation tests

Combined Ecogrout- carbonation tests were performed by assembling the set-ups used in the previous phase, as reported in Figure 3.12, and following the experimental procedures described in Paragraph 3.4.2.1 and Paragraph 3.4.2.2. The tests were performed at concentrations of CaCl<sub>2</sub> and NaHCO<sub>3</sub> equal to 125, 250, 300 mM and 250, 500, 600 mM, respectively, and employing the class containing also the finest particles (Fraction A: < 0.84 mm) of the SS slag, since this size fraction showed the best results in the column carbonation tests in terms of the achieved CO<sub>2</sub> uptakes. All the combined Ecogrout – carbonation tests were performed in duplicate. After 90 minutes, slag samples were collected from the top, middle and bottom level of the column and analyzed to determine their carbonate content by calcimetry analysis of HCl-digested slag using a Dietrich-

Frülingh calcimeter. Selected unmilled samples were collected for the leaching tests (EN 12457-2).



Figure 3.12. Small set-up used to perform the combined Ecogrout-carbonation test.

In order to closely reproduce real scale conditions, a combined test was performed using a larger reactor with the aim of estimating the differences in the carbonation degree as a function of the slag layer height as well as identify the possible criticalities of the coupled process when applied in a real scale scenario. The set-up used to perform the test is reported in Figure 3.13. A reactor with an internal diameter of 94 cm and an internal height of 46 cm was poured with approximately 70 L of deionized water. Subsequently, about 300 kg of a uniform fine gravel ( $d_{95} = 2 \text{ mm}$ ) were inserted and compacted with a proper device. A blank test was performed by continuously injecting for 8 h 375mM CaCl<sub>2</sub> and 750 mM NaHCO<sub>3</sub> solutions at 100 ml/min along the entire height of the gravel by means of two different injection wells positioned at the centre of the reactor.



Figure 3.13. Large set-up used to perform the combined Ecogrout-carbonation test.

The level of the water inside the reactor was kept constant by means of an extraction well located at 40 cm from the injection wells. During the test, the produced gas was conveyed to a sealed steel chamber equipped with a Digitron CO<sub>2</sub> sensor (model HLX 85) connected to a data logger (Grant Instruments, model Squirrel SQ2010). The combined test was performed applying the same procedure and employing Fraction D of the SS slag, i.e. all the bulk material available. For the combined test, a properly designed layer of an inert porous material was located above the gravel to prevent the direct contact of the slag with water while all the available slag (about 7.5 kg) was placed on top of the layer and homogenously spread along the entire cross section of the reactor, providing a final height of the SS layer of about 2 cm. After 8 h, 11 slag samples of about 10 g each were collected from the points shown in Figure 3.14 and analyzed to determine the carbonate content of the entire material as well as of the finer size fraction of the slag (<

0.84 mm) by calcimetry analysis of HCl-digested slag using a Dietrich-Frülingh calcimeter.



Figure 3.14. Sampling points of the SS slag inside the reactor after the combined Ecogroutcarbonation test.

# 3.4.3 Results and discussion

## 3.4.3.1 Carbonation tests

In Figure 3.15, the main results obtained from the column carbonation tests performed on the slightly weathered SS slag are reported. Specifically, CO<sub>2</sub> uptake kinetics resulting for slag samples collected at different column heights are shown as a function of particle size. As can be observed, the highest CO<sub>2</sub> uptakes were attained for Fraction A (< 0.84 mm) and Fraction C (< 2 mm) of the SS slag, probably due to the fact that these size classes included the portion < 0.177 mm of the SS slag, which resulted to be highly reactive with CO<sub>2</sub> (see results shown in Paragraph 3.3.2). In fact, maximum CO<sub>2</sub> uptakes

of 11.3 and 10.1 % were obtained at a reaction time of 24 hours for Fraction A and Fraction C, respectively (see Figure 3.15a and Figure 3.15c). The finest portion of the SS slag seemed to exert a relevant influence also on the rise of CO<sub>2</sub> through the column. In fact relevant differences in the CO<sub>2</sub> uptake values obtained at different heights were particularly evident for Fraction A and Fraction C at the 1 h and 2 h tests. In spite of this, no pressure drop through the column was observed and for reaction times longer than 8 h the material appeared to react homogeneously with  $CO_2$ . In Figure 3.15b, the  $CO_2$  uptake kinetics resulting from the column carbonation tests performed on Fraction B (0.177 – 0.84 mm) are reported. It can be noted that carbonation kinetics proved to be slightly slower than that observed for the same fraction of the freshly produced SS slag, reported in Figure 3.5 of Paragraph 3.3.2. This result may be possibly ascribed to the partial conversion of fast-reacting phases such as Ca(OH)<sub>2</sub> into calcite as a result of natural weathering, which generally account for the first steep increase in the rate of CO<sub>2</sub> uptake with time (Huijgen et al., 2005). In spite of this, the slightly weathered SS slag showed an average CO<sub>2</sub> uptake comparable to that observed for the fresh slag for the 1 h and 2 h tests and slightly higher for the 8 h test (see Figure 3.5a). The size Fraction D of SS slag, which included the finest portion (< 0.177 mm) as well as the coarser one (> 2 mm) of the tested material, showed to react homogeneously with CO<sub>2</sub> already after 1 h, i.e. no significant differences of the CO<sub>2</sub> uptakes were noted at different column depths. Furthermore, despite the presence of coarse SS particle (> 2 mm), accounting for 25% of the bulk material, a maximum CO<sub>2</sub> uptake similar to that obtained for Fraction B was achieved after 24 h, highlighting the relevant influence of the finest portion (< 0.177 mm) on the global reactivity of the SS slag.

The SS size Fraction A, which showed the best results in terms of the achieved  $CO_2$  uptakes, was subjected to the standard compliance leaching test EN 12457-2. Moreover, the test was carried out also on Fraction B (0.177 - 0.84 mm), in order to assess potential differences in the leaching behaviour of the slightly weathered SS slag in comparison with that obtained for the freshly produced SS slag. The main results in terms of the eluate pH are reported in Figure 3.16.



Figure 3.15. CO<sub>2</sub> uptakes kinetics for the slightly weathered SS slag as a function of particle size at different column depths (T = 23-25 °C, P = 1 bar, L/S = 0.2 l/kg, water added by mixing); a) Fraction A: d < 0.84 mm; b) Fraction B: 0.177 < d < 0.84 mm; c) Fraction C: d < 2 mm; d) Fraction D: d < 10 mm.

As shown in Figure 3.16, the native pH of the eluates was high, above 12, and very similar for both size fractions. The results of the EN 12457-2 leaching compliance test after carbonation denoted a decrease in pH for all the carbonated samples. For Fraction B, the pH decreasing trend was slightly more pronounced and very similar to that obtained for the fresh slag (results shown in Paragraph 3.3.3.2). Moreover, longer reaction times (24 h) allowed the pH of the treated Fraction B to decrease further, to a value of 10.


Figure 3.16. Results of the EN 12457-2 test in terms of the eluate pH for fraction A (d < 0.84 mm) and fraction B (0.177 < d < 0.84 mm) as a function of reaction times.

The main results of the EN 12457-2 test in terms of leaching of major and regulated elements are reported in Figure 3.17. For the elements whose concentrations resulted lower than the instrumental quantification limit, the corresponding limit of quantification (LOQ) is reported and indicated in Figure 3.17 with a star. The leaching behaviour of the untreated SS slag was found to be very similar for both size fractions investigated, the only remarkable difference being noticed for Ba. As far as major elements are concerned, the results obtained for Fraction B were comparable to those obtained for the same fraction before natural carbonation occurred (see Paragraph 3.3.1), thus suggesting that the slight weathering of the SS slag did not imply significant modifications of the properties of the material and that several mineralogical species, e.g. Ca-Al silicates, where available to react with CO<sub>2</sub>. This finding could also explain the CO<sub>2</sub> uptake values obtained for Fraction B (see Figure 3.15b) which were found to be comparable or even higher than those observed for the fresh slag (see Figure 3.5a). The elements which resulted to be mainly influenced by carbonation were Ca and Si. For both size fractions, Ca concentrations in the eluates of the carbonated slag were significantly reduced, up to one order of magnitude, revealing the formation of less soluble phases, e.g. calcite, than that characterizing the untreated slag (Huijgen and Comans, 2006; Baciocchi et al., 2010a;

van Zomeren et al., 2011). Conversely, Si leaching concentrations increased upon carbonation, due to the conversion of the original silicate minerals into more soluble phases (Huijgen and Comans, 2006). The result of the compliance leaching test performed on carbonated samples revealed a similar behaviour for both size fractions in terms of leaching of regulated elements.



Figure 3.17. Comparison of the EN 12457-2 test results of SS slag before and after column carbonation as a function of size fractions: (a) Fraction A (d < 0.84 mm); (b) Fraction B (0.177 < d < 0.84 mm). Black stars refer to the limit of quantification of the specific element.

Besides, the release of Ba, Cr, Mo and V from the 2 h and 8 h carbonated samples proved similar to that already found as a result of the preliminary column carbonation tests (compare Figure 3.17 with Figure 3.4). Moreover, a further mobilization effect of

carbonation was observed at longer reaction times for Mo and V, while Cr leaching remained substantially unchanged.

#### 3.4.3.2 Ecogrout tests

The main results of the Ecogrout tests are reported in Figure 3.18. Specifically, Figure 3.18a reports the results of two duplicate tests performed employing 250 mM of CaCl<sub>2</sub> and 500 mM of NaHCO<sub>3</sub> in terms of pH of the Ecogrout solution and of the measured CO<sub>2</sub> flow rates as a function of time. During the first 20 minutes of the test, the gas flow rates were found to increase sharply with time while the pH values progressively decreased up to a minimum value of about 5.5, achieved at 20 minutes. At this time, a corresponding maximum gas flow rate equal to 420 ml/min was obtained. The Ecogrout reaction seemed to reach completion after about 40 minutes; indeed for longer times a relevant modification of the pH as well as of the gas flow rates did not occur. Figure 3.18b reports the obtained CO<sub>2</sub> flow rates as a function of the CaCl<sub>2</sub> and NaHCO<sub>3</sub> injection concentrations.



Figure 3.18. Results of the Ecogrout tests in terms of: a) pH and CO<sub>2</sub> flowrates for the test performed at 250 mM CaCl<sub>2</sub> and 500 mM NaHCO<sub>3</sub>; b) CO<sub>2</sub> flowrates as a function of CaCl<sub>2</sub> and NaHCO<sub>3</sub> injection concentrations.

The average CO<sub>2</sub> volume produced as a result of the Ecogrout reaction, estimated from the measured flow rates, was found to be around 7.5 and 9.5 L for the 250, 300 mM CaCl<sub>2</sub> tests, respectively. This result was not really in line with the stoichiometric CO<sub>2</sub> volumes potentially achievable, estimated by assuming CO<sub>2</sub> as a perfect gas and a constant temperature of 22 °C, which were found to be of around 6 and 7.2 L for the 250, 300 mM CaCl<sub>2</sub> tests, respectively. However, the differences between the estimated CO<sub>2</sub> volumes and the stoichiometric ones could be due to the combination of several factors, among others the assumptions made as well as the possible errors in the measurements of the actual CO<sub>2</sub> flow rates.

Regarding the 125 mM CaCl<sub>2</sub> test, the achieved CO<sub>2</sub> flow rates did not allow to obtain a sufficient CO<sub>2</sub> volume to replace completely the air volume of the headspace. Indeed, the estimated CO<sub>2</sub> volume was found to be lower than the headspace volume and around 2 L.

#### 3.4.3.3 Combined Ecogrout-carbonation tests

The main results of the combined Ecogrout –carbonation tests performed employing the set-up shown in Figure 3.12 are reported in Figure 3.19. Specifically, the CO<sub>2</sub> uptakes obtained for Fraction A of the SS slag at different column heights are reported as a function of the CaCl<sub>2</sub> and NaHCO<sub>3</sub> concentrations. As can be noted, the CO<sub>2</sub> uptakes obtained from the test performed at the lowest concentrations of CaCl<sub>2</sub> and NaHCO<sub>3</sub> were appreciable only at the bottom of the column. These results confirmed those attained in the Ecogrout tests, i.e. an insufficient CO<sub>2</sub> volume to completely replace the headspace of the Ecogrout reactor and flow through the SS slag inside the column. For higher CaCl<sub>2</sub> and NaHCO3 concentrations, the CO2 released from the Ecogrout reaction seemed to react quite homogenously with the SS slag, allowing to achieve an average CO<sub>2</sub> uptake of 7.2 and 7 % for the 250 and 300 mM CaCl<sub>2</sub> tests, respectively. Furthermore, the achieved CO<sub>2</sub> uptakes were found to be significantly higher than those obtained as a result of column carbonation tests performed at similar reaction times (see Figure 3.19b). This result was ascribed to the higher CO<sub>2</sub> volumes attained as a result of the Ecogrout reaction compared to that employed to perform carbonation tests, i.e. about 1.2 L at 2 h of treatment



Figure 3.19.  $CO_2$  uptakes resulting from the combined Ecogrout - carbonation tests as a function of CaCl<sub>2</sub> and NaHCO<sub>3</sub> concentrations at different column heights (a) and comparison with the average  $CO_2$  uptakes kinetics obtained as a result of the column

carbonation tests (b).

Moreover, this result suggested that appreciable  $CO_2$  uptakes may be possibly achieved at low contact times between  $CO_2$  and SS slag. Indeed, the estimated contact times between  $CO_2$  and the SS slag for the 250 and 300 mM CaCl<sub>2</sub> tests were around 8 and 10 times lower than those observed for the column carbonation tests, respectively.

The significant carbonation degree of the slag was confirmed by the standard compliance leaching test performed on the carbonated SS slag obtained from the 300 mM CaCl<sub>2</sub> test, whose main results are shown in Figure 3.20. Besides allowing a decrease of the eluate pH to 11, the combined treatment also influenced the leaching behaviour of both major and regulated elements, providing similar qualitative effects to those found as a result of the column carbonation tests performed of the same size fraction and at similar reaction times (see Figure 3.17a). Nevertheless, probably due to the higher CO<sub>2</sub> volumes involved, the effects of carbonation were more pronounced for the SS slag resulting from the combined process.



Figure 3.20. Comparison of the results of the leaching test on Fraction A (d < 0.84 mm) of SS slag before and after the combined Ecogrout – carbonation test (300 mM CaCl<sub>2</sub>; 600 mM NaHCO<sub>3</sub>) in terms of: a) major elements and b) regulated elements. Black stars refer to the limit of quantification of the specific element.

Regarding the test performed in the larger reactor, the theoretical CO<sub>2</sub> volume releasable as a result of the Ecogrout reaction at the set CaCl<sub>2</sub> concentration (375 mM) was estimated to be around 440 L, this amount being sufficient to replace the headspace volume (147 L) up to three times. However, the CO<sub>2</sub> concentrations measured at the outlet of the reactor during both the blank and the combined test were slightly higher than the CO<sub>2</sub> concentration in the air and significantly lower than  $10^6$  ppm, i.e. around 700 ppm. This result was probably due to the poor stirring conditions achieved in the large set-up, which may hinder the mixing of CaCl<sub>2</sub> and NaHCO<sub>3</sub> and therefore the Ecogrout reaction. This hypothesis may be confirmed by further analysis aimed at determining the Ca<sup>2+</sup> concentrations in water and/or the amount of calcite precipitated in the pores of the gravel as a result of the Ecogrout reaction. As far as the carbonation of SS slag is concerned, negligible CO<sub>2</sub> uptakes were obtained for all the collected samples, regardless of the distance of the sampling points from the injection wells as well as of the size fraction analyzed. This result could be attributed to the weak mixing of reagents as well as to the formation of preferential pathways through the slag layer for CO<sub>2</sub> escape. While the latter drawback could be possibly avoided by discarding the coarser fraction of SS slag, the influence of the regime and mixing conditions on the Ecogrout reaction must be further elucidated.

# 4 CONCLUSIONS AND FINAL REMARKS

Brownfield regeneration is a relevant issue in the European Union, where two contradictory socio-economical phenomena are occurring: on the one hand an increasing number of industrial activities are being shutdown, resulting in large abandoned Brownfields, whereas on the other hand Greenfields are still being consumed for new commercial and residential construction projects. In order to make Brownfields more attractive, different actions can be taken. These include actions aimed at making their regeneration easier and more sustainable. Making reference to the specific issue of excavated soil and residues, the traditional bottom-up approach used in selecting the best technology for the clean-up of a contaminated Brownfield site has to be coupled with a top-down one, which starts from the identification of the services required, to drive the selection of the technologies that allow to obtain them. As excavated soil and residues are generally characterized by a certain extent of contamination, selected remediation technologies which are able to meet specific remediation objectives, while also producing a material with specific properties, were discussed in Chapter 1. Furthermore, in order to establish a link between input materials available at the Brownfield site and the required output materials, combination of technologies (i.e. technology trains) were proposed, which allow to provide an effective answer to the issue of reusing excavated materials originating from the Brownfield regeneration process. Specifically, technology trains based on coupling stabilization/solidification, granulation and carbonation with each other and other preliminary treatments were shown to be promising options to obtain "products" with environmental and mechanical properties that may be suitable for civil engineering applications, such as road pavements or concrete production.

A step forward for the assessment of the applicability of a specific technology train to a Brownfield metal-contaminated soil was addressed in Chapter 2. Specifically, the effects of a combined S/S - granulation treatment applied to the fine fraction (d < 2 mm) of an

industrial soil sampled from a Brownfield site were evaluated in terms of the particle size, mechanical strength and leaching behaviour resulting for the produced aggregates. The results obtained from the treatment of the natural soil, besides confirming previous findings of the granulation process, i.e. the relevant influence of the L/S ratio on the growth and compaction of the granules, helped to define the preliminary operating windows of the combined process. Specifically, the findings showed that the type of cement employed was the factor that most influenced the particle size and mechanical strength (measured in terms of ACV) of the aggregates. In particular, the use of a highperformance cement (R 52.5) seemed to be the most prominent requirement for obtaining granules with mechanical properties approaching those of natural gravel (ACV  $\sim 20\%$ ), while the type and amount of superplasticizer proved to be less relevant. Moreover, the outcome of the preliminary tests allowed to identify an optimum operating range for the tested technology train also in terms of binder content and suggested that the use of cement to solid ratios higher than 30% wt. may result in a significant decrease of the mechanical performance of the final product, regardless of the type of cement employed. The results obtained applying the proposed technology train at the industrial soil highlighted the relevant role of both soil properties and binder composition on the properties of the resulting product. Indeed, the use of the acrylic additive (at 2% wt.) and especially of a higher cement content (30% wt.) appeared to yield a noteworthy improvement of the mechanical performance of the aggregates obtained from the S/S – granulation treatment of the soil characterized by the highest fraction of organic carbon. The treatment proved to be less efficient in improving the environmental behaviour of the treated soil in terms of the release of certain metals, especially Cu. Nevertheless, the increased mobilization of Cu, Ba and Cr was mainly ascribed to the characteristics of the cement used as a binder, which showed to release significant concentrations of these metals. In addition, the leaching of the above mentioned elements is pH dependent and can increase in the alkaline environment produced as a result of the cement-based treatment. Despite the increased release of certain elements, the result obtained in this work suggested that the proposed technology train may be an effective treatment for obtaining a product with mechanical and environmental properties suitable for

construction applications from a Brownfield contaminated soil, once that the appropriate type and amount of binder are selected.

The feasibility of in-situ carbonation as a treatment technique aimed at improving the environmental behaviour of alkaline industrial materials and to store the CO<sub>2</sub> generated from remediation/regeneration processes in a Brownfield site was demonstrated through lab-scale carbonation column tests performed on stainless steel slags at operating conditions expected for field-scale application, i.e. ambient temperature and 1 bar CO<sub>2</sub>. The results showed that, even at the mild operating conditions tested, a significant degree of carbonation could be achieved. Namely, an average CO<sub>2</sub> uptake of 6% was obtained for the intermediate size fraction of the material (0.177 - 0.84 mm) after 8 hours of reaction. Despite this value being significantly lower than the 14% uptake achieved for the same reaction time by carbonation of the fine size fraction (d < 0.177 mm) at enhanced operating conditions (T =  $50^{\circ}$ C, P = 10 bar), the tested column carbonation treatment significantly affected the mineralogy and environmental properties of the slag. The XRD patterns indicated a clear decrease of portlandite and a slighter one of Ca-Al silicate and melilite peaks, as a result of the carbonation reaction, that was confirmed by the relevant increase of calcite peaks as well as by the results of IC analysis of the treated samples. As far as the leaching behaviour is concerned, the results of the compliance test showed a decrease of the eluate pH well below the limit for reuse set by the Italian national legislation. As to the behaviour of regulated trace compounds, barium and chromium leaching was improved after carbonation, although the eluate concentration was still above the limit for reuse for the latter element; the opposite behaviour was observed for vanadium and molybdenum, whose eluate concentration remained anyhow below the corresponding limits. Based on the results obtained from pH-dependence tests, the behaviour observed for chromium and molybdenum was explained by the reduction of eluate pH occurring after carbonation, that of barium with the possible formation of Ba-Ca carbonate solid solutions, whereas that of vanadium was attributed to its incorporation in Ca phases, such as dicalcium silicate, that react during carbonation. The results of the acid neutralization test also showed that a further reduction of the eluate pH to fairly neutral values could be expected in a long-term perspective upon contact with water. The

coupling of the carbonation treatment with the Ecogrout process showed that significant CO<sub>2</sub> uptakes (around 7%) could be potentially achieved in a relatively short timeframe (90 min) and that the release of both major and regulated elements may be strongly affected in a combined scenario. Hence, the results obtained in this work suggested that an in-situ carbonation process which exploits a CO<sub>2</sub> upward flow at mild operating conditions may be a feasible option for the improvement of the environmental properties of alkaline residues in Brownfield sites. However, the combined Ecogrout – carbonation tests performed at larger scale highlighted that the poor mixing of the CaCl<sub>2</sub> and NaHCO<sub>3</sub> solutions within the porous medium may hinder the Ecogrout reaction, and consequently the CO<sub>2</sub> release, to a relevant extent. As far as the conditions of applicability of the combined process are concerned, this finding suggests that the soil texture is one of the key factors which mainly influence the performance of the combined process in a real scale scenario and that its application in presence of a soil with a fine texture could be not recommended. Moreover, the influence of the injection conditions of the CaCl<sub>2</sub> and NaHCO<sub>3</sub> solutions into the subsoil on the Ecogrout reaction must be further elucidated, e.g. by performing blank tests varying the relative position as well as the depths of the injection wells and the injection mode of the reagents (continuous or pulsed).

Thus summarizing, the techniques investigated in this work may represent a feasible opportunity for increasing the role of in-situ technologies aimed at soil reuse within remediation and Brownfield regeneration projects. Nevertheless, the results obtained for the more consolidated technique investigated in this work, the S/S one, showed how the success of the proposed technologies very strongly depend upon the operating conditions applied and the properties of the starting materials. The possibility of applying the carbonation concept, especially in the framework of the Ecogrout process, is surely more intriguing and the proof of concept was positive, but more efforts are eventually required to make it ready for field application and the conditions for its application need to be made more clear.

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## **PUBLICATIONS**

### Scientific journal

Capobianco, O., Costa, G., Thuy, L., Magliocco, E., Hartog, N., Baciocchi, R., 2014. Carbonation of stainless steel slag in the context of in situ Brownfield remediation. Minerals Engineering 59, 91-100.

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### In preparation

- Capobianco, O., Costa, G., Baciocchi, R.. Cement-based granulation of Brownfields soil for aggregates production. In preparation.
- Capobianco, O., Costa, G., Baciocchi, R.. Technology trains as a tool for reusing Brownfield's excavated materials. In preparation.