Università degli Studi di Cagliari

Facoltà di Ingegneria
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Stabilization of MSW combustion residues by accelerated carbonation treatment and their potential carbon dioxide sequestration

Dott. Martina Piredda

Tutor: Prof. Ing. Aldo Muntoni and
Dott. Ing. Giovanna Cappai

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Abstract

The main objective of the Integrated Waste Management System is to consent an environmentally and economically advantageous way to sustain the continuous increasing volumes of municipal waste products.

Nowadays thermal treatment of municipal solid waste represents the main option for reducing the volume by up to 90 %; nevertheless the combustion process generates solid residues, as well as atmospheric emission, the latter containing acid gases and about 12 % of carbon dioxide which require proper treatment.

In particular, municipal solid waste (MSW) combustion residues, produced during the waste to energy (WtE) process, are landfilled or reused. Landfill space limitations and EU Landfill Directive (CEU 1999) push to adopt reuse and recycling strategies. Recycling of waste material is becoming the main objective in the field of integrated waste management system.

The material residues produced by thermal treatment are represented by bottom ash (BA), fly ash (FA) and flue gas cleaning ash. Bottom ash is the most significant product of combustion, in fact it accounts for 85 %; FA and flue gas cleaning are commonly collected together in electrostatic precipitators or fabric filter devices. This side product is normally called air pollution control (APC) and represents 1.5 – 2 % of the total waste mass combusted.

In several European countries, BA is used as a secondary building material; in fact the sand and gravel fractions can be used in concrete bricks, in road sub-bases or in foundations, whilst APC might be used in cement production.

Municipal solid waste combustion BA and APC residues are considered respectively as a non hazardous and a hazardous waste material, because they potentially release metals, toxic organic substances and soluble salts into the environment, thus landfilling or recycling options require a pre-treatment.

Many treatments have been proposed and are used to reduce the mobility of the hazardous compounds, generally contained in all combustion residues, thus reducing the impact of the landfilling or reusing of these materials. Among the different treatment options, the ageing processes (weathering) and the water washing treatment have been recently introduced.

Regarding the ageing process, carbonation is one of the main reactions involved during the process and seems to be one of the most interesting techniques to reduce the metal release by metals immobilization. The carbonation process stabilises the material by changing its mineralogical characteristics and, it has shown a positive effect on heavy metal mobility. Nowadays, in France for 64 % of BA a period of ageing treatment is required before reuse and BA is stocked for several months in weathering areas. In the case of BA, the source of carbon dioxide in weathering areas could be the carbon dioxide contained in the air, however, other flue gas rich in CO_2 might be used, as well as the adoption of several parameters during the process which help to improve the kinetics of the reaction, which are generally quite slow.

Carbon dioxide (CO_2) represents 0.039 % of the atmosphere and it is considered a greenhouse gas deriving largely from human activity. It is mostly released by the energy production process which is based on the combustion of fossil fuels and biomass, from the burning of forests and by industrial and resource extraction processes. One of the ultimate objectives of the United Nations Framework Convention of Climate change (UNFCCC) is “the stabilisation of greenhouse gas concentrations in the atmosphere at a level that prevents dangerous anthropogenic interference with the climate system”. For this purpose, the capture of CO_2, contained in stack gas, also produced by thermal treatment of waste, might contribute to decrease the emission of greenhouse gas.

In this contest, carbonation treatment of combustion residues might combine the clearly positive effect caused on reduction of metal mobility and, as a consequence, on metal release, with the side effect of carbon dioxide reduction.

When dealing with residues with high content of soluble chlorides and sulphates, such as APC ash, the water washing treatment seems to be the best option in order to remove soluble salts. Unfortunately, when ash is mixed with water, not only chlorides pass into the solution, but some heavy metals are leached out. In this frame, a first carbonation treatment, which might produce metals immobilisation, followed by a water washing treatment, that removes chlorides and sulphates might help to obtain a stabilized APC residue and a wastewater deprived of heavy metals.

The main objectives of this doctoral thesis were to: (i) investigate the effects of the direct aqueous accelerated carbonation process, applied on BA, its particle size fractions and APC ash residues, in order to gain new insight on the chemical and mineralogical changes for each type of material; (ii) evaluate the effect of a combined treatment "carbonation + washing", applied on APC ash in terms of chlorides and metal release; (iii) evaluate the CO_2 sequestration capacity of residues under investigation. The first objective was reached by applying the direct aqueous accelerated carbonation on MSW combustion BA and its particle size fractions. It was performed by placing moistured (20 % by weight) samples into a CO_2 incubator chamber. The temperature was set at 40 °C. The BA was exposed to an atmosphere characterized by a 10 – 20 % by volume CO_2 content. The effects produced by carbonation treatment on the metals mobility was investigated by different leaching tests, performed on untreated and carbonated material.

In the case of APC ash, the accelerated carbonation treatment was applied on residue in the slurry phase (L/S = 2.5) and by bubbling 100 % by volume of CO_2. The temperature was set at 20° - 25 °C. In order to asses the best conditions to reduce metals mobility, the process was interrupted at different levels of final pH. A sample of the slurry phase was collected, dried and the leaching test was performed.

The second objective was reached by applying the water washing treatment on carbonated APC ash. The washing treatment was studied by adopting several L/S ratio (2.5, 5, 7 e 10) and several times of contact (1, 15, 30, 60 e 120 min). The best conditions were selected on the basis of the chlorides and metals release and by comparing from the behaviour of fresh and carbonated APC ash.

The third objective focused on the application of accelerated carbonation treatment on residues under investigation in order to asses the potential of the process in terms of sequestration of the CO_2 emitted from WtE plant. To evaluate the CO_2 uptake of ashes, thermal analysis and calcimetry were performed on untreated and carbonated residues.

As for the effects of accelerated carbonation on the metal leaching behaviour of the studied alkaline residues, significant results were obtained for both BA and APC residues.
In the case of BA residue, carbonation treatment proved to be effective in reducing the mobility of Pb and Cu, whilst increased the Mo mobility and did not show any significant effect on Zn and Cr. When the single size fractions were considered, the effects on Pb (decreased mobility) and Mo (increased mobility) were fairly homogenous for all the size fractions, whilst the overall positive effect on Cu mobility seemed to derive mainly from the particles having < 1.0 mm in size. The effect of carbonation on Cr mobility seemed to be negative for fractions as above particle size < 1.0 mm. Carbonation treatment on APC

ash was able to reduce the release of Pb, Zn, Cr, Cu and Mo, with an optimal final pH, identified on the basis of the demobilization effect, close to 10.5. Nevertheless, along the whole studied pH range ($13.17 < pH < 8.22$), a mobilization effect was noticed for Sb. No effect was observed in chlorides release in the pH range studied.

On the basis of the experimental findings, it could be assessed that the aqueous accelerated carbonation treatment, applied on BA and APC ash residues, exerted a immobilization effect on several elements, but the combination with other process might be necessary to immobilise some oxyanion metals (e.g. Cr, Sb or Mo), as well as to reduce the chloride release by APC ash. In this contest, the application of a water washing treatment could help to remove soluble chloride and metal from fresh and carbonated APC ash. The process have shown good results in terms of chloride reduction in residue when a L/S = 2.5 l/kg and a washing time between 1 – 15 minutes were used. When the treatment was applied on carbonated APC ash (final pH= 9.60), the metal release was reduced respect to it showed for the fresh residue (except Sb and Cr). The Sb and Cr mobility is strongly influenced by the extent of carbonation, thus it implies that the first step of the combined process should be opportunely performed, for example by a strict control of pH during the process.

The CO_2 sequestration capacity of BA was about 5 - 9 % by weigh of residue in the finest particle fraction and between 3 - 4 % in the coarse fraction. In the case of APC ash, the estimated CO_2 uptake was close to 20 %. These results are consistent with several other experiences reported in the literature.

The carbonation treatment can be thus considered as a potentially viable option in order to improve the environmental behaviour of combustion residues and reduce CO_2 emissions from Waste to Energy plants. In case of APC ash, the application of the carbonation treatment to reduce the CO_2 emissions appears not a feasible process, because the scarcity of residue produced in spite of the high sequestration capacity.

Sommario

Il Sistema Integrato dei Rifiuti ha il fine sostenere il continuo incremento dei volumi di rifiuti prodotti attraverso che permetta di una gestione economicamente vantaggiosa e rispettosa dell’ambiente.

Attualmente, il trattamento termico dei rifiuti rappresenta l’opzione principale per ottenere una riduzione del volume del materiale fino al 90 %; tuttavia la combustione è un processo che produce residui solidi, così come emissioni che contengono gas acidi, e circa il 12 % di anidride carbonica, contribuendo all’inquinamento atmosferico.

I residui solidi prodotti durante il processo di termovalorizzazione dei rifiuti solidi urbani (frazione secca residua) possono essere smaltiti in discarica o riutilizzati/riciclati. La Direttiva dell’UE (CEU 1999), insieme alla difficoltà di reperire spazi disponibili per la realizzazione di nuove discariche, spingono ad adottare le strategie del riutilizzo e del riciclo. Riciclare i materiali di scarto è infatti uno dei principali obiettivi del sistema integrato di gestione dei rifiuti.

I residui solidi prodotti dalla combustione dei rifiuti sono sostanzialmente le scorie di fondo, le ceneri volanti e le ceneri prodotte dal trattamento dei gas acidi.

Le scorie di fondo rappresentano il residuo più abbondante, circa l'85 %; le ceneri volanti e le ceneri prodotte dal trattamento dei gas acidi sono generalmente raccolte insieme nei sistemi filtranti. Il materiale residuo ottenuto è denominato ceneri APC (air pollution control) e rappresenta l’1,5 – 2 % della massa totale combusta.

In diverse nazioni della Comunità Europea, le scorie di fondo sono spesso utilizzate come materie prime seconde per costruzioni, infatti le frazioni sabbiosa e ghiaiosa possono essere adoperate per produrre mattoni, nei sotto fondi stradali o nelle fondazioni; le ceneri volanti possono essere utilizzate nella produzione di cemento.

Le scorie di fondo e le ceneri APC sono considerate rispettivamente un rifiuto non pericoloso e pericoloso a causa del rilascio nell’ambiente di metalli pesanti, sostanze organiche tossiche e sali solubili; inoltre i cloruri contenuti nelle ceneri APC possono corrodere l’acciaio. Date queste considerazioni, prima di smaltire il residuo in discarica o di riutilizzarlo/riciclarlo, è quasi sempre necessario un pre-trattamento.

Sono stati messi a punto molti trattamenti per ridurre la mobilità di composti tossici e pericolosi contenuti nei residui da combustione dei rifiuti. Tra questi processi rientrano

l'invecchiamento artificiale delle scorie di fondo e il lavaggio delle ceneri APC. La carbonatazione è la principale reazione chimica coinvolta nel processo di invecchiamento naturale e sembrerebbe la tecnica attualmente più interessante ai fini della riduzione del rilascio dei metalli dai residui da combustione. La carbonatazione determina variazioni chimiche e mineralogiche del residuo che spesso hanno come conseguenza l'immobilizzazione di metalli tossici.

In Francia il 64 % delle scorie di fondo è sottoposto ad un processo di carbonatazione della durata di alcuni mesi, realizzato attraverso stoccaggio delle scorie in specifiche aree.

Nel caso delle scorie di fondo, per realizzare il processo di carbonatazione, la sorgente di anidride carbonica può essere l'aria; tuttavia potrebbe anche essere utilizzata la stessa corrente gassosa emessa in atmosfera in seguito alla combustione. Il processo può inoltre essere condotto in modo da migliorare la cinetica della reazione, abbastanza lenta in condizioni naturali.

L'anidride carbonica (CO_2) costituisce lo 0.039 % dell'atmosfera ed è considerata un gas serra, prodotto soprattutto da attività umane. E' uno dei gas rilasciati dalla combustione del carbone fossile e delle biomasse, dalla combustione provocata dagli incendi delle foreste, da processi industriali ed estrattivi. Uno degli ultimi obiettivi della United Nations Framework Convention of Climate Change (UNFCCC) è "la stabilizzazione delle concentrazioni dei gas serra nell'atmosfera a livelli tali da prevenire pericolose interferenze antropogeniche con il sistema climatico". A tale scopo, il sequestro della CO_2 contenuta nella corrente gassosa prodotta dal trattamento termico dei rifiuti, potrebbe portare al duplice vantaggio di ridurre le emissioni del gas serra e migliorare il comportamento ambientale dei residui attraverso la riduzione della mobilità dei metalli.

Nel caso delle ceneri APC, il trattamento più vantaggioso per rimuovere i cloruri e i solfati è il lavaggio con acqua, adottato. Sfortunatamente, quando la cenere è miscelata con l'acqua, in soluzione passano anche alcuni metalli pesanti. Ciò suggerisce una potenziale integrazione tra i due trattamenti di carbonatazione e washing, il primo inteso a ridurre la mobilità dei metalli, il secondo, applicato a valle del primo, volto alla rimozione dei sali solubili, con produzione di un'acqua di rifiuto con bassi livelli di contaminazione da metalli pesanti.

I principali obiettivi di questa tesi di dottorato sono stati: (1) valutare gli effetti causati della carbonatazione accelerata in fase acquosa applicata alle scorie di fondo (distinguendo anche la risposta delle diverse frazioni granulometriche) e alle ceneri APC, attraverso lo studio delle trasformazioni chimiche e mineralogiche dei materiali; (2) valutare l'effetto del trattamento combinato "carbonatazione + lavaggio" applicato alle ceneri APC in termini di rilascio di cloruri e metalli; (3) valutare la capacità di sequestro della CO_2 da parte dei residui oggetto di indagine.

Il primo obiettivo è stato raggiunto trattando con la carbonatazione accelerata le scorie di fondo e le relative frazioni granulometriche. Il trattamento è stato effettuato all'interno di un incubatore ad anidride carbonica, operante ad una temperature di 40 °C, su campioni di scoria umidificati al 20 % e con un'atmosfera caratterizzata dal 10 – 20 % in volume di CO_2.

Nel caso delle ceneri APC, il trattamento di carbonatazione accelerata è stato eseguito in fase slurry (L/S = 2.5 l/kg), insufflando il 100 % in volume di CO_2.

La temperatura di esercizio è stata mantenuta a 20° - 25 °C. Con il fine di individuare le migliori condizioni che consentissero la riduzione della mobilità dei metalli, il processo è stato interrotto al raggiungimento di differenti valori prefissati di pH.

Gli effetti prodotti dalla carbonatazione accelerata sulla mobilità dei metalli sono stati verificati tramite prove di lisciviazione su campioni di scorie e ceneri APC non trattati e cartonatati.

Il secondo obiettivo è stato raggiunto applicando il lavaggio con acqua alle ceneri APC carbonatate. Il lavaggio con acqua delle ceneri APC è stato eseguito utilizzando diversi rapporti L/S (2,5 – 5 - 7 e 10 l/kg) e diversi tempi di contatto (1, 15, 30, 60 e 120 minuti). Le condizioni migliori sono state selezionate sulla base del rilascio di cloruri e metalli pesanti e confrontando il comportamento delle ceneri APC fresche e carbonatate (eccetto per Sb eCr). La mobilità del Sb e Cr è notevolmente influenzata dal livello di carbonatazione, così il primo passaggio del trattamento combinato dovrebbe essere opportunamente controllato, per esempio attraverso di uno stretto controllo del pH.

Il terzo obiettivo poneva l'attenzione sull'applicazione della carbonatazione accelerata ai residui oggetto di studio per valutare la capacità di sequestro della CO_2 emessa dagli impianti di termovalorizzazione.

Per valutare la CO_2 captata da scorie e ceneri, è stata eseguita l'analisi del contenuto di carbonato tramite la termogravimetria e la calcimetria, sia su campioni freschi che carbonatati.

Con riferimento agli effetti provocati dalla carbonatazione accelerata sulla lisciviazione dei metalli pesanti da parte dei residui da combustione studiati, sono stati ottenuti risultati significativi, sia nel caso delle scorie di fondo, sia nel caso delle ceneri APC.

Nel caso delle scorie di fondo, il trattamento di carbonatazione accelerata ha effettivamente provocato la riduzione della lisciviazione di Pb and Cu, mentre si è verificato un incremento della lisciviazione del Mo e nessun effetto significativo sulla lisciviazione di Zn and Cr.

Considerando le singole frazioni granulometriche, l'effetto sul Pb (riduzione della mobilità) e sul Mo (aumento della mobilità) è risultato omogeneo su tutte le frazioni considerate, mentre l'effetto positivo mostrato dal ridotto rilascio del rame da parte delle scorie, è sembrato dipendere principalmente dalle particelle con dimensione < 1,0 mm. L'effetto della carbonatazione sulla mobilità del Cr ha mostrato risultati negativi per le frazioni di scoria con dimensione < 1,0 mm.

Il trattamento di carbonatazione accelerata sulle ceneri APC, considerando un pH di fine trattamento prossimo a 10,5, ha permesso di ridurre i rilasci di Pb, Zn, Cr, Cu e Mo. Tuttavia all'interno del campo di pH studiato (13,17 < pH < 8,22), si è verificato un effetto di mobilizzazione dell'Sb. Nessun effetto provocato dalla carbonatazione è stato osservato nel rilascio dei cloruri nel campo di pH adottato.

Sulla base dei risultati sperimentali ottenuti, si è potuto evidenziare che la carbonatazione accelerata in fase acquosa, applicata su scorie e ceneri APC, è in grado di provocare effetti positivi in termini di riduzione della mobilità di alcuni metalli pesanti; tuttavia l'utilizzo di un processo aggiuntivo potrebbe comunque essere necessario per immobilizzare alcuni metalli presenti come ossi-anioni (e.g. Cr, Sb or Mo), così come per ridurre il rilascio di cloruri da parte delle ceneri APC. In questo ultimo caso, applicando il lavaggio con acqua alle ceneri APC precedentemente carbonatate a pH ~ 10, il risultato migliore, in termini di rimozione del cloruro e consumo di acqua di lavaggio, è stato ottenuto utilizzando un rapporto L/S = 2.5 L/kg.

Il sequestro di CO_2, valutato per le scorie di fondo, è stato del 5 - 9 % in peso nelle frazioni più fini ed ha assunto valori inferiori, pari al 3 - 4 %, nelle frazioni grossolane. Nel caso delle ceneri APC, la CO_2 sequestrata è risultata pari al 20 % in peso, in concordo con i dati ottenuti da altre sperimentazioni.

La carbonatazione accelerata può dunque essere considerata una tecnica capace di migliorare il comportamento ambientale dei residui da termovalorizzazione e ridurre le emissioni di CO_2 prodotte dalla combustione dei rifiuti. Nel caso delle ceneri APC, l'applicazione della carbonatazione sul residuo ai fini del sequestro di CO_2 rende il processo non realizzabile, infatti la quantità di cenere prodotto è scarsa sebbene la capacità di sequestro sia alta.

Introduction

Nowadays the necessity to reduce the negative effects caused by the increasing amount of waste produced by human activities is the main problem to take into account in the waste management system. The Integrated Waste Management System represents the best opportunity to improve the cycle of waste and reduce their negative impact on the environment. It is based on the reuse or recycling of several waste materials, such as plastic, glass, aluminium, paper and organic fraction which are separated from municipal solid wastes.

In particular, the recycling option involves the transformation of a waste material into a new product, reducing the consumption of fresh raw material; as a consequence, it brings about better use of available resources. Furthermore, less solid residues need to be treated and landfilled, thus the energy usage, the air pollution (from thermal treatment) and water pollution (e.g. from landfilling) decrease, reducing the costs of water and air decontamination.

However, after the recycling option, a residual waste fraction remains and it must be treated before reusing or landfilling. The residual waste fraction can be mechanically-biologically pre-treated (MBT) or combusted during the waste to energy (WtE) process. The first option is often considered as an alternative waste treatment to incineration and it consists in mechanical sorting and biological treatment (composting, stabilization and anaerobic digestion) stages. Nevertheless, new solid residues are produced during both processes. In the case of thermal treatment, solid materials (such as bottom ash, fly ash and gas flue cleaning) and acid gases (e.g. SOx, NOx, halogenidric acids and carbon dioxide) are produced.

The solid residues, produced after thermal treatment, require a treatment before landfilling or recycling, overcoming the potential release of toxic organic compounds, metals (e.g. Pb, Zn, Cu, Cd, Cr, Mo and Sb) and soluble salts into the environment. These elements are always present in the initial solid waste and, after the combustion process, their contents in residue material increases. The mineralogical alterations which occur as a consequence of the combustion reaction are another aspect to consider. For example, after the quenching process of BA, new mineralogical phases are formed which are metastable under atmospheric condition. In a short time, the alkalinity of these combustion solid residues brings about the leach out of these compounds and elements. The extent of the release is largely dependent on the mineralogical alterations which naturally occur as a consequence of the contact with atmospheric agents. Another very important aspect is the necessity of predicting the pH change in a long term period for the management of a landfill site, after it is closed.

Several pre-treatments are applied on BA and APC ash and they are included in the following classes: (a) physical separation, (b) chemical separation, (c) chemical stabilisation and (d) thermal treatment. Some of them are carried out in the full scale (e.g. size separation, magnetic separation, washing, blending with cement), while others are more innovative (natural weathering and carbonation). The effect produced by some processes studied till now is to move contaminants from the residue to other phases, which have to be treated because they are polluted. For example, with respect to the washing treatment, water soluble salts, such as chlorides and sulphates, are easily removed from residues; furthermore a wastewater riches, not only in soluble salts, but also in heavy metals and organic compounds, is produced thus a new problem, linked to wastewater treatment, will require a solution in order to solve the problem.

The ideal solution might be to find treatment capable to immobilise contaminants in residue and producing an environmentally stable material in a short and long time scale.

Regarding to innovative processes, the *weathering* of alkaline residues is the result of several reactions (e.g. hydrolysis, oxidation/reduction, carbonation) which cause chemical and mineralogical changes, affecting the leaching behaviour of contaminants from solid residue. One of the most well-known weathering processes is the one based on the carbonation reaction. After carbonation treatment, the most evident effect produced is the decrease of pH which affects the compounds mobility. In this respect, several studies have shown, as consequence of treatment, a positive effect in terms of metal immobilisation. Another beneficial aspect is that the treated residue maintains or increases the buffering capacity, thus it is more stable when it is exposed to environmental conditions.

As a result, in several European Countries, the ageing process has already been used at a full scale to stabilise BA; for example, in France about 64 % by weigh of residue is stocked several months on a weathering area, before its reuse in road construction.

Regarding the carbon dioxide (CO_2) emission produced by thermal treatment, according to Intergovernmental Panel on Climate Change (IPCC), most of the warming observed is attributable to human activities and CO_2 is the greenhouse gas which makes the largest contribution. The ultimate objective of the UN Framework Convention on Climate Change is to achieve the reduction of greenhouse gas concentration by adopting several technological options. These include: reducing energy consumption, increasing the use of renewable energy source, sequestering CO_2 by biological adsorption, as well as CO_2 capture and storage (CCS), chemically or physically. The CO_2 capture takes place by separating the gas under investigation from a gas stream, adopting solid materials (e.g. biological or waste solid material) rich in calcium (portlandite, Ca-silicates such as wallostonite and ettringite). Several studies were carried out to evaluate the potential use of the MSW combustion residues to achieve the CO_2 capture and storage (CCS). In the case of MSW combustion APC ash residues, a high CO_2 uptake potential was observed, as well as MSW combustion BA and stainless steel slag, but in this case, the maximum sequestration capacity was dependent on its particle size fractions. The maximum value of CO_2 was measured in the finest fractions whilst it was lower in coarse fractions.

The objective of this doctoral thesis was to investigate the effect of the direct aqueous accelerated carbonation process on chemical and mineralogical property of both MSW combustion BA and APC ash and to evaluate the CO_2 potential sequestration of these residues. In Chapter 1 and 2 the accelerated carbonation process and carbon dioxide sequestration are discussed. In particular, the main applications of accelerated carbonation on different alkaline residues and the general effects produced on the metal leaching are reported.

In Chapter 3, the effects of the aqueous accelerated carbonation applied on BA and its particle size fractions is discussed in terms of metal leaching and CO_2 sequestration capacity. In order to better understand the effect caused on metal release by carbonation treatment, several leaching tests, a geochemical modeling and a sequential extraction procedure were adopted.

In Chapter 4, the results obtained by performing the accelerated carbonation process on APC residue are reported and discussed. In particular, the optimum pH of the carbonated APC ash, in terms of reduced metal leaching, might be in a limited range of pH, probably between 10.0 – 10.5, thus the study of effects on metal release from APC residue, was performed by stopping the process at fixed pH, in a range between 8.2 – 13.0. Leaching tests were performed on fresh and carbonated material collected during treatment to evaluate the metal mobility. Generally, carbonation treatment applied on APC residue seems not to decrease significantly the chlorides, sulphates and fluorides leaching and their release appears to be pH independent. In this contest, the washing process of the residue represents the main option used to decrease salts mobility. In Chapter 5, results of preliminary water washing tests is reported. Experimental tests were carried out to asses the effectiveness of the single step process and both the time and liquid-solid (L/S) ratio were varied, respectively from 2.5 to 10 l/kg and from 60 to 120 minutes. Furthermore, by applying the washing treatment, other contaminants, such as heavy metals, are dissolved. In this contest a combined pre-treatment of APC residues appeared to be interesting, by using both carbonation and washing process. The application of the carbonation treatment, such as first step of a pre-treatment, and of washing process, as second step, might be an optimum solution to achieve a selective removal of soluble salt during the water washing.

In this doctoral thesis, the influence of several parameters on the previewed combined treatment was evaluated in order to achieve information on the optimal operative conditions, which might improve the metals and salts leaching.

The experimental work of this research was carried out in the laboratories of the Geoengineering and Environmental Technologies Department of the Cagliari University (Italy).

Chapter 1. Accelerated carbonation and technical applications

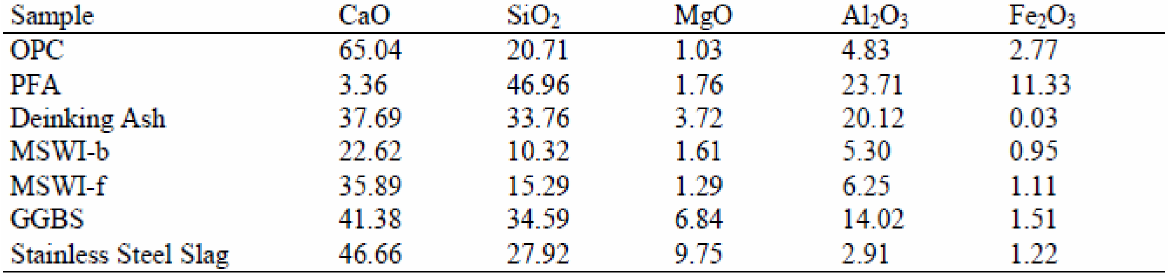
1.1 Mineral carbonation

Mineral carbonation or mineral sequestration is based on the reaction of CO_2 with metal oxides, normally contained in natural raw minerals, e.g. silicate, and in many waste materials, to form the corresponding insoluble carbonates. The products of mineral carbonation are stable solids that would provide storage capacity on a geological time scale. Carbonation is recognised as one of the most important reactions occurring during the *ageing* process of alkaline materials, when they are exposed to atmospheric conditions. Moreover, magnesium and calcium silicate deposits are sufficient to fix the CO_2 that could be produced from the combustion of all fossil fuels. To fix a tonne of CO_2 about 1.6 to 3.7 tonnes of rock is required (IPCC, 2005). From a thermodynamic point of view, inorganic carbonates represent a lower energy state than CO_2; hence the carbonation reaction is exothermic and can theoretically yield energy.

Several studies (Sabbas *et al.*, 2003; Freyssinet *et al.*, 2002; Meima *et al.*, 2002) pointed out the chemical and mineralogical alterations which are involved during the ageing process and in particular, after the carbonation of solid residues obtained by combustion process.

Solid residues obtained by thermal treatment are considered strongly alkaline materials because of their high amount of calcium and magnesium oxides content. A typical composition of residues is shown in Table 1.1.

Table 1.1. Chemical composition of alkaline residues tested for carbonation treatment (% by weigh of each oxide) (Johnson 2000).



Sample	CaO	SiO_2	MgO	Al_2O_3	Fe_2O_3
OPC	65.04	20.71	1.03	4.83	2.77
PFA	3.36	46.96	1.76	23.71	11.33
Deinking Ash	37.69	33.76	3.72	20.12	0.03
MSWI-b	22.62	10.32	1.61	5.30	0.95
MSWI-f	35.89	15.29	1.29	6.25	1.11
GGBS	41.38	34.59	6.84	14.02	1.51
Stainless Steel Slag	46.66	27.92	9.75	2.91	1.22

During the mineral carbonation process, metal-oxides (MO) are easily carbonated, according to the following chemical reaction:

$MO\ (s) + CO_2\ (g) \rightarrow MCO_3\ (s) + heat \quad (\Delta H < 0)$ [1]

where M is a divalent metal, e.g. Ca, Mg or Fe. The products of mineral carbonation are carbonates, which are stable solid compounds that would provide storage capacity on a geological time scale. The amount of heat produced by reaction depends on the bivalent metal contained in oxide compounds. In the case of Ca-(hydro)oxide, e.g. portlandite, calcite is the solid product, according to the reaction:

$Ca(OH)_2\ (s) + CO_2\ (g) \rightarrow CaCO_3\ (s) + H_2O\ (l) + 178\ kJ/mol_{CO_2}$ [2]

Others classes of compounds, generally contained in industrial residues, are Ca-silicates, such as wollastonite and ettringite. These mineral phases were found in many waste materials derived from thermal process (Johnson, 2000). Carbonation of Ca-silicate can be written as:

$CaO\cdot nSiO_2\cdot mH_2O + CO_2\ (g) \rightarrow CaCO_3\ (s) + nSiO_2\ (s) + mH_2O$ [3]

In the case of ettringite, the reaction can be represented by the following chemical equation:

$3CaO\cdot Al_2O_3\cdot 3\ CaSO_4\ 32H_2O$ (ettringite) $+ CO_2\ (g) \rightarrow 3CaCO_3\ (s) + 3CaSO_4\cdot H_2O$ (gypsum) $+ Al_2O_3\cdot xH_2O$ (alumina gel) $+ (26 - x)\ H_2O$ [4]

Carbonation process might take place in different conditions: at low pressure, by bubbling CO_2 into the residue in slurry phase or exposing the moistured residue to a stream rich in this gas and or high pressure, in a closed reactor. In the first case, only soluble Ca minerals and ettringite can be carbonated; in the second case, also Ca-silicates can react with CO_2 gas. Considering the different carbonation process routes used to mineral CO_2 sequestration, such as the *direct* and *indirect* methods, the same treatments might be applied to residues (figure 1.1). In *direct* methods, the gas is directly put in contact with material which is in solid or aqueous phase; in the case of *indirect* methods, the alkaline metals are extracted from matrix and then they can react with CO_2. The most common method applied on waste residues, is the *direct* carbonation treatment, *gas-solid* or *aqueous route*; in the last case, the process does not require the extraction of alkaline metals, which are water soluble.

The carbonation reaction in aqueous phase involves the following steps: (a) the CO_2 diffusion from the air through the porous system; (b) the $CO_{2\ (g)}$ dissolution in water film surrounding each particles; (c) $CO_{2\ (aq)}$ hydration to carbonic acid and its ionization, (d) the reaction of $CO_{2\ (aq)}$ with $Ca(OH)_2$ present in water solution. These mechanisms can be described by a modelling approach, considering the following differential equation (Arickx *et al.*, 2006):

$$\varepsilon_{air} \frac{\delta C^{g}}{\partial t} CO_2 = D_{eff} \frac{\partial^2 C^{g}{}_{CO_2}}{\partial x^2} - R_{CO_2} \qquad [5]$$

In the equation, a constant porosity ε_{air} and the effective diffusion coefficient D_{eff} are assumed.

Carbonation can be considered a second order reaction, with respect to $Ca(OH)_2$ and CO_2 concentration in the aqueous phase ($R_{CO_2} = e_{water} K_r C^{l}_{CO_2} Cl^{l}_{Ca(OH)_2}$). Assuming $Ca(OH)_2$ concentration constant, the reaction becomes pseudo-first order ($R_{CO_2} = e_{water} K\ C^{g}_{CO_2}$) and might be integrated. The degree of carbonation is strongly dependent upon the calcium content and the absence or low quantity of $Ca(OH)_2$ and/or the deposit of other compounds might influence the diffusivity and reactivity of the carbon dioxide (Rendek *et al.*, 2006).

Carbonation reaction affects the physical-chemical properties and the mineralogical composition. From a physical point of view, the reaction leads to an 11.8 % increase in solid volume which causes, as a consequence, a reduction of porosity. (Fernandez-Bertos *et al.*, 2004).

Regarding chemical modification, the new calcite phase causes a pH reduction, from a range of 11 - 13 to 8 - 9 and might improve the buffer capacity of solid residue.

Metals speciation and solubility may be modified, as a consequence of several interrelated chemical and physical processes: complexation, hydration, hydrolysis, dissolution/precipitation, oxidation/reduction, sorption and mineral neo-formation. In this respect, several studies examined the MSW combustion BA and APC ash to evaluate the involved modifications, after carbonation treatment. In the case of BA, it was observed that Al minerals, amorphous aluminosilicates, $Al(OH)_3$, and Fe oxides are likely to precipitate during carbonation (Stumm and Morgan, 1981; Meima and Comas, 1997) and sorption of contaminants on neo-formed solid might be an important mechanism that causes metal leaching reduction (Meima and Comas, 1998; Zevembergen *et al*., 1994). A similar result was obtained treating APC ash which, after carbonation treatment, showed a different metal leaching behaviour (Baciocchi *et al*., 2007; Wang *et a*l., 2010).

Accelerated carbonation has shown: (i) a positive and significant effect especially on lead zinc and copper leaching on both BA and APC ash (Li et al., 2007; Kim et al., 2003; Wang *et al*., 2010; Polettini *et al*., 2005; Rendek *et al*., 2006; Arickx *et al*, 2006); (ii) no effect or negative effect on antimony and molybdenum leaching (Van Gerven *et al*., 2005; Polettini *et al*. (2005); (iii) a non clear behaviour on chromium leaching.

Natural carbonation process usually requires long periods, therefore, in order to make an effective technical exploitation possible, the adoption of specific conditions (i.e. high CO_2 pressure, optimal water content) or material pre-treatments (i.e. preliminary mineral phases dissolution), is currently under evaluation.

1.2 Accelerated carbonation

At the low partial pressure of carbon dioxide in atmosphere (0.03 – 0.06 % v/v) and at temperature ambient, carbonation of metal oxides occurs spontaneously, through geological scales (Robie *et al*., 1978; Lasanga and Berner, 1998). It has been demonstrated that after seven months weathering period, bottom ash could be adsorbed (Kaibouchi *et al*., 2003). The carbonation treatment can be accelerated by adopting several parameters which affect the kinetic reaction: (a) the CO_2 pressure, (b) moisture content of residue, (c) temperature and CO_2 percent of air, (d) material sieving. The CO_2 pressure plays a major role on the kinetic of the whole process (Rendek *et al*., 2006); the gas solubility in the water, content in pores, is directly related to its partial pressure (P_{CO_2}) in the surrounding gaseous phase as described by Henry’s law:

$$C_{CO_2} = K_{CO_2} P_{CO_2} \qquad [6]$$

Where K_{CO2} is the Henry constant, depending on temperature (K_{CO_2} = 34.13 mol m^{-3} bar^{-1} at 20 °C). Taking into account the Henry’s equation, the CO_2 concentration (C_{CO_2}) calculated, considering the pressure at 2 and 17 bar, is included in a range values from 68 mol m^{-3} to 580 mol m^{-3}. Consequently, the increase of CO_2 concentration accelerates the carbonation reaction (Rendek *et al*., 2006).

The effect exerted by temperature parameter on the carbonation reaction, is positive and it might be due to the Ca^{2+} leaching from the particle of solid; however, since the reaction is exothermic, the formation of carbonate is thermodynamically favoured at low temperature (Fernandez-Bertos *et al*. 2004).

Water is necessary to promote the reaction of CO_2, in fact it dissolves and hydrates CO_2 and Ca^{2+} ions; however, too much water can limit the reaction, because it blocks pores in solid, reducing the surface of contact of gas-solid (Fernandez-Bertos *et al*. 2004; Rendek *et al*., 2006; Van Gerven *et al*., 2005).

The degree of carbonation is strongly dependent on the Ca content, however, some waste residues seem do not follow this tendency. It might be ascribed to compounds deposit, e.g. Ca-hydro(oxides), formed during the process, which could influence the effective diffusivity and reactivity of the CO_2 (Rendek *et al*., 2006).

1.3 Accelerated carbonation of alkaline residues

Accelerated carbonation of alkaline residues has been found to represent an effective way to achieve CO_2 sequestration from industrial point sources, an interesting additional benefit in view of the decrease of greenhouse gases (Huijgen and Comans, 2003; Fernández-Bertos *et al*., 2004; Baciocchi *et al*., 2007, Sipilä *et al*., 2008).

Industrial residues obtained by thermal treatment are considered strongly alkaline materials, because of the high amount of calcium and magnesium content. Calcium is the main alkaline metal found in industrial residues and it is the most reactive specie, with respect to CO_2; thus it is carbonated more quickly than Mg (Hujgens *at al*., 2003).

The initial composition and the mineralogy of the many industrial residues were evaluated and an example of mineralogy study is given below (Table 1.2).

Table 1.2. Mineralogical studies on fresh and weathered residues.

Residue	Unweathered	Weathered
MSWI bottom ash	(Kirby and Rimstdt, 1993) Tedjar, 1999) (Freyssinet *et al*., 2002) Zevenbergen, 1994)	(Tedjar, 1999) (Zevenbergen *et al*., 2004) (Piantone *et al*., 2004)
MSWI electrostatic precipitator ash	(Eigmy *et al*., 1995)	
Coal fly ash	(Reddy *et al*., 1994) (Schramke, 1992) (Warren and Dudas, 1995) (Sarbak and Kramer-Wachoviak, 2001)	(Reddy *et al*., 1994) (Schramke, 1992) (Warren and Dudas, 1995)
Coal combustion fluid bed combustion	(Fauth *et al*., 2002)	(Fauth *et al*., 2002)
Steel slag	(Yan *et al*., 2000) (Johnson *et al*., 2003)	(Johnson *et al*., 2003) (Huijgen *et al*., 2004)
Oil shale solid residue	(Essington, 1991) (Reddy *et al*., 1991) (Reddy *et al*., 1994)	(Essington, 1991) (Reddy *et al*., 1991) (Reddy *et al*., 1994)
Coal APC residues	(Tawfie *et al*., 1995)	(Tawfie *et al*., 1995)

The leaching of inorganic salts or organic compounds is an important aspect with regard to the beneficial utilisation of the carbonation products. Accelerated carbonation has been shown to have a potential for improving the chemical stability and the leaching behaviour of both bottom ash and APC residues obtained by municipal wastes combustion. Lead and zinc in BA are reported to be trapped in newly formed carbonates (Freyssinet *et al.,* 2002).

Recently the use of accelerated carbonation to neutralise red mud (RM) has been investigated. The storage of red mud is the main problem due to its caustic nature ($10 < pH < 12.5$) and the reuse of this residue was studied to remove phosphate, nitrate, fluoride, heavy metals, as well as organics compounds, e.g. phenols, and bacteria from wastewater (Shaobin *et al*., 2008). After neutralisation of pH, RM has exhibited a promising adsorption capacity with respect to the previewed contaminants and it can be used, for example, in wastewater treatment.

Gunning (2010) considered the use of accelerated carbonation process for the treatment of industrial wastes to reduce their toxicity. By comparing the leaching behaviour of the untreated and carbonated wastes to the regulatory limits for inert, stable non-reactive and hazardous landfills, carbonation proved effective in reducing the leaching of Pb ad Ba, but increased Sb and Cr. The mobility of As, Cu, Mo and Ni as well as many anions were largely unchanged. The corrosive nature of wastes was reduced by partial neutralisation of pH. As a result, the carbonation reduced the waste acceptance criteria classification of many wastes, but the mobility of some metals can remain problematic.

The effects of accelerated carbonation on the leaching behaviour of pulverized coal fly ash and oil shale ash was first analyzed by Reddy *et al*. (1991; 1994). Treating the humidified samples (20 % moisture) with 100 % of CO_2 at ~ 3 bar, for 120 hours, lowered the pH of the residues from 12.3 - 12.8 to 8.8 - 9.7 and caused calcite precipitation (Reddy *et al*., 1994).

1.3.1 Accelerated carbonation on MSW combustion BA and its particle size fractions

Energy recovery and material recycling are mandatory goals in the framework of the integrated waste management system. Bottom ash from municipal solid waste thermovalorization has a high recycling potential: the sand and the gravel fractions can be used in concrete production or as material for building and road foundations; recently BA was also proposed as adsorbent to removing metals from wastewater, due to its high porosity and large surface area (Sim and Lee, 2001).

From an environmental point of view, some BA recycling options are hindered by metals release and in many European countries its recycling is usually limited by strict regulations. Several techniques have been proposed to reduce the metal leaching, such as physical treatment, e.g. sieving and electro mechanical separation, washing, chemical treatment, e.g. solvent extraction, solidification and/or stabilisation and thermal treatment (Sabbas *et al*., 2003).

Weathering processes is applied to promote mineralogical changes, as a consequence of mineralogical phase’s alteration in MSW combustion residues over time. A first important effect of the ageing process is a pH decrease, from 11 - 12 to 8 – 9, which causes several interrelated processes: complexation, hydration, hydrolysis, dissolution/precipitation, carbonation, oxidation/reduction, sorption and mineral neo-formation. In this respect, All minerals, amorphous aluminosilicates $Al(OH)_3$ and Fe oxides are likely to precipitate during carbonation (Stumm and Morgan, 1981; Meima and Comas, 1997) and sorption of contaminants on neo-formed solid might be an important mechanism that causes metal leaching reduction (Meima and Comas, 1998; Zevembergen *et al*., 1994).

Focusing on the carbonation reaction, the natural process usually requires long periods, thus large areas would be needed to stock the material for natural weathering, before reuse/landfilling. Therefore, in order to make an effective technical exploitation possible, the adoption of specific conditions (i.e. high CO_2 pressure, optimal water content) or material pre-treatments (i.e. preliminary mineral phases dissolution or sieving), is currently under evaluation. In general, it has been several years since the interest arose on technical applications of the carbonation treatment as a possible solution to improve the environmental properties of alkaline residues. The time required for the carbonation process depends on the following parameters: CO_2 content in the gas phase, water content in solid residue, pressure and temperature of the system. In case of normal atmospheric conditions, the optimum values of CO_2 and water content were evaluated respectively, between 10 – 20 % by weigh of residue and close to 20 % and the temperature required were estimated to be 30° - 40 °C (Van Gerven *et al*., 2005). Rendek *et al*. (2006) evaluated the effect of CO_2 partial pressure on BA carbonation treatment, performing several experiments in a range from 2 to 17 bar and by using a moisture content of sample close to 20 % by weigh of residue, at room ambient. The time required to have a complete carbonation was 3 hours and 30 minutes, at 17 bar and more than 2 days at 2 bar.

However, a better understanding of the key reaction mechanisms proper of each type of material to be treated and of the influence of chemical and physical parameters, e.g. differences between particle size fractions, is still an acknowledged need. Several studies have shown the different roles played on the leaching behaviour by several chemical and physical factors, and among the others, by particle size distribution in the BA (Van Gerven *et al*., 2005; Rendek *et al*., 2006). According to this study, the elementary composition of BA fractions was different in each class, according to their particles size: Ca and Si content respectively increased and decreased in the smallest fractions. Carbonation treatment seems to have a little influence on the gravel fractions that consist of inert material such as SiO_2 (Arickx *et al*., 2006).

1.3.2 Accelerated carbonation on MSW combustion APC ash

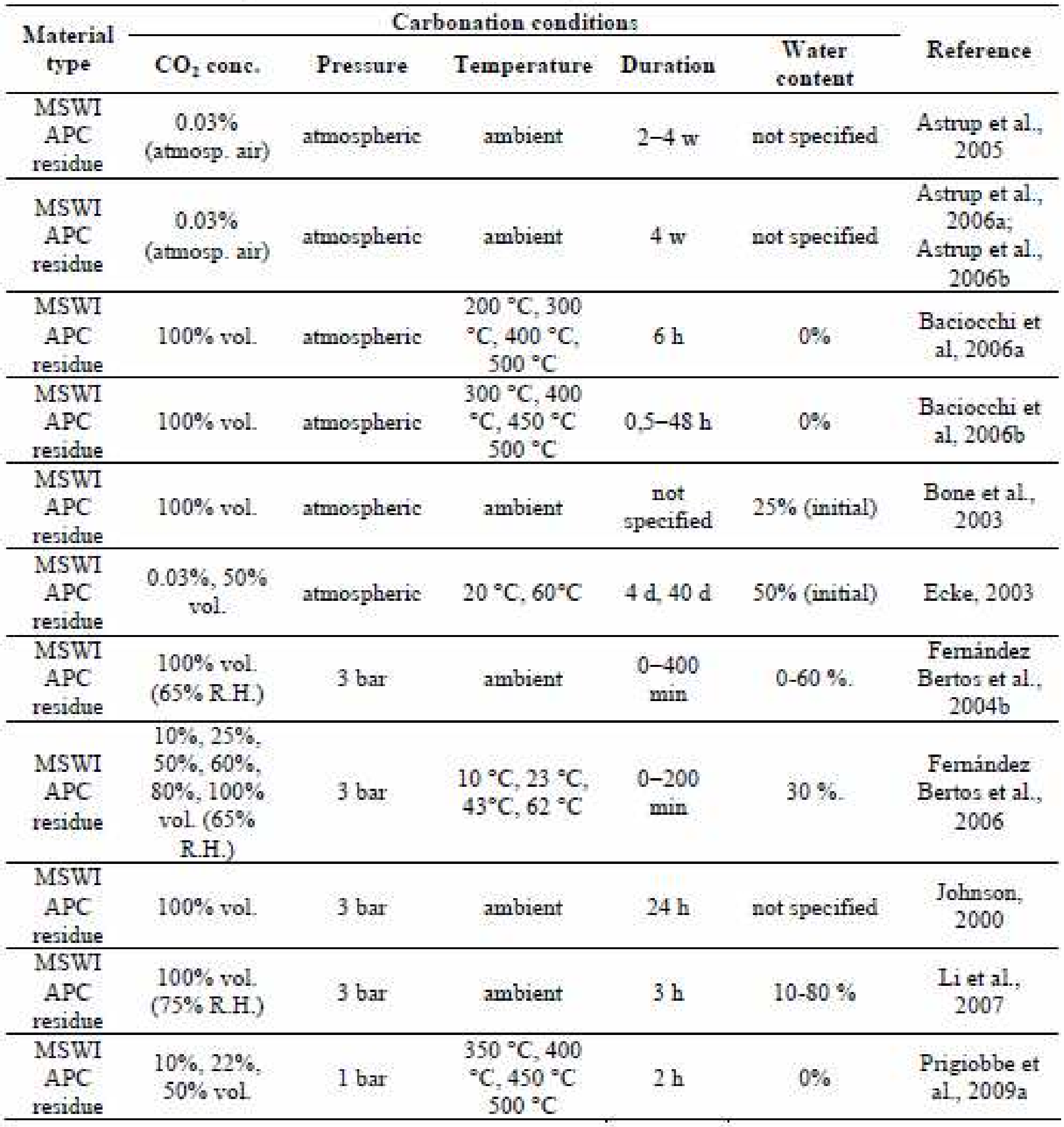
Fly ash and flue gas cleaning ash, produced by thermal treatment of MSW, are generally collect together in electrostatic precipitations and bag filters; the mix obtained is called air pollution control (APC) residues and represents about 2 - 3 % of the waste mass combusted. The high amount of soluble salts, especially chloride and sulphate, heavy metals and organic toxic compounds, contend in APC residue, are considered during managing options, because these contaminants might be leached out in specific environmental conditions, thus a pre-treatment or combined processes has to be applied prior land disposal or reuse. Because of the high content of SiO_2 and CaO, the reuse options of APC ash in raw cement material is hindered by the chloride contented which corrodes steel (Glass and Buenfeld, 1997; Montemor *et al.*, 2002). Among the treatments used to reduce the release of these compounds, carbonation and water washing processes, applied on APC ash, have shown promising results; the first process seems to effectively reduce the metals mobility and the second one allows the removal of heavy metals and chlorides (Kim *et al.*, 2003; Chimenos *et al.*, 2005; Zhu *et al.*, 2010).

Accelerated carbonation treatment on APC ash is now under evaluation, and several studies have been carried out to find out the best conditions to optimize the kinetic process by adopting several parameters, such as the liquid to solid (L/S) ratio and L/S contact time, temperature and pressure of process and CO_2 gas content in the air (Table 1.3). The optimum L/S ratio was found 0.25, under this value the reaction time seems to require 7 hours to reduce the initial alkaline pH to 9.5 – 10.5 (Wang *et al.*, 2010). Baciocchi *et al.* (2007) showed the dependence of carbonation treatment especially on L/S ratio and temperature.

The most evident effect produced by carbonation treatment is a strong pH reduction, from value of 12 - 13 to 7 - 8, which causes, as a consequence, several mineralogical changes. Furthermore, after treatment, a significant immobilisation of several metals was observed (Baciocchi *et al.*, 2007; Wang *et al.*, 2010). Baciocchi *et al.* (2006) studied the direct gas-solid carbonation of APC residues at different temperatures (the acid neutralization capacity and metal leaching as function of pH are respectively showed in Figure 1.3 a-b) and they found Cu, Cr and Cd concentrations in the leachate obtained by EN 12457-2 test were below the limits imposed by the Italian regulation for disposal in non-hazardous waste landfills, whereas Pb concentration still exceeded the corresponding limit value.

With the aim to study the effect of several carbonation degrees, on metals release, Wang *et al*. (2010) concluded that applying the treatment on APC ash and stopping it when the fix final pH value was reached, the optimum pH of the carbonated APC ash was between 9.5 – 10.5. In this pH range, Pb, Zn and Cu leaching decreased significantly, while the Cd and Sb release increased.

Table 1.3. Summarises of the operating conditions adopted for the accelerated carbonation of MSWI APC ash.



Material type	Carbonation conditions					Reference
	CO_2 conc.	Pressure	Temperature	Duration	Water content	
MSWI APC residue	0.03% (atmosp. air)	atmospheric	ambient	2–4 w	not specified	Astrup et al., 2005
MSWI APC residue	0.03% (atmosp. air)	atmospheric	ambient	4 w	not specified	Astrup et al., 2006a; Astrup et al., 2006b
MSWI APC residue	100% vol.	atmospheric	200 °C, 300 °C, 400 °C, 500 °C	6 h	0%	Baciocchi et al, 2006a
MSWI APC residue	100% vol.	atmospheric	300 °C, 400 °C, 450 °C 500 °C	0,5–48 h	0%	Baciocchi et al, 2006b
MSWI APC residue	100% vol.	atmospheric	ambient	not specified	25% (initial)	Bone et al., 2003
MSWI APC residue	0.03%, 50% vol.	atmospheric	20 °C, 60°C	4 d, 40 d	50% (initial)	Ecke, 2003
MSWI APC residue	100% vol. (65% R.H.)	3 bar	ambient	0–400 min	0-60 %.	Fernández Bertos et al., 2004b
MSWI APC residue	10%, 25%, 50%, 60%, 80%, 100% vol. (65% R.H.)	3 bar	10 °C, 23 °C, 43°C, 62 °C	0–200 min	30 %.	Fernández Bertos et al., 2006
MSWI APC residue	100% vol.	3 bar	ambient	24 h	not specified	Johnson, 2000
MSWI APC residue	100% vol. (75% R.H.)	3 bar	ambient	3 h	10-80 %	Li et al., 2007
MSWI APC residue	10%, 22%, 50% vol.	1 bar	350 °C, 400 °C, 450 °C 500 °C	2 h	0%	Prigiobbe et al., 2009a

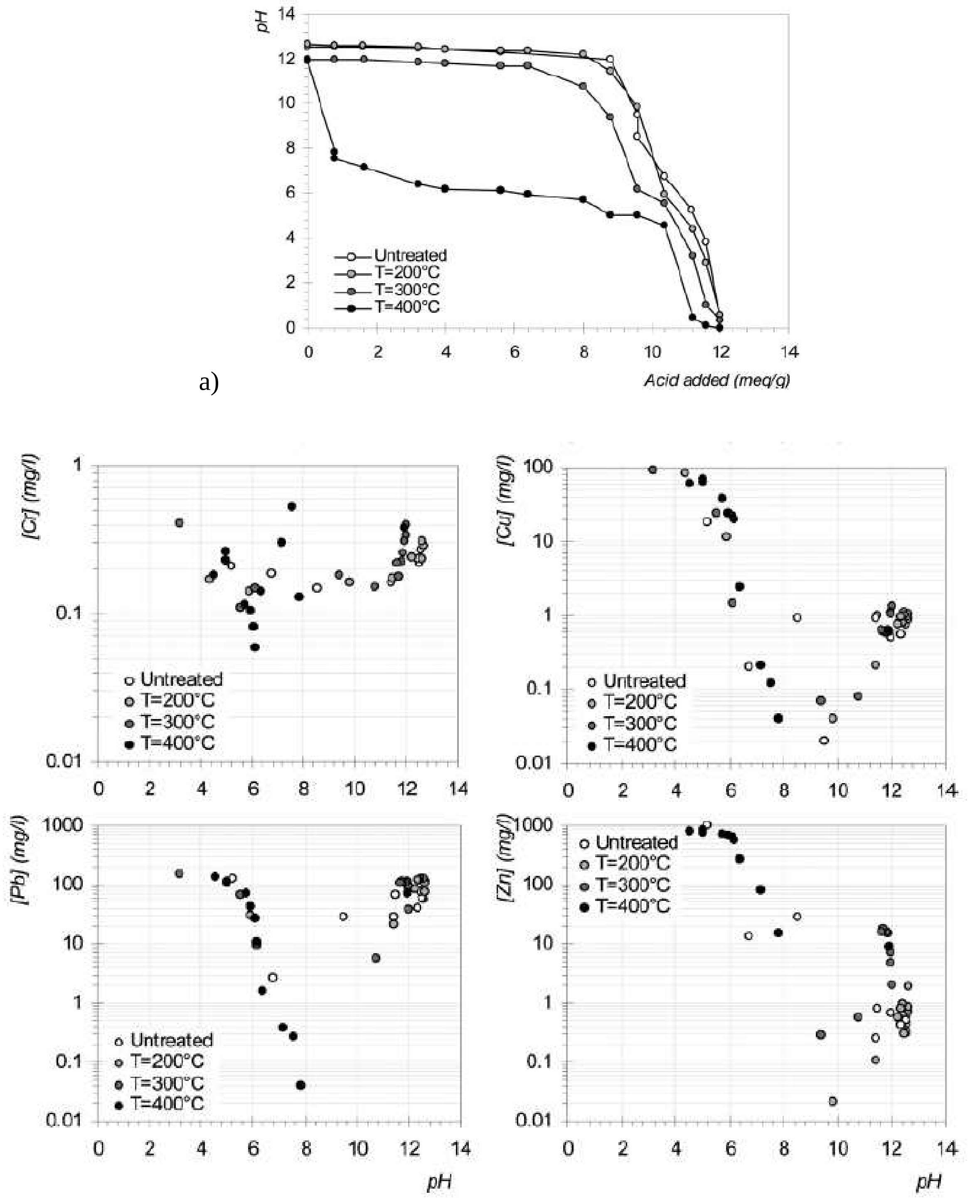


Figure 1.3. Acid neutralization capacity (ANC) curves (a) and metal leaching as function of pH, in ANC test (b) for untreated and carbonated APC ash at different temperature (Baciocchi *et al.*, 2006).

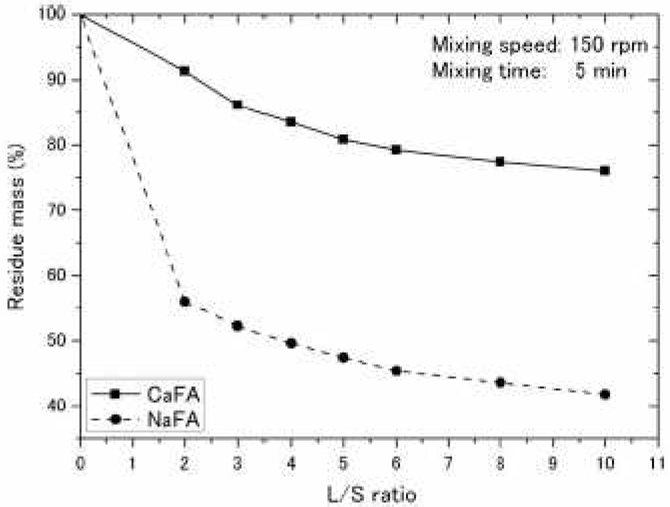
1.4 Municipal solid waste combustion APC ash: general aspects of the washing treatment

Sulphates and chlorides are the main soluble salts released from BA and APC ash. In the case of the reuse of APC ash as raw cement material, the amount of chlorides in the residue must be reduced because it will corrode steel (Glass and Buenfeld, 1997; Montemor *et al*., 2002).

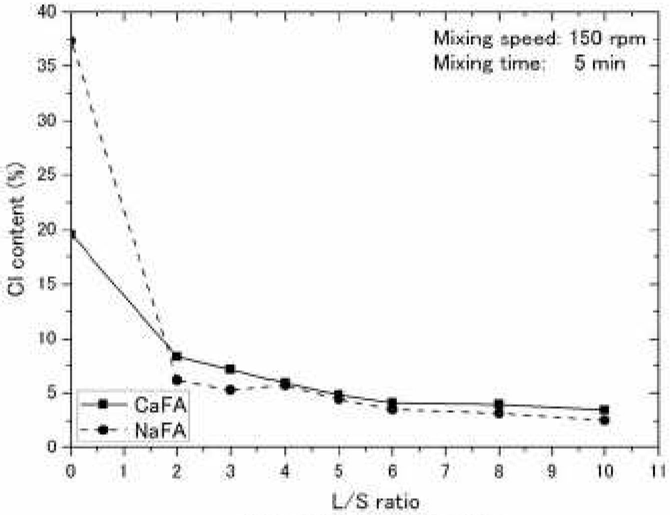
Several studies suggest the water washing treatment of MSW combustion BA and APC ash to remove soluble salts, before applying another stabilisation process (Abbas *et al*., 2003; Bertolini *et al*., 2004; Mangialardi, 2003; Piantone *et al*., 2003; Chimenos *et al.*, 2005; Hyks *et al*., 2009; Liu *et al*., 2009). Researchers focused on finding out the best process conditions, by modifying the liquid-solid (L/S) ratio and the mixing time of the two phases. In the case of the single washing treatment, they applied several L/S ratios, from 2 to 100 l/kg and used mixing time from 5 minutes to 2 hours; the best conditions which allow to reduce the chloride content in residue were at a L/S ratio between 3 and 5 l/kg and a mixing time close to 5 minutes (Kim et al., 2003; Zhu *et al*., 2009) (e.g. see Figure 1.3).

The main disadvantage of the washing treatment is the use of a large amount of water which must be subsequently treated, thus other studies focused on the application of a multi-step process on APC (Chimenos *et al*., 2005; Zhu *et al*., 2009), eventually applied on its different size fractions (De Boom *et al*., 2009). In this case, the fraction of easily soluble chlorides dissolved in water in the first stage of the process and the remaining salts did not dissolve or hardly dissolved during the other steps. However, the washing frequency had a greater influence on reducing chlorides content than the L/S ratio or the mixing time. Zhu *et al.* (2009) found the best conditions, in terms of L/S ratio and mixing time, to apply in the double and triple washing treatment for reducing the amount of chlorides in APC ash (e.g. Figure 1.4).

During washing process, others elements dissolve in water, such as heavy metals, thus before the APC ash recycling or the final disposal with the aim of reducing the leaching of hazardous elements, the use of the carbonation process might be adopted (Wang *et al*., 2010). In this case, the benefit of both treatments might improve the management of APC ash and its environmental impact.

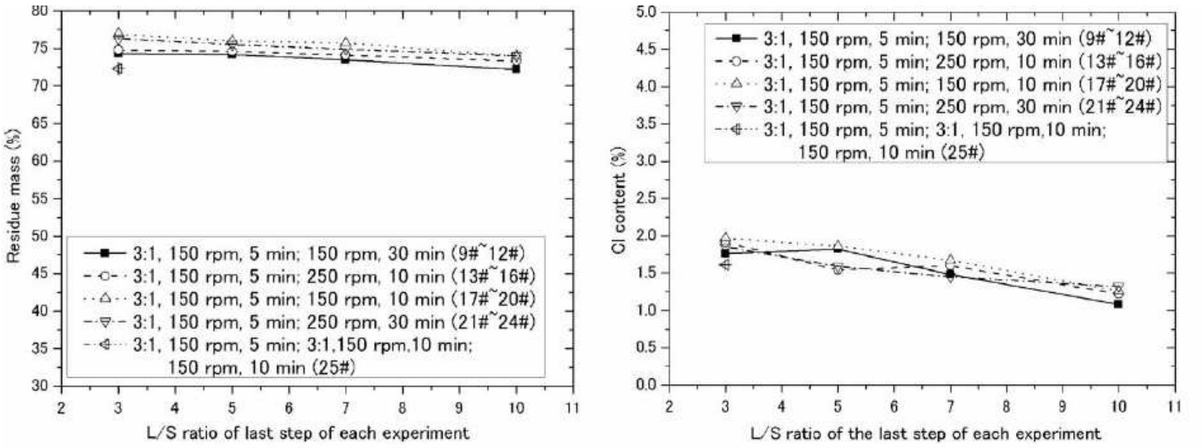


(a) Amount of residue

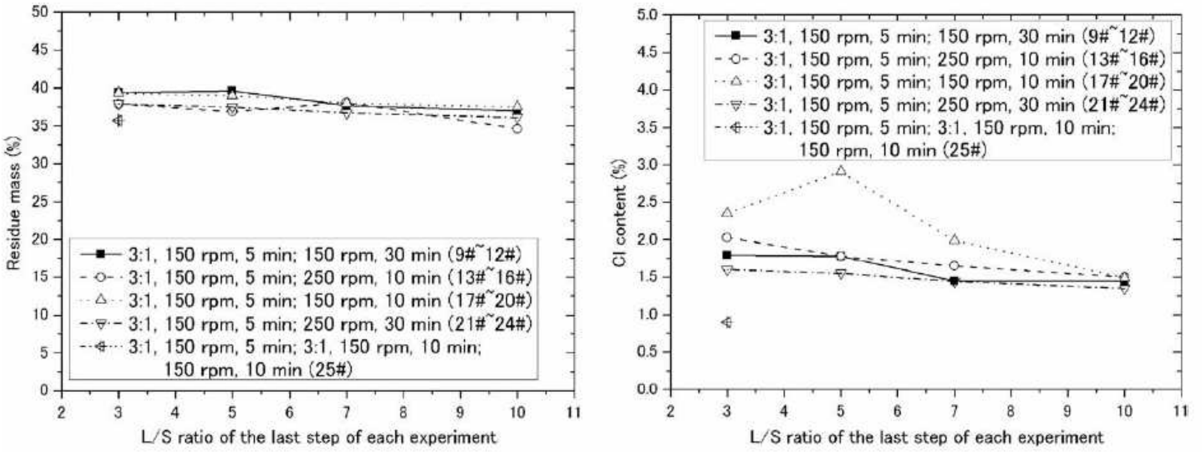


(b) Cl content in the residue

Figure1.3. Single washing treatment applied on fly ash (FA) treated in the dry scrubber with $Ca(OH)_2$ (CaFA) or $NaHCO_3$ (NaFA). Effects on residue mass (a) and chloride content in residue (b) as function of L/S ratio (Zhu *et al*., 2009).



(a) Residue mass of CaFA (b) Cl content in the residue of CaFA



(c) Residue mass of NaFA (d) Cl content in the residue of NaFA

Code	L/S	Experimental conditions
9#	3–3	150 rpm, 5 min–150 rpm, 30 min
10#	3–5	150 rpm, 5 min–150 rpm, 30 min
11#	3–7	150 rpm, 5 min–150 rpm, 30 min
12#	3–10	150 rpm, 5 min–150 rpm, 30 min
13#	3–3	150 rpm, 5 min–250 rpm, 10 min
14#	3–5	150 rpm, 5 min–250 rpm, 10 min
15#	3–7	150 rpm, 5 min–250 rpm, 10 min
16#	3–10	150 rpm, 5 min–250 rpm, 10 min
17#	3–3	150 rpm, 5 min–150 rpm, 10 min
18#	3–5	150 rpm, 5 min–150 rpm, 10 min
19#	3–7	150 rpm, 5 min–150 rpm, 10 min
20#	3–10	150 rpm, 5 min–150 rpm, 10 min
21#	3–3	150 rpm, 5 min–250 rpm, 30 min
22#	3–5	150 rpm, 5 min–250 rpm, 30 min
23#	3–7	150 rpm, 5 min–250 rpm, 30 min
24#	3–10	150 rpm, 5 min–250 rpm, 30 min
25#	3–3–3	150 rpm, 5 min–150 rpm, 10 min–150 rpm, 10 min

Figure 1.4. Double (9# - 24#) and triple (25#) washing tests. Residue mass (a - c) and chloride content (b -d) in residue as function of L/S ratio by adopting different conditions (Zhu *et al.*, 2009).

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Chapter 2. Carbon dioxide sequestration

2.1 Introduction

Carbon dioxide (CO_2) is the most common component of the earth's atmosphere after nitrogen, oxygen, and argon, when water vapour is disregarded. The amount of CO_2 in the atmosphere has increased significantly and rapidly in recent years. The steep increase in CO_2 concentration is alarming, and it is believed to be cause of the increase in the earth's temperature. In order to avoid the potentially devastating consequences of global warming and climate change, the CO_2 emissions into the atmosphere, caused by anthropogenic activities, must be reduced considerably.

There are several ways to achieve this reduction, and one of these is the carbon dioxide capture and storage (CCS) (see Figure 2.1) which has already able to meet the enormous demand for reduction.

Carbon dioxide capture and storage (CCS) is a process consisting in the separation of CO_2 from industrial and energy-related sources, transport to a storage location and long term isolation from the atmosphere. Emission of CO_2 arises from different sources, mainly fossil fuel combustion in the power generation, industrial and transport sector. Over 7,500 large CO_2 emission sources have been identified, distributed in North America, North West Europe, South East Asia and Southern Asia. According to projections for the future, the number of emission sources from the power and industry sectors is likely to increase, especially in Asia. Comparing the geographical distribution of the emission sources with geological storage sites, it can be seen that there is a good agreement between sources and storage sites. To reduce CO_2 emissions through the use of CCS, it is also necessary to solve problems related to the transport phase and the relative costs, especially when CO_2 source and storage locations are far apart.

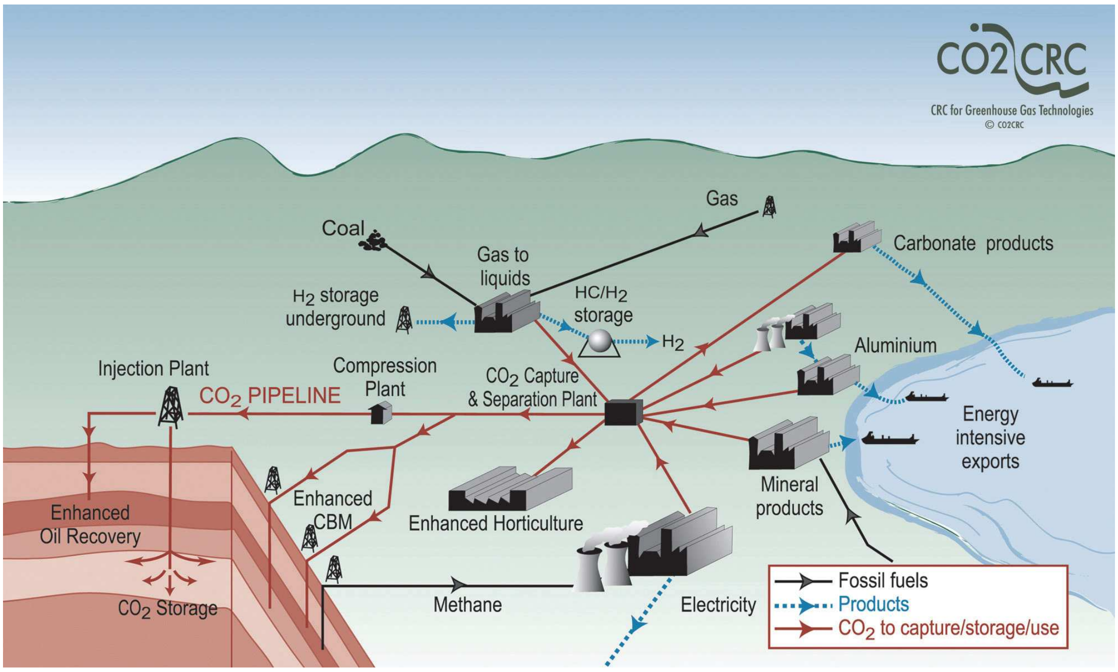

Figure 2.1. Schematic diagram of various CCS alternatives (*CO$_2$*CRC, 2007).

The main systems of CO_2 capture are (Figure 2.2): (a) the capture from industrial process streams; (b) the post-combustion capture; (c) the oxy-fuel combustion capture and (d) the pre-combustion capture. Focusing on the case of post-combustion capture, the CO_2 content in the flue gases, produced by combustion of fossil fuels and biomass, is passed through a device (e.g. a chemical sorbent or solvents) which separates most of CO_2 from the others gases. The CO_2 is then stored and the remaining flue gas is discharged in atmosphere. For example, the absorption process is based on the contact of flue gas with an alkaline organic solvent (e.g. monoethanolamine, MEA) and the subsequent chemical reaction between CO_2 and alkaline compounds. The use of solid sorbent (usually material containing metal oxides) allows the gas-solid reaction and after that, the sorbent material is quickly regenerated. The use of CaO to separate the CO_2 at $T > 600$ °C, leads to $CaCO_3$ formation which, by calcining at $T > 900$ °C, gives back CaO and CO_2. Abadanes *et al*. (2004) proposed the use of CaO in fluidized bad to capture CO_2 directly from combustion gases.

The fixation of CO_2 in the form of inorganic carbonates is known as “mineral carbonation” or “mineral sequestration” and the purpose of fixing the CO_2 as carbonates was studied in the 90s (Seifritz, 1990; Dunsmore, 1992; Lackner *et al*., 1995). Suitable materials to apply in the process might be serpentine and olivine minerals, which contain Mg-rich silicates, or alkaline industrial residues (e.g. fly ash or slag from steel production).

In a recent study**,** Teir *et al.* (2007) investigated the stability of calcium and magnesium carbonate when subjected to an acidic aqueous environment, such as acidic rain. The conclusion of the study was that Ca or Mg carbonates should be resistant enough to prevent local environmental effects at a mineral carbonate storage site.

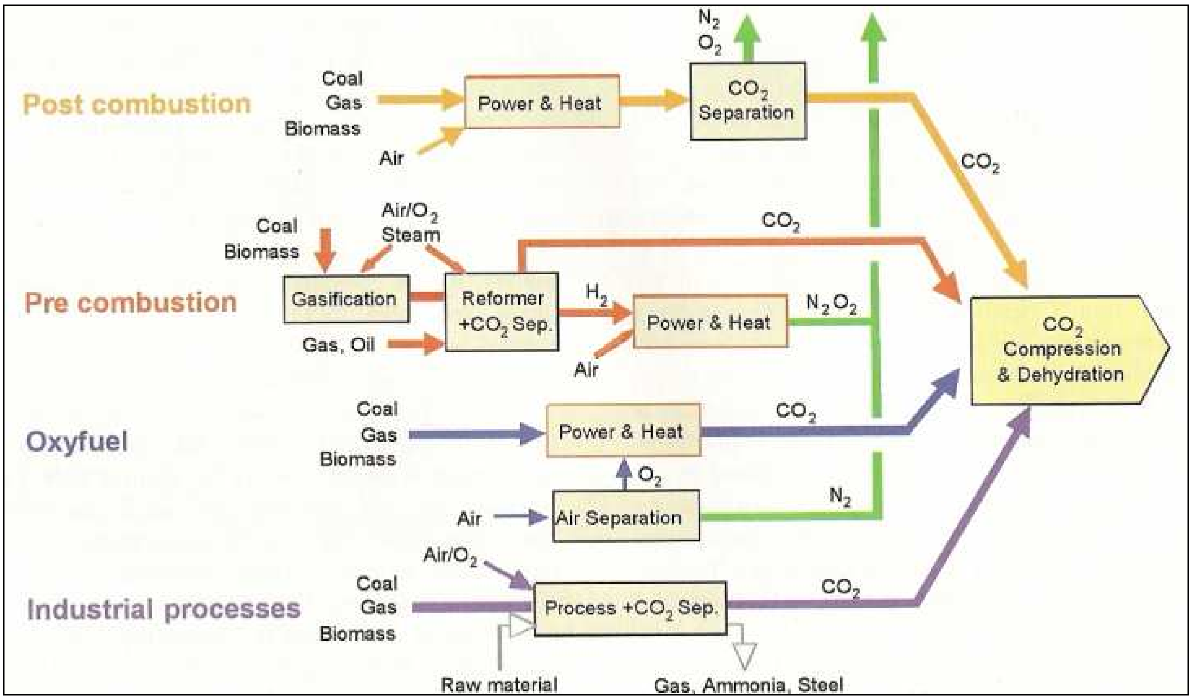

Figure 2.2. Overview of CO_2 captures processes and systems (IPCC, 2005).

Carbon dioxide uptake can be related to elemental composition by using Steinour formula:

$$CO_{2,\ uptake}\ (\%) = 0.785\ (CaO - 0.7SO_3) + 1.091\ Na_2O + 0.935K_2O \qquad [3.1]$$

Gunning *et al*. (2010) compared the Steinour formula to the measured CO_2 uptake of many solid residues and observed that the measured uptake were lower than the theoretical uptakes. In particular, in Figure 2.3 the relationship between Ca content of some alkaline residues and CO_2 uptake is reported.

The advantage of using alkaline residues is that they are a waste stream instead of a natural material and are available at low costs. Nowadays several studies of carbon dioxide sequestration by solid residues have been published as consequence of several researches which studied the natural ageing of material residues and the effects of carbonation reaction on metal mobility (Zenvenbergen and Comas, 2004; Meima and Comas, 1997, 1999; Bone *et al*., 2003; Polettini *et al*., 2004; Van Gerven *et al*., 2005; Rendek *et al*., 2006 Arickx *et al*., 2006).

Considering the residues produced by WtE process, BA could reduce the CO_2 emission by 0.4 - 1 % by weigh of residue (Van Gerven *et a*l., 2005; Baciocchi *et al*., 2006; Rendek *et al*., 2006) and as the finest fractions are richer in Ca element, than the coarse fractions, the particle size is an important parameter which control the carbonation process (Rendek *et al*., 2006; Fernandez-Bertos *et al*., 2004). In the case of APC ash, the CO_2 potential uptake has been evaluated from 7 % by weigh of residue (Fernandez-Bertos *et al*., 2004) to 12 - 13 % (Johnson 2000; Baciocchi *et al*., 2006). Differences in values depend on the carbonation conditions used during experimental work (e.g. aqueous or solid-gas route). This APC ash has a great CO_2 sequestration capacity, but it is only a little fraction of the total waste mass combusted (around 2 %), thus it can be responsibly of a limited reduction in CO_2. However, the stack gas emission of WtE plant approximately contains 10 % of CO_2; therefore it is possible to study a possible solution (Arickx *et al*., 2006) which considers the carbonation of residues produced in the WtE process. Many others solid residues have a high CO_2 potential sequestration, e.g. red mud, wood ash, steel slag and biomass ash.

Red mud is a caustic waste material of bauxite processing for alumina extraction. The Bayer process produces approximately 30 million metric cubic tons/year are globally produced (Khaitan *et al.*, 2009) and many problems are associated with their disposal, especially the strong alkaline pH, due to presence of NaOH and Na_2CO_3. The theoretical CO_2 sequestration capacity was found to be between 2.1 g CO_2/100 g RM (Samer *et al.*, 2009) and 2.3 g CO_2/100 g RM, at a pressure of 6.9 MPa (Enrick *et al*. 2001). Bonenfant et al. (2008) found a carbonation capacity of 4 g of CO_2/100 g of RM at ambient conditions. Recent study found a CO_2 sequestration capacity of 7.02 g CO_2/100 g of RM by adopting ambient condition and a gas flow rate of 5 ml/min (Ramesh *et al*., 2010). Generally, the amount of CO_2 sequestered by residue is small if compared to annual CO_2 emission (110 MMT/year) for Bauxite refining. Nevertheless, CO_2 neutralization is considerate a green process economically advantageous, thus a further studies continue study in this field are required.

Another kind of industrial residue susceptible of carbonation treatment is steel slag, produced during steel manufacturing. This residue is generally considered a non hazardous material, however it might be classified as a hazardous waste if the Cr release is upper than fixed limit (Shen *et al*., 2003). A recent experimental work has evaluated the potential use of steel slag in full scale filters, designed to remove phosphorus (P) from wastewaters. Baciocchi *et al*. (2009) studied the CO_2 sequestration of stainless steel slag by applying the carbonation treatment at a CO_2 pressure of 3 bar and using a L/S ratio of 0.4. The process was completed in around 2 hours and the maximum CO_2 uptakes was 13 g CO_2/100 g residue, detected in the finest fractions (< 0.105 mm) (Figure 2.2).

The CO_2 sequestration of concrete demolition waste has also been studied, owing to the high contents of both free lime and calcium silicates present in this material (Iizuka *et al.*, 2004; Shtepenko *et al*., 2006; Stolaroff *et al*., 2005). Others material residue such as wood ash achieved an uptake of 7 g/ 100 g RM, whilst steel slag and biomass ash have a little reaction with CO_2 gas (CO_2 uptake $\leq$ 1 %).

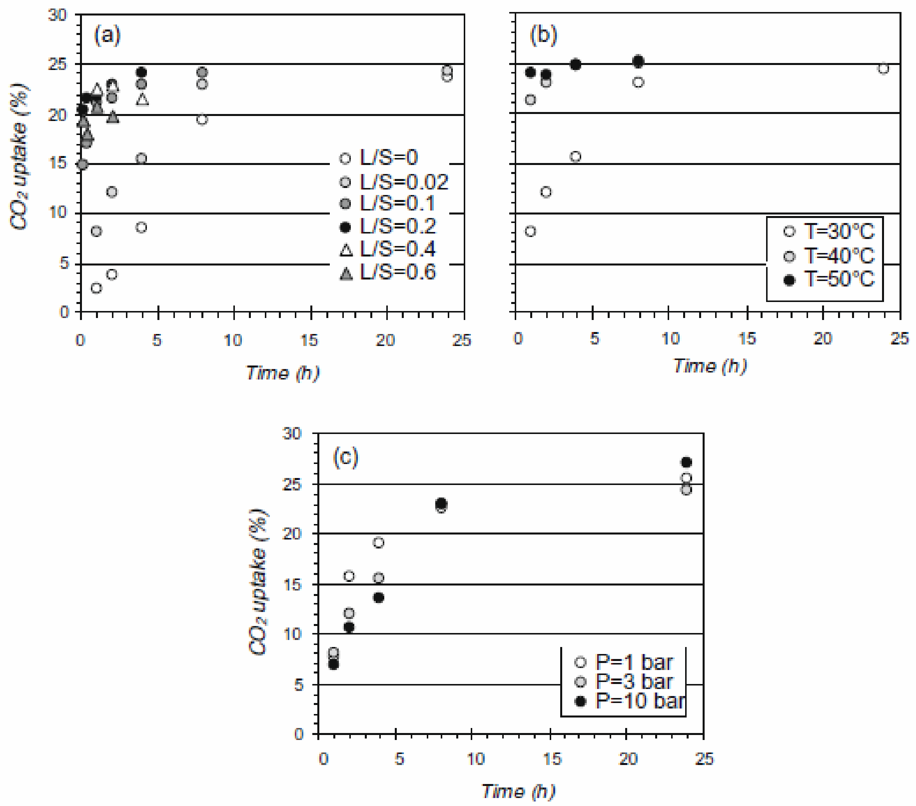

Figure 2.2. CO_2 uptake kinetic in steel slag as function of a) L/S ratio (30 °C, 3 bar), b) temperature (3 bar, L/S 0.02 l/kg and c) pressure (30 °C, L/S ratio 0.02 l/kg) (Baciocchi *et al.*, 2009).

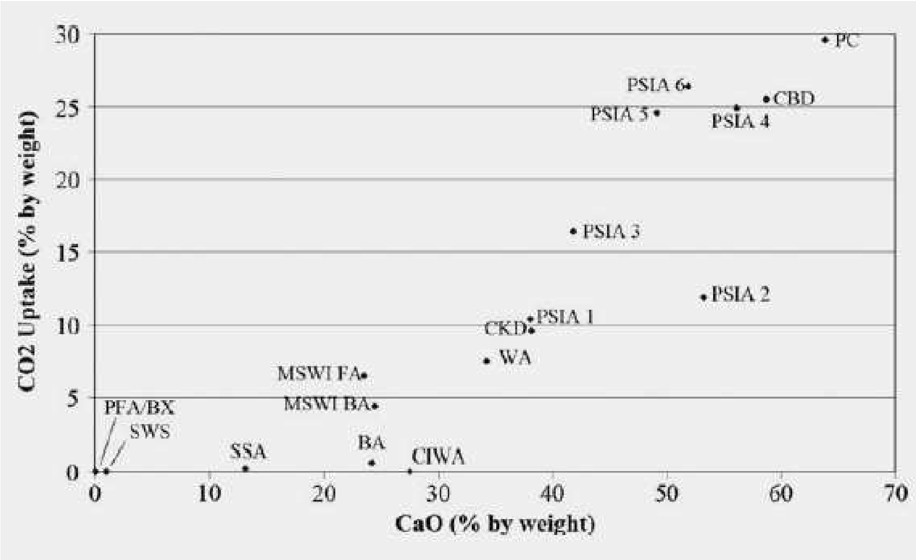

Figure 2.3. Relationship between calcium content and CO_2 uptake (Gunning *et al.*, 2010). BX= bauxite, BA= biomass ash, CKD= cement kiln dust, CBD= cement bypass dust, CWIA= clinical waste incinerator ash, MSWI BA and FA= municipal solid waste bottom ash and fly ash, PSIA1-6= six paper sludge incinerator ashes from different producers, PFA= pulverised fuel ash, SSA= sewage ash incinerator ash, SWS= steel wastewater sludge, WA= wood ash.

2.2 Applications

Several experimental works were performed applying the carbonation treatment on solid residues; essentially, the process can be distinguished in: (i) at low pressure and (ii) at elevated pressure. In the first case, Ca salts and ettringite dissolve in water and are carbonated; in the second case, Ca bound tightly can be carbonated, increasing the CO_2 sequestration capacity.

Many process routes have been developed to achieve the CO_2 sequestration by using primary minerals, but they are also applied on solid residues. Two routes are considered (Figure 2.4): (i) the *indirect carbonation route* and (ii) the *direct carbonation route.*

In the case of *indirect* method (multi step carbonation process), the alkaline elements is extracted by the solid matrix and then precipitate as carbonate. The solvents used to extract alkaline metals are strong and weak acids (Pundsack, 1967; Lackner *et al.*, 1995, Fouda *et al.*, 1996; Park *et al.*, 2003; Maroto-Valer *et al.*, 2005), bases (Blencoe *et al.*, 2003) and chelating agents to extract SiO_2 or MgO from solid (Park *et al.*, 2003; Carey *et al.*, 2003; Park and Fan, 2004). The process includes a solvent recycling step; generally, the required operating conditions are moderate. All these additives compounds have been proven to enhance the dissolution of silicates minerals, but only in case of acid acetic, the process scheme adopted in wallostonite carbonation is complete (Kakizawa *et al*., 2001).

The *direct* carbonation route (one step carbonation process) is preferred to apply on solid residues; the reaction could occur in both aqueous phase or in the gas-solid interface.

In case of the aqueous route, to improve the kinetic of treatment, O'Connor (2005) often added salts (e.g. sodium chloride or sodium bicarbonate). However, when the soluble salts amount content in solid residues is high (e.g. MSW combustion BA), it will not require an addition of salts. In case of gas-solid route, the reaction proceeds very slowly at room temperature, but kinetic can be accelerated by increasing this parameter. However, a high temperature may shift the equilibrium of carbonation reaction to CO_2 gas and causes the calcinations reaction. In this contest, a study of carbonation of alkaline residues was performed by Jia *et al*. (2000), by adopting temperatures above 400 °C, a pressure between 0.1 and 1.1 MPa and 100 % CO_2 atmosphere. The higher pressure increased the number of CO_2 molecules inside the pores and at higher temperature the gas diffuses faster and thus makes more CaO accessible for carbonation.

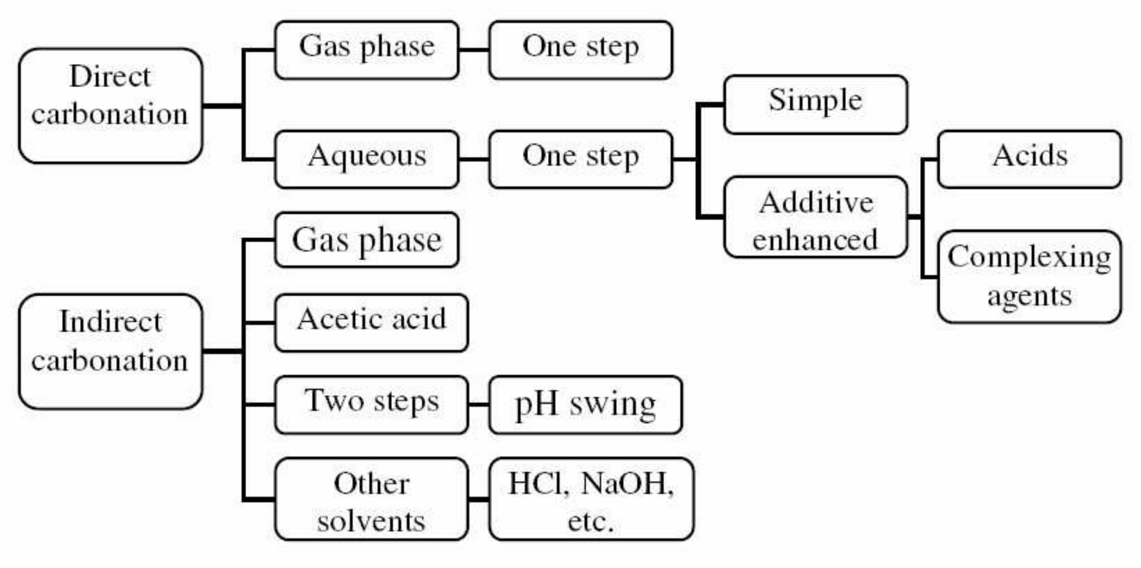

Figure 2.4. Main process routes tested for accelerated carbonation of minerals (Uibu, 2008).

Carbonation can be carry out either *ex-situ* (Figure 2.5) in a chemical processing plant after mining and pre-treating the silicates, or *in-situ*, by injecting CO_2 in silicate-rich geological formation or in alkaline aquifers. Industrial residues on the other hand can be carbonated in the same plant where they are produced. *In situ* carbonation is process similar to geological storage, while *ex-situ* carbonation involves processing steps requiring additional energy input that are difficult to compensate for with the energy released by the carbonation reaction. With the present technology there is always a net demand for high grade energy to drive the mineral carbonation process that is needed for: (i) the preparation of solid reactants including mining, transport, grinding and activation when it is necessary; (ii) the processing, including the equivalent energy associated with the use, recycling and possible losses of additives and catalysts; (iii) the disposal of carbonates and by-products. The relative importance of the three items differs depending on the source of the metal oxides, fr example whether they are natural silicates or industrial wastes.

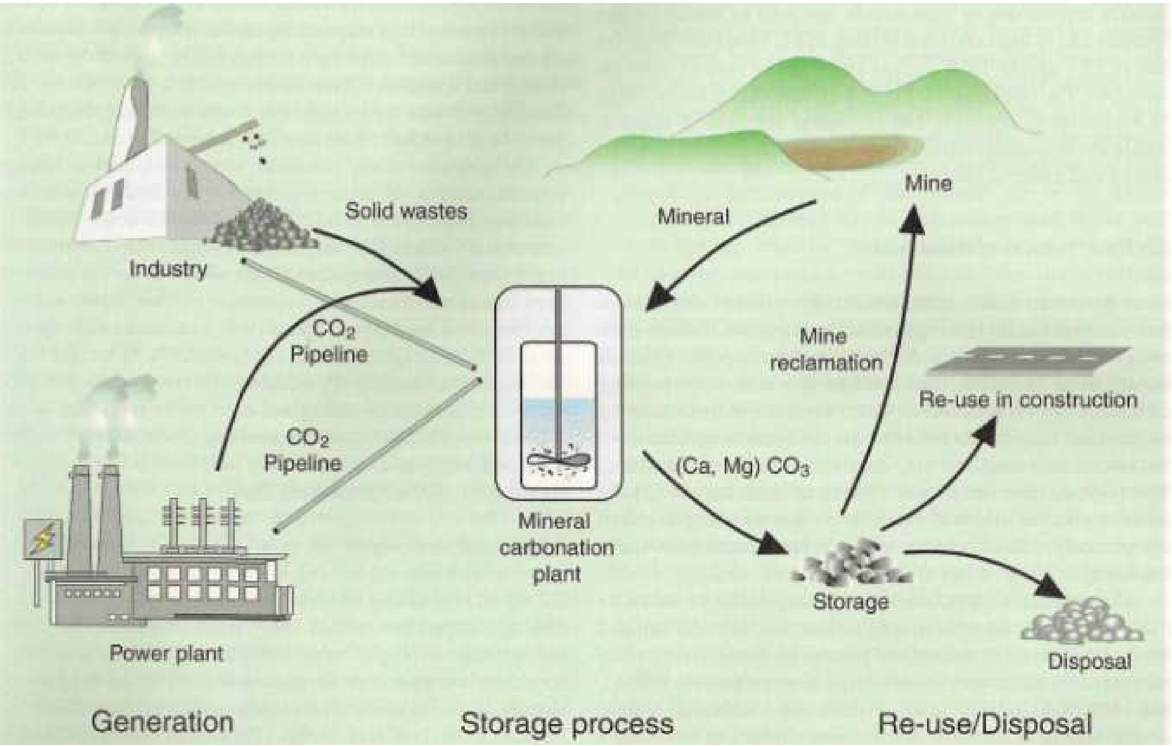

Figure 2.5. Material fluxes and process steps associated with the *ex-situ* mineral carbonation of silicate rocks or industrial residues (Courtesy Energy Research Centre of the Netherlands (ECN)).

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Chapter 3. Accelerated carbonation on MSW combustion BA and its particle size fractions

3.1 Introduction

Waste recycling is the main objective in the field of waste management. This option requires energy and material consumption; however, compared to the needs required for a new production, the result, in term of mass balance, has shown that the recycling is efficient, especially considering glass and aluminium (Grosso *et al*., 2007).

The thermal treatment (combustion) of municipal solid waste is the last option, after the recycling or the reuse of waste; however during the combustion process, new residues are produced (bottom ash, fly ash and flue gas cleaning) and they require a pre-treatment before landfilling. In most European countries, the legislation allows, under special rules, the reuse of bottom ash (BA) as construction material and the utilisation is even especially regulated. Another possibility is to reuse BA or its specific fractions as additives in cement production.

Considering the reuse of BA, the quality of residue requires a special attention to avoid any problem in terms of environmental pollution. BA is classified as a non hazardous waste according to the European Waste Catalogue. Soluble salts, like chlorides and sulphates, organic compounds and heavy metals are generally leached out from residue during exposed to atmosphere conditions. Frequently, the contaminants concentration in leachates produced in regulatory leaching tests exceed the local limit values required for landfilling. Furthermore, in these tests, long-term changes in mineralogical composition and in chemical properties of residue are not taken into account, and as a consequence, the contaminants concentration in leachates does not respect the real environmental behaviour of material. On the basis of this assumption, the metal leaching from fresh and treated BA has been the topic of several researches. The main parameters which affect the metal leaching are the follow: i- pH, ii- saving, iii- geochemical processes.

The pH affects many phenomena (e.g. dissolution, precipitation, adsorption of contaminants, CO_2 absorption or activity of microorganisms) in the short and in the long period, thus the prediction of pH in function of time is an important parameter. In case of BA, the alkalinity, especially due to high CaO, gypsum and ettringite content (Meima and

Comas, 1997), promotes the metal mobility in the short time, but it is important to predict be the potential metal release in the long term.

With regard to the different role played by particle size distribution in the BA, Van Gerven *et al.* (2005) and Arickx *et al.* (2006) compared the metal leaching concentration of the fresh BA with the Flemish limit values for recycling of granular material in construction applications. In particular, the sand ($0.2 < D < 2$ mm) and the sludge ($D < 0.1$ mm) fractions were not in compliance with limit values.

By considering the effect of the chemical composition on metal leaching, Zomeren and Comas (2004) showed the dependence of the Cu leaching from dissolved organic carbon (especially of the fulvic acid type components), detected in BA leachates.

Geochemical processes, such precipitation/dissolution of common minerals, control the leaching of major and trace elements from BA (Comas et al., 1993; Kirby and Rimstidt, 1994; Meima and Comas, 1997). Other observations confirm that sorption processes may control metal leaching; for example, amorphous iron and aluminium (hydr)-oxides are known to strongly sorb heavy metals and Mo (Stumm and Morgan, 1981; Dzombak and Morel, 1990; Meima and Comas, 1998). As is common knowledge, the leaching of several elements, such as Cu, Pb and Zn decrease as a result of weathering. The use of a geochemical modelling method (e.g. MINTEQA2) might help to understand which geochemical processes are involved during the ageing of residue. In this way, the metal leaching behaviour might be predicted in the long time.

Many treatments options have been proposed prior BA reuse or landfilling, such as chemical extraction, ageing, carbonation, size separation magnetic separation. Nowadays, the aim of a treatment is to accelerate the chemical and mineralogical transformations which would occur in the medium and long term. Among recent treatments propose, *natural weathering* and *carbonation* process are the most innovative and economically advantageous techniques.

Carbonation has been recognised as one of the important ageing process that causes chemical and mineralogical changes in BA; it involves the adsorption of CO_2 by alkaline minerals which entails calcite precipitation and pH decrease. Metals speciation and solubility may be modified, also as a result of several interrelated processes: complexation, hydration, hydrolysis, dissolution/precipitation, oxidation/reduction, sorption and mineral neo-formation. In this respect, Al minerals, amorphous aluminosilicates, $Al(OH)_3$ and Fe oxides are likely to precipitate during carbonation (Stumm and Morgan, 1981; Meima and Comas, 1997) and sorption of contaminants on neo-formed solid might be an important mechanism that causes metal leaching reduction (Meima and Comas, 1998; Zevembergen *et al.*, 1994). This process depends on pH: neutral and alkaline pH values favour cation binding, whilst low pH values favour oxyanion binding (Dzombak and Morel, 1990).

The time required for the BA carbonation process depends on CO_2 content and pressure in the gas phase, as well as water content and temperature in the system. In case of atmospheric conditions, the optimum value of CO_2 and water content was estimated between 10 - 20 % and close to 20 %, respectively, whilst optimal temperature was assessed between 30° – 40 °C (Van Gerven *et al.*, 2005). The degree of carbonation is strongly dependent also upon the calcium content and in this respect the absence or low contents of $Ca(OH)_2$ and/or the deposit of other compounds might influence the diffusivity and reactivity of the carbon dioxide.

The natural carbonation process usually requires long periods, thus large areas would be needed to stock the material for natural weathering before reuse/landfilling. Therefore, in order to make possible an effective technical exploitation, the adoption of specific conditions (i.e. high CO_2 pressure, optimal water content) or material pre-treatments (i.e. preliminary mineral phases dissolution), is currently under evaluation. In general, although the interest on technical applications of the carbonation treatment as a possible solution to improve the environmental properties of alkaline residues arose several years ago, a better understanding of the key reaction mechanisms proper of each type of material to be treated and of the influence of chemical and physical parameters, e.g. differences between particle size fractions, is still an acknowledged need.

Another aspect to evaluate concerns the organic matter which is not completely mineralized, during combustion process, thus a portion remains in BA. The organic matter might provide a substrate for microbial activity (Belevi *et al*., 1992; Ferrari *et al*., 2002). Microbial degradation of organic matter in BA release organic acid (Dugenest *et al*., 1999) and CO_2 which might react with calcite contributing to the carbonation reaction during the ageing process. Rendek *et al*. (2006) reported that the biodegradation of organic matter is probably an important factor in BA carbonation during ageing process; they hypothesized that atmospheric CO_2 increased by the CO_2 produced during the biodegradation processes.

In this framework, a study was performed aimed at assessing the effects of direct aqueous carbonation treatment on the characteristics of the BA produced at an integrated platform for solid and waste-water treatment located in Italy. As the first general goal the effects of the treatment in terms of modification of the BA mineral phases and reduction of metals release were assessed. Furthermore, the assessment of the above-mentioned goals was extended to different BA particle size fractions in order to study the influence of the particle specific surface and of the possible differences in chemical composition among the different considered particle size fractions. Another objective of this research study was evaluating the CO_2 sequestration capacity of the considered BA and of the different particle size fractions.

Experimental study consisted of: (a) monitoring solutions composition obtained by leaching tests on BA and its particle size fractions, before and after carbonation treatment, (b) monitoring solutions composition obtained by leaching tests on BA at fixed pH and identification of solubility-controlling minerals phases by geochemical modeling, (c) achieve more information on BA metals mobility by adopting a sequential extraction method on BA sample, before and after treatment (d) performing calcimetry and thermal analysis on the single particle fraction, before and after carbonation treatment.

3.2 Materials and methods

Bottom ash samples were collected after quenching at a waste-to-energy (WtE) plant in Cagliari - Sardinia (Italy). The sampled BA was air dried for 4 days, homogenized and quartered in order to produce representative laboratory samples to be used for preliminary determination of total metal concentration and related leaching potential, loss on ignition (LOI), acid neutralization capacity (ANC). A sample of approximately 5 kg was sieved in order to produce the following particle size fractions: 0-0.106 mm (A), 0.106 mm-0.212 mm (B), 0.212-0.420 mm (C), 0.420-1 mm (D), 1- 4 mm (E), 4-10 mm (F), and > 10 mm (G). Each fraction was reduced to < 0.10 mm size and analysed in order to assess total organic carbon (TOC), loss on ignition (LOI) and total metal content. Calcium carbonate contents in untreated and carbonated BA was evaluate by both calcimetry and thermal analyses. Characterization by X-ray diffractometry (XRD) and metal leaching tests were performed on each particle size fraction.

Trace elements content in BA samples was determined by microwave acid digestion, according to EPA method n. 3052, by adding 4 ml of hydrofluoridric acid, 9 ml of nitric acid and 3 ml of hydrochloridric acid to 0.3 - 0.4 g of dry sample. The vessel was sealed and heated in the microwave system. The temperature profile is specified to permit specific reactions and incorporates reaching (180 ± 5) ºC in approximately less than 5.5 minutes and remaining at (180 ± 5) ºC for 9.5 minutes for the completion of specific reactions. After cooling, the vessel contents may be filtered, diluted to volume of 100 ml, and analyzed by the ICP-OES (Varian 710 ES).

Macro element content was determined by alkaline digestion, adding to 0.2 – 0.4 g of dry sample, 2.0 – 2.5 g of metaborate lithium in platinum melting pots. The mix was heated at 1050 °C, followed by dissolution of the melted material in a 10 % HNO_3 solution (V_{final} = 100 ml) and the measurement of element concentrations in solution was performed by ICP-OES.

With the aim of assessing the water content and the amount of non volatile organic matter in BA, a sample was dried overnight in an oven at (105 ± 3) °C, according to EN 14346 method. After that, non volatile organic matter was evaluated measuring the loss on ignition (LOI), by applying the method EN-15169. The procedure applied was performed heating a sample in a furnace up to (550 ± 25) °C for at least 1 hour. It should be noted that any content of elementary carbon and volatilisation of organic materials or chemical reactions by inorganic compounds, is included in the LOI.

Total organic carbon (TOC) was measured using a TOC analyzer (SHIMADZU, TOC-VCSN) with a solid sample module (SHIMADZU, SSM-5000 A). The test was performed in triplicate.

Calcium carbonate content was determined by the calcimetry analysis which was performed using a Dietrich-Frülingh calcimeter. The method is based on the measure of volume of CO_2 released when 10 ml of HCl (1:1) are added to 1 g of dried sample. It is necessary now to calculate the carbon dioxide volume (V°) at dry condition and at 0 °C temperature and at 760 mmHg pressure, by the following formula:

$$V^0 = \frac{[V*(B-w)]*273}{760*(273+t^0)} \qquad [3.1]$$

Where:

B = barometric pressure in mmHg

w = water vapour tension at t° temperature in mmHg
V = reading in ml

It is necessary to calculate the water vapour tension at 20 °C in mmHg by simple linear interpolation.

The carbonate content was assessed by thermo-gravimetric analysis (TGA). The procedure is based on the determination of changes in sample weight during heating. A derivative of weight loss allows assessing the point at which weight loss is most apparent. The loss weight due to calcium carbonate decomposition occurs in a range between 700° - 900 °C.

Differential thermo analysis (DTA) is a test where the material under study and an inert reference are made to undergo identical thermal cycles, while recording any temperature difference between sample and reference. This differential temperature is then plotted against time, or against temperature. Changes in the sample, either exothermic or endothermic, can be detected relative to the inert reference, thus, a DTA curve provides data on the transformations that have occurred, such as glass transitions, crystallization, melting and sublimation.

Thermo-gravimetric (TG) and differential thermo analyses (DTA) were performed by using a analyzer in air atmosphere (Stanton Redford, model STA 780) equipped with a Pt/Rd crucible (V= 135 mm^3, D= 6 mm) at a heating rate of 15 °C/min.

The pH of material was evaluated by mixing the residue with distillate water (L/S= 10 l/kg) for 24 hours. The measure was carried out on the solution filtered. The neutralization capacity (ANC) allows assessing the consequences of external influences on the pH of the material. From the amount of acid required to cover the pH range (from 4 to 12), the ANC of the material is determined. The method applied was the UNI CEN/TS 15364. The method was applied on sieved (D < 4.0 mm) untreated BA. Separated test portions are separated a fixed L/S ratio (L/S= 10 l/kg) with leachants containing pre selected amounts of nitric acid (1 and 10 M) in order to reach stationary pH values at the end of the extraction period (48 h). After filtration at 0.45 µm, the metals concentrations in the solution were measured with ICP-OES spectrometry. The test was performed in duplicate.

The partitioning of Cu, Zn, Pb, Cr and Mo in BA was investigated by performing the three steps of the sequential extraction (SE) procedure proposed by the Standard, Measurement and Testing Program (SMTP) of the European Union. The method was carried out on 1 g of dry sample. An additional fourth step with strong acid attack was performed for mass balances calculations (Bruder-Hubscher *et al*., 2001). Details on each SE step are reported in Table 3.1. The principle of the method is based on the fractional of the metals contended into the matrix in different fractions which can be destroyed by using specific reagents. Metals bound to each fraction destroyed are then released in solution. The solid phase is separated by the solution phase (centrifugation and filtration) and metals concentration in solution phase is analysed by ICP-OES. The fraction studied generally are: (a) exchangeable (metals are extracted by solution containing electrolytes or slightly acid); (b) carbonate fraction (metals bound to carbonate, soluble in acid solution); (c) iron and manganese oxides (metals bound to soluble in a reducing solution, followed by an acid treatment which allows to precipitate metal bound); (d) natural organic matter (metals bound to organic compounds or sulphides, soluble in oxidizing conditions).

The residual fraction contains silicates and other minerals which retain elements in crystalline structure and it can be destroyed by an acid digestion. To evaluate the effect of carbonation treatment on metal partitioning, SE was performed on both untreated and carbonated BA samples

Table 3.1. Sequential extraction procedure (Bruder-Hubscher *et al.*, 2002).

Extraction step	**Reagents**	**Extracted fractions**
1	Acetic acid 0.11 M	Water, acid soluble (carbonates) and exchangeable
2	Hydroxylammonium chloride 0.1 M, adjusted to pH=2 with HNO_3	Easily reduceable (Fe and Mn hydro- oxides)
3	Hydrogen peroxide (H_2O_2) 8.8 M, ammonium acetate 1.0 M, adjusted to pH=2 with HNO_3	Oxidizable (sulphides and organic matter)
4	Hydrochloridric/nitric/hydrofluoridric acid (9 ml: 3 ml: 5 ml)	Residual

The crystalline minerals present in the solid residue were identified using X-ray powder diffraction analysis and TG/DTA. The XRD scan was conducted on untreated and carbonated dried BA samples. The diffractometric analyses were performed using a

RIGAKU device with Cu-Kα radiation (copper tube operated at 30 kV and 30 mA).

Accelerated carbonation treatment applied on BA and its particle size fractions was performed by placing moistured (20 % by weight) samples into a CO_2 incubator chamber (PBI, 2123 TC), provided with a bottom water storage in order to keep a constant internal atmosphere humidity. Temperature was set at 40 °C. Bottom ash samples were exposed to an atmosphere characterized by a 10 – 20 % by volume of CO_2 and were spread out in thin layers, in order to optimize CO_2 diffusion. The process was interrupted when a pH of 8.3 was reached (usually after 24 - 48 h).

The effect of carbonation on metals mobility was assessed by performing the compliance leaching test EN 12457-2 test on the untreated and carbonated BA and on the considered particle size fractions. The method consisted of mixing 10 - 20 g of BA (after a size reduction to less than 4 mm) in 100 - 200 ml of distillate water (L/S= 10) for 24 h, the mass of the sample depending on the particle size fraction studied: 10 g were selected for classes < 0.425 mm size and 20 g for the other classes. After filtration at 0.45 µm, the metals concentration in the solution was measured with ICP-OES spectrometry (Varian, 710 ES). All the tests were performed in triplicate.

The influence of pH on metal leaching from untreated and carbonated BA was evaluated by means of pH-Stat leaching tests: 20 g of dry material were mixed with 200 ml of distillate water (L/S= 10) for 24 h, maintaining a constant pH by addition of small amounts of analytical grade HNO_3/NaOH by an automatic potenziometric titrator (KEM, AT 510). The suspension was filtered and analyzed as described above. All the pH-stat tests were performed in duplicate. The range of pH studied was from 4.0 to 10.0.

3.3 Geochemical modeling

The geochemical modeling was performed adopting the Visual MINTEQ code, using as the input the metal concentrations measured in solution from untreated and carbonated BA produced by means of EN 12457-2 leaching tests; all solids precipitation was suppressed and pH was fixed at the measured value. Potential solubility-controlling phases were selected among those proposed by the model and having a saturation index (SI) close to zero (-1 < SI < +1). The solution composition in equilibrium with the selected minerals was estimated as a function of pH (in the range 4.0 - 10.0), and by adding at each run one of the selected minerals as infinite solid. The equilibrium curves calculated by modeling were compared with experimental data obtained by the leaching tests.

Bottom ash pH may be controlled by the solubility of one mineral phase or by the coexistence of several mineral phases.

3.4 Results and discussion

Accelerated carbonation treatment showed effects on chemical and mineralogical properties and on metal leaching. In this section results of CO_2 sequestration capacity are reported.

3.4.1 Effects of accelerated carbonation on chemical and mineralogical properties

The chemical composition (trace element), water content, LOI and TOC assessed on fresh BA are reported in table 3.2. The grain size distribution curve of fresh BA is shown in figure 3.1. Total element composition, LOI and TOC of each particle size fraction studied are reported in Table 3.3. The grain size distribution showed a gentle slope of the curve which indicated a good gradation. As a matter of both, fresh BA is a heterogeneous material and it is classified as a sandy and gravel soil by considering the Unified Soil Classification System (USCS).

The TOC content was higher in the smallest size fractions and decreased with increasing particle size, confirming the results previously obtained by Zhang *et al.* (2004). Organic carbon in BA includes compounds formed during and after combustion (Rubli *et al.*, 2000; Van Zomeren and Comas, 2003) and unburned organic matter, since some organic compounds might persist at the lower temperature range of 300° - 600°C, locally occurring in the furnace bed.

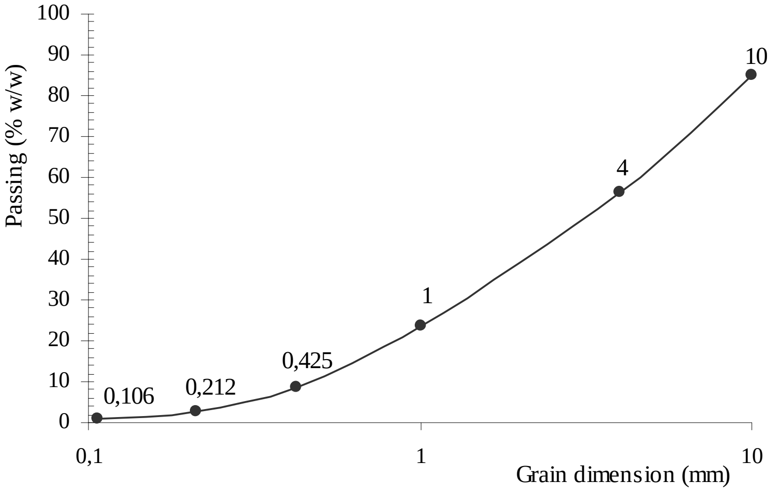


Figure 3.1. Grain size distribution curve of fresh BA.

Table 3.2. Trace element content (mg/kg dry wt.), water content (%), LOI (%) and TOC (%) assessed for the fresh BA.

Element	Concentration (mg/kg)
Pb	2579 ± 212
As	12.00 ± 3.34
Cr	264 ± 41.62
Zn	3182 ± 294
Mo	8.34 ± 1.28
Sb	85.30 ± 22.25
Cu	3022 ± 396
Ni	85.00 ± 3.50
Cd	6.14 ± 0.45

Chemical property	Value (% w/w)
Water contet	12
LOI	1.38
TOC	0.80

Table 3.3. Total metal content (mg/kg dry wt.), LOI (%) and TOC (%) assessed for the particle size fractions.

Class	A	B	C	D	E	F	G
	< 0.106	0.106 - 0.212	0.212 - 0.425	0.425 - 1.00	1.00 - 4.00	4.00 - 10.00	> 10.00
Element							
Pb	2847	3503	3140	4119	1450	2144	3163
As	11.91	14.85	11.40	11.35	9.31	8.81	15.72
Cr	292	278	225	233	124	262	291
Zn	4476	3876	2417	2551	3844	1239	3380
Mo	65.68	18.55	3.40	<	<	N.D.	<
Sb	554	420	358	285	100	N.D.	280
Cu	2542	3696	4934	6453	2964	7217	2692
Ni	124	146	138	101	107	97.00	49.84
Cd	16.28	13.37	10.63	14.37	5.42	< D.L.	7.53
Al	29185	32614	36721	47335	50632	43083	51353
Ca	264074	232096	183136	155172	149951	296442	298786
Mg	16666	15530	14184	12539	13631	11857	14939
K	7407	10353	14184	17241	13631	7905	9337
Fe	23703	36238	48857	62695	52580	55335	56022
Na	2037	2588	3467	3605	7789	11857	9337
Mn	1666	1207	1103	1097	1168	790	5415
Si	82592	115271	192119	192633	223953	233201	220354
LOI	6.75	6.77	4.62	3.60	3.58	1.40	1.34
TOC	0.995	0.700	0.560	0.309	-	0.336	-

Silicium and Al content were higher in the coarser fractions (D > 0.425 mm), which in fact displayed quartz as main mineral phase during diffractometric analyses (Figure 3.3). Bottom ash contains numerous crystalline phases, however, the detection limit of XRD is about 2 % and only major phases could be identified. The main component of BA detected was quartz and calcite, and analysing each particle size fraction, also lead (as metal), hematite (Fe_2O_3), hardystonite ($Ca_2ZnSi_2O_7$), CaO and ramsdellite (MnO_2) were found. As for the finest fractions, ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}$ 26 H_2O), clinozoisite ($Ca_2(AlFe)Al_2(SiO_4)_3OH$), Pb (as metal), hematite and CaO were detected. Fresh BA contained lime and portlandite which are quickly carbonated into calcite in the aged sample.

As far as the speciation of metals was concerned, table 3.4 sums up metal partitioning as obtained from the SE applied on both the untreated and carbonated BA, the latter discussed above. The percent metal recovery was calculated as the sum of all the SE steps concentrations related to the total content. Copper and lead were extracted mainly under oxidizing conditions (metal bound to organic matter and sulphides), with a recovery of 30 % and 34 % w/w, respectively. Lead release under oxidizing conditions could be explained by the possible presence of sulphides, which were detected by XRD analysis in class D of untreated BA. Over 70 % by weigh of the total Zn was extracted under slightly acidic conditions, meaning that the metal can be mobilized from BA when pH changes occur.

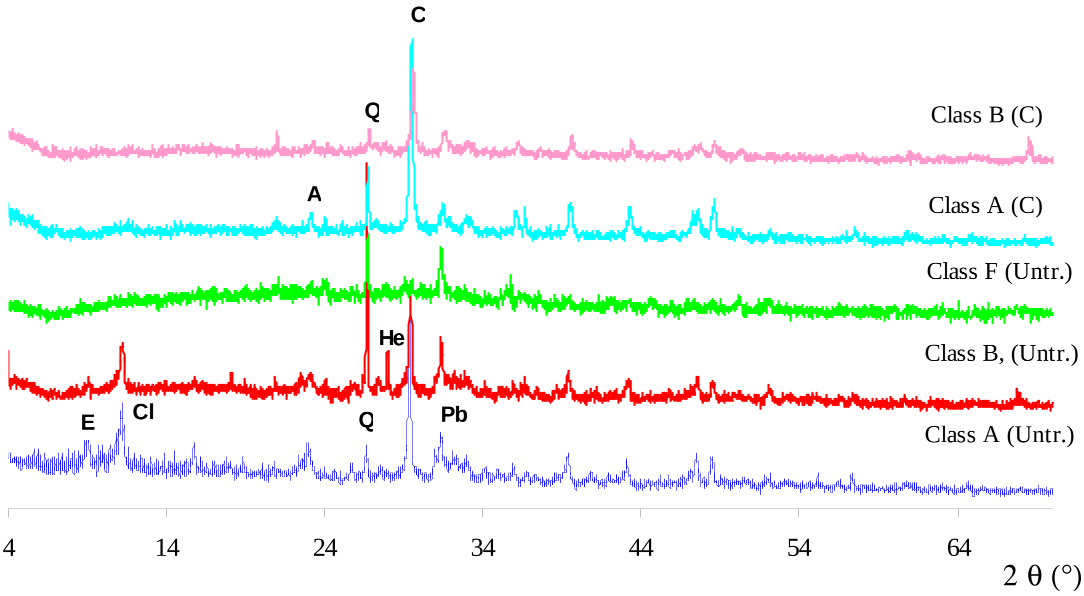


Figure 3.3. Diffractometric analysis on untreated (Untr.) and carbonated (C) BA fractions; E = ettringite, Cl = clinozoisite, Q = quartz; Pb = lead as metal, **C** = calcite, He = hematite, A = anglesite.

Table 3.4. Metal partitioning as obtained from the sequential extraction applied on both untreated and carbonated BA (mg/kg dry wt.) and percent recovery (w/w).

Element		1 step	2 step	3 step	4 step	% Recovery
Cr	Untr.	8.93±1.61	7.70±0.93	27.48±1.30	218±8.42	99
	C	6.76±1.84	7.71±0.23	31.80±2.92	209±32.60	79
Cu	Untr.	437±4.89	341±32.00	943±59.00	1325±23.73	101
	C	239±38.00	95.00±7.89	1122±315	1854±23.43	110
Zn	Untr.	1911±321	281±6.00	378±17.00	576±50.00	106
	C	1899±271	634±129	389±75.00	309±40.00	108
Pb	Untr.	576±179	344±107	922±322	881±179	106
	C	417±44.70	299±89.00	878±120	1622±67.00	114
Mo	Untr.	0.32±0.10	1.06±0.39	0.20±0.01	7.48±0.65	108
	C	1.40±0.47	0.65±0.25	0.03±0.001	5.56±1.25	92

Most of the total Cr and Mo were found in the residual fraction (> 80 % by weigh of total Cr), suggesting that they tightly bound to the matrix and therefore scarcely releasable under natural environmental conditions. Analytical results provided by SE showed a high standard deviation, in agreement with other studies. It should be stressed that 1 g of material is hardly representative of matrices, such as BA, due to its typical low homogeneity and high complexity (Brudere-Hubscher *et al.*, 2001).

As far as the effect of carbonation on the general characteristics of the material was concerned, the pH of the BA decreased from 12.34 ± 0.58 to 8.49 ± 0.72. The natural pH for untreated BA pH was likely to be related to the co-existence of ettringite, calcite, gypsum and portlandite, since the equilibrium pH of a pure system, containing the above mentioned minerals, was expected to be 12.39.

As compared with the untreated BA, carbonate formation resulted in an ANC increase, from 1.0 meqH$^+$/g of BA to 2.0 meqH$^+$/g of BA at pH = 8.00 (Figure 3.4). The pH decrease observed during carbonation was stronger for the BA fine particle size fractions than for the coarser ones, and it was respectively of 8.20 and 9.50, the difference being probably due to the higher quartz content in the latter. Polettini *et al*. (2003), by applying accelerated carbonation treatment on BA, found an increase of ANC value from 0.46 – 0.48 to 0.88 meq/g (at pH 5).

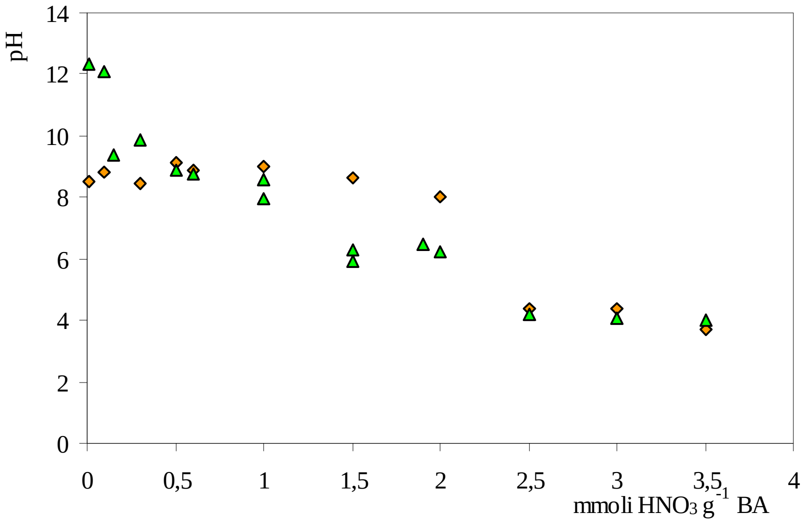


Figure 3.4. ANC curves obtained by ANC tests on untreated (△) and carbonated (▲) MSW combustion BA

3.4.2 Effects of accelerated carbonation on metal leaching and modeling

Molybdenum, Cr, Cu, Zn and Pb concentrations in the solution obtained by the EN 12457-2 leaching tests performed on the BA and on each particle size fractions before and after carbonation, are shown in Table 3.5. The overall Cr release was not modified by carbonation, although the treatment increased Cr release in almost all the fractions having particle size < 1 mm (about 22 % by weight of the total material). As far as the metal partition was concerned, differences due to carbonation in Cr partitioning were not appreciable (Table 3.4). As for Zn, the overall release was not modified by carbonation; moreover, no clear influences on Zn mobility were observed when each particle size fraction was considered. The Zn leaching behaviour was in accordance with the results obtained by SE performed before and after carbonation, which showed no appreciable differences in terms of metal bound to the soluble and exchangeable fraction. After the treatment, Mo concentration in BA solution increased as much as 63 % and the mobility was fairly homogenous for all the size classes. It has to be considered that the diffractometric analysis showed the presence of ettringite in the smallest fractions; a possible replacement of SO_4^{2-} in the mineral by oxyanions such as MoO_4^{2-}, CrO_4^{2-}, SbO^{3-} has been highlighted, among the others, by Kumarathasan *et al.*, (1990). This mechanism could explain the higher Mo and also Cr release noticed after the treatment. In fact, ettringite can only persist at alkaline pH and, when pH decreases below 9 - 10 (e.g. during carbonation), sulphate, Cr, Mo and Sb are released in solution. However, since a higher Mo release was assessed for all the size fractions, other mechanisms besides ettringite dissolution should be involved. In agreement with this, sequential extraction performed on the carbonated material showed an increase of Mo bound to soluble, exchangeable and carbonate fractions. The carbonation treatment resulted in a reduction of Cu and Pb release of 22 % and 40 %, respectively. As well known, enhanced leaching of Cu from untreated BA is probably due to dissolved organic carbon (DOC), in particular the fulvic-like components present in the material (Belevi *et al*, 1993, Meima *et al.*, 1999; Van Zomeren and Comas, 2004). As for the speciation of Cu (Table 3.4), a post-treatment reduction of both the soluble, exchangeable and carbonate, (from 14 % to 7 % w/w) and the reducible fractions (from 7 % to 3 % w/w) was observed. The increase of Cu bound to the oxidizable fraction, however, did not lead to an increase of Cu leaching from the treated BA, most likely because, at pH ~ 8.3, Cu bound to DOC decreased due to co-precipitation with amorphous Al-minerals (Meima *et al.*, 2002). As far as the Cu release from the different BA fractions was concerned, it can be stressed that the release reduction had to be ascribed to the finest fractions. In the case of Pb, the reduction of solubility from the carbonated BA was evident for each of the considered size classes. The results obtained by SE indicated that the Pb bound to soluble and exchangeable fraction decreased and an increase of the metal bound to the residual fraction was also observed; nevertheless, the experimental data are not reliable due to the high standard deviations. In the untreated material, most of the Pb was bound to organic matter and sulphides, as seen for Cu, hence it can be supposed that a similar mechanism of immobilization (e.g. co-precipitation) does occur, as also previously described by Meima and Comas (1998) for Cd.

Table 3.5. Metals concentration in solutions obtained by EN 12457-2 test (mg/l) performed on both untreated (untr.) and carbonated (C) BA, as well as on each particle size fractions.

Element	Mo		Cr		Cu		Pb		Zn	
Fraction size (mm)	Untr.	C	Untr.	C	Untr.	C	Untr.	C	Untr.	C
< 0.106	0.243	0.200	0.111	0.604	0.267	0.109	0.113	< 0.0015	0.323	0.023
0.106 ÷ 0.212	0.016	0.230	0.187	0.093	0.269	0.104	0.092	0.051	0.061	0.076
0.212 ÷ 0.425	0.087	0.094	0.090	0.165	0.150	0.106	0.142	0.080	0.052	0.070
0.425 ÷ 1.00	0.049	0.080	0.053	0.094	0.092	0.062	0.190	0.032	0.044	0.038
1.00 ÷ 4.00	< 0.0005	0.003	0.025	0.030	0.055	0.053	0.109	0.014	0.073	0.022
4.00 ÷ 10.00	< 0.0005	0.016	0.016	0.006	0.045	0.047	0.043	0.071	0.091	0.009
> 10.00	< 0.0005	0.017	0.012	0.008	0.017	0.012	0.042	0.060	0.019	0.007
Untr. BA	0.054	0.088	0.072	0.068	0.089	0.069	0.072	0.043	0.049	0.056

Figure 3.5 reports the metals concentrations in the solution as obtained by the pH-stat leaching test, along with the results of the geochemical modelling. As for the general leaching trends observed, it can be assessed that leachability was largely controlled by the pH in solution. As for Cu, the shape of the leaching curve was similar for both untreated and carbonated BA. Moreover, the positive effect of carbonation could be observed, since leaching data for carbonated BA are below the ones obtained from untreated material in the neutral to alkaline pH range. Geochemical modeling suggested that the solubility-controlling phase was $Cu(OH)_2$ for both carbonated and untreated BA. Another research identified malachite ($Cu_2(OH)_2CO_3$) as solubility-controlling phase for treated BA

(Polettini *et al.*, 2002), whilst in this work the model did not suggest any evidence of Cu carbonate precipitation. As seen for Cu, also Pb showed a similar leaching curve before and after treatment, with a V shape typical of amphoteric elements. Furthermore, after carbonation it was evident a lower metal leaching in the alkaline pH range. Geochemical modeling did not provide any useful indication for the untreated BA, whilst it identified $Pb(OH)_2$ as solubility-controlling phase for the carbonated material. As for Zn, again a leaching trend typical of amphoteric elements was observed. The phases controlling Zn solubility in carbonated MSW combustion BA were zincite (ZnMnO) and hydrozincite ($Zn_5(CO_3)_2(OH)_6$) at pH close to 8; when pH decreases to 6, the solubility-controlling phase seemed to be zinc carbonate. In the case of the untreated material, modeling did not evidence any possible Zn solubility-controlling phase. When considering Mo leaching, the negative effect on metal mobility was easily assessed, since leaching from carbonated BA was generally higher than from the untreated material. Modeling predicted molibdates (i.e. $CuMoO_4$ and $PbMoO_4$) as the possible solubility-controlling phases, in both untreated and treated material, in line with previous studies (Meima *et al.*, 1999, Polettini *et al.*, 2005) that suggested powellite ($CaMoO_4$) as the solubility-controlling mineral phase. In the case of Cr, for both the treated and untreated BA, the influence of pH on metal release could not be unambiguously assessed; the concentrations in the solution seemed to be lower at neutral pH and higher under acidic and alkaline conditions. Modeling did not show any possible solubility-controlling phase: however, the leaching pattern previously evidenced might be due to sorption phenomena on amorphous Fe and Al oxides, as suggested by Meima *et al.* (2002).

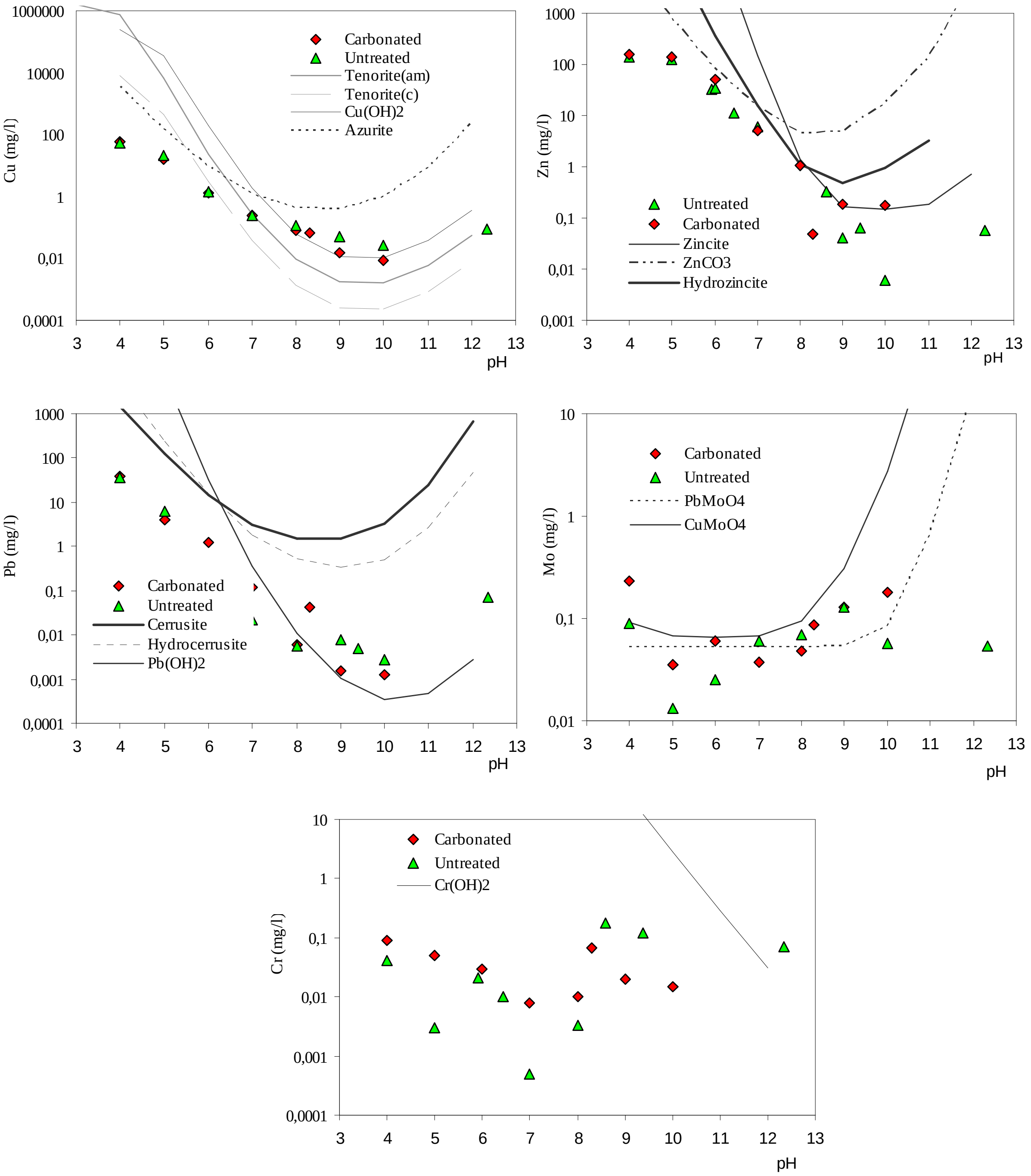


Figure 3.5. Metals concentration in pH-stat test solution and solubility-controlling phases as suggested by geochemical modeling.

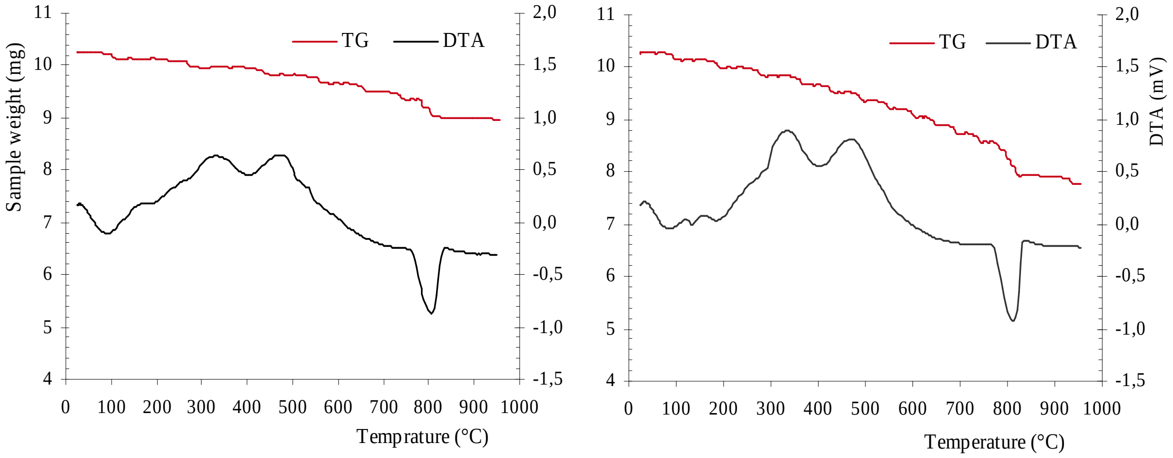
3.4.3 Carbon dioxide sequestration capacity

The CO_2 sequestration potential capacity of BA particle size fraction was evaluated by both calcimetry and TG/DT analyses. As it is well known, during the TG analysis the loss weight that occurs in the range of 650° – 850 °C could be directly linked to the carbonate decomposition. Figure 3.6 (a) reports the TG/DTA curves obtained by analysing class A fraction sample: the shape of loss of weigh curve, shows three steps, in particular a first one between 300°- 400 °C, associated to organic matter oxidation (exothermic reaction); the second one between 400° – 600 °C probably caused by $Ca(OH)_2$ decomposition and a third at 800 °C due to carbonate decomposition. The BA fraction required to be milled before analysis, thus it is consistent with a partial natural carbonation of the material when it is expose to air atmosphere. In figure 3.6 (b) the TG curves obtained by carbonated BA sample, shows in a range between 300°- 400 °C the oxidation of organic matter, and at 850 °C the loss of weight due to carbonate deposition.

The CO_2 uptake was evaluated by the percent loss weight at 600° – 850 °C, before and after accelerated carbonation, with respect to the initial weight. The amount of CO_2 sequestrated by residues, on the basis of TG analysis, was estimated by calculating the difference, after and before treatment, of the weight loss in the range of 700° – 900 °C, with respect to the initial weight of residue sample, taking into account the weight increase upon carbonation:

$$CO_2\ uptake\ (\%) = \frac{CO_{2,\ final}(\%) - CO_{2,\ initial}(\%)}{100 - CO_{2,\ fiunal}(\%)} \times 100 \qquad [3.1]$$

Calcimetry and TG analyses results indicate a CO_2 uptake of about 5 - 9 % by weight of total sample for the class A and a decreasing value to 3 - 4 %, in the case of class D. These results is consistent with several other experiences that indicated a maximum value of weight gain of BA sample, upon carbonation, between 3.0 – 6.5 % (Johnson, 2000; Fernandez-Bertos *et al.*, 2004; Rendek *et al.*, 2006). The study, concerning the CO_2 uptake capacity by BA particle size fractions, showed that sieving is an important factor during the carbonation process, according to the results obtained by other authors (Van Gerven *et al.*, 2005; Rendek *et al.*, 2006). The explanation might be due to Ca-minerals, like portlandite and ettringite, detected by XRD analysis, in the smallest fraction, which are the easy reactive mineral phases. Another explanation is that accelerated carbonation has a little influence on the gravel fraction because it consists of inert material such as SiO_2 (the ratio Ca/Si measured in the fine fractions was of 2 – 3, against 1 – 1.5 found in the coarse fractions).



a) (b)

Figure 3.6. TG/DTA obtained for class A (D < 0.106 mm) before (a) and after (b) carbonation treatment.

The maximum theoretical sequestrating capacity was also estimated by assuming the full stechiometric conversion to carbonates of the overall CaO and MgO content (kodama *et al.*, 2008). Finally, on the basis of the CO_2 emission factors available for the WtE plant, the reduction of CO_2 emissions potentially achievable has been evaluated. As resumed in Table 3.6, the residue under investigation showed different CO_2 uptakes, depending especially on the size fraction, mineralogy and specific surface area. The measured CO_2 uptakes were in general quite lower than the maximum theoretical values, indicating that by adopting appropriate operating conditions and/or using chemical/physical pre treatments the storage potential of the different fractions could be increased.

Table 3.6 - CO_2 sequestration capacity of the different residues under investigation and reduction of the CO_2 emissions achievable at the different combustion plants.

Residue	CO_2 uptake (kg CO_2/ kg residue)	Maximum theor. CO_2 uptake (kg CO_2/ kg residue)	Plant Emission factors (kgCO_2/ kg residue)	Reduction of CO_2 emissions * (%)	Maximum Reduction of CO_2 emissions ** (%)
MSW combustion BA	0.023	0.18	4.71	0.48	3.82
< 0,106 mm (1.07%)	0.086	0.22			
0,106-0,212 mm (1.81%)	0.051	0.19			
0,212-0,425 mm (5.81%)	0.057	0.15			
0,425-1 mm (14.92%)	0.037	0.13			
1,0-4,0 mm (32.64%)	0.024	0.12			
4.0-10 mm (28.88%)	0.010	0.24			
> 10 (14.87%)	0.000	0.25			

*Calculated on the basis of the measured uptake
** Calculated on the basis of the maximum theoretical uptake

3.5 Conclusions

The present study has pointed out the effect of accelerated carbonation on BA and on its particle fractions. Accelerated carbonation was able to modify some important macroscopic properties such as buffering capacity and mineralogy of BA. In particular, the observed buffering capacity doubled at pH 8; as far as the metals mobility was concerned, carbonation proved to be effective in reducing the mobility of Pb and Cu, whilst increased the Mo one and did not sort any significant positive effect on Zn and Cr.

If the single size fractions are considered, the effects on Pb (decreased mobility) and Mo (increased mobility) were fairly homogenous for all the size fractions, whilst the overall positive effect on Cu mobility seemed to derive mainly from the particles having size < 1.0 mm. The effect of carbonation on Cr mobility seemed to be negative for fractions having particle size < 1.0 mm.

On the basis of the experimental findings, it could be assessed that the carbonation treatment exerted opposite effects on metals mobility when applied on the BA. Furthermore, different effects were noticed also when the treatment was applied to the considered particle size fraction, even when the single metal was concerned.

The carbonation treatment combined with other treatments (e.g. addition of sorbing agents such as Bauxol) might improve and make uniform the leaching behaviour of the residue.

As far as the capacity of capturing the CO_2 is concerned, the results obtained underlined that it is higher for the smaller BA particles (about 5 - 9 % by weigh of sample). Therefore the eventual implementation of the carbonation treatment, in order to contribute to the reductions of CO_2 point source emissions, should require careful evaluations concerning the opportunity of applying it to the whole BA mass or to selected fractions more capable to sequestrate the gas.

3.6 References

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Chapter 4. Accelerated carbonation on MSW combustion APC ash

4.1 Introduction

The Waste to Energy treatment while being a feasible option for recovering energy and reducing the mass of municipal solid waste fractions to be landfilled is known to entail concentration of inorganic contaminants in the post-combustion by-products such as bottom ash, fly ash and flue gas cleaning residues (Hjelmar *et al.*, 1996; IAWG, 1997; Sabbas *et al.*, 2003). In particular, the solid by-products generated by flue gas treatment, named APC residues, are composed by the flue gas condensation and reaction products and the excess of sorbent material (usually lime or activated carbon) injected into the stack gas, but include also the fly ash particles carried over from the combustion chamber if they are not separately captured upstream. APC residue, corresponding to about 3 % of the incinerated total waste mass, is classified as hazardous wastes according to the Commission Decision 2000/532/EC. The main concern related to the disposal or reuse of these residues is represented by the potential release of metals and soluble salts (Quina et al., 2009); so that a pre-treatment is required in order to reduce the associated environmental impact. In the literature, several treatment technologies have been proposed as appropriate treatments for APC residues, including solidification and/or stabilization, physical and chemical separation and thermal processes (see e.g. Quina *et al.*, 2008 and references therein). Among these options, accelerated carbonation has been described as an important treatment technology capable of improving the environmental and technical behaviour of different types of combustion residues, consisting in the adsorption of CO_2 by alkaline materials which causes pH decrease and calcite precipitation (Meima et al., 2001; Ecke *et al.*, 2003; Huijgen *et al.*, 2006; Costa *et al.*, 2007; Baciocchi *et al.*, 2009; Wang *et al.*, 2010) This process, that occurs also spontaneously under ambient conditions, results in a number of chemical/mineralogical transformations which involve also the immobilization of several inorganic contaminants of concern. Furthermore, accelerated carbonation of alkaline residues has been found to represent an effective way to achieve CO_2 sequestration from industrial point sources, an interesting additional benefit in view of the decrease of the emissions of greenhouse gases (Huijgen *et al.*, 2005; - Fernández-Bertos *et al.*, 2004; Baciocchi *et al.,* 2007; Bertos et al., 2007; Sipilä *et a*l., 2008).

However, despite the widespread experimental studies carried on so far, several aspects still need to be elucidated, especially pertaining to both the optimal operating conditions to be adopted and the leaching behaviour of some heavy metals and oxyanion-forming elements (e.g., Cr, Mo, As and Sb) for which inconsistent results in terms of reduction of mobility have been reported in literature (Van Gerven *et al*., 2005; Astrup *et al*., 2006; Cornelis *et al*., 2006; Costa *et al*., 2007).

Baciocchi *et al.* (2009) presented the results of an experimental work performed on carbonated APC ash to study the CO_2 uptake kinetic and the metal leaching-controlling mechanisms. The dependence of CO_2 uptake upon the L/S ratio, temperature and CO_2 pressure, had shown: (i) the L/S ratio had a strong impact on the CO_2 uptake, (ii) the increase of temperature from 30° C to 50 °C could improve kinetic of reaction, (iii) pressure, from 1 to 10 bar, seemed not influence kinetic of carbonation. After 1 – 1.5 hours, the CO_2 uptake was of over 250 g/kg of APC ash, by adopting a L/S = 0.2 l/kg and maintaining the system at P = 3 bar and temperature at 30 °C. In this condition, the Pb, Zn, Cu and Cd leaching was considerably reduced. The carbonation treatment has shown only a slight influence on Cr, chlorides and sulphates release, instead it seemed to cause a Sb mobilisation. To evaluate the mineralogical phases which controlled the metals release in solution during leaching tests, Visual Minteq geochemical speciation code was used. In case of Pb, Zn and Cu, metal concentration in solution were essentially controlled by hydroxides, carbonates and chlorides, depending on the pH range considered.

The present study focused on the application of an accelerated carbonation treatment to APC residue, in order to assess the potential of the process in terms of sequestration of the CO_2 emitted from WtE point sources as well as the influence on the environmental behaviour of the residue under concern.

4.2. Materials and methods

Municipal solid waste combustion APC samples were collected at a WtE plant in Cagliari, Sardinia, where the flue gas treatment system produces a residue composed of ashes coming from the heat exchanger (boiler ashes) and the particulate matter collected by the bag filters after addition of dry hydrated lime to neutralize acid components. The samples were homogenized in order to produce representative laboratory subsamples to be used for preliminary characterization: metal and anion content, total carbon content (TC) and loss on ignition (LOI). In order to investigate the effect of the accelerated carbonation treatment on the APC ash mineralogy and, consequently, on the inorganic contaminant leaching behaviour, and to estimate the CO_2 sequestration capacity of APC ash, release and partitioning of metals (Pb, Zn, Cr, Cu, Mo and Sb), APC ash buffering capacity and mineralogy were evaluated. The APC ash mineralogy was studied by means of X-ray diffractometry (XRD), calcimetry and thermo gravimetric (TG) analyses performed on both untreated and carbonated APC ash subsamples.

The metals content was determined by digesting 1 g of dried APC sample with a concentrated acid mix 3 ml of nitric acid, 9 ml of hydrochloridric acid and 5 ml of hydrofluoridric acid. After digestion, the residue was diluted to 100 ml by distilled water and HNO_3 (1 %). The macro elements content was evaluated by alkaline fusion with lithium metaborate (1050 °C). The metal concentration in solutions obtained was evaluated by ICP-OES analysis.

Water content and loss on ignition were determined respectively by the EN 14346 and EN-15169 methods. TC content was measured using a CHN analyzer (LECO, model CHN 1000). The analyses were performed in triplicate.

The pH of material was evaluated by mixing the residue with distillate water (L/S= 10) for 24 hours. The suspension was filtered and pH was measured on the solution. The buffering capacity of both untreated and carbonated APC ash was evaluated by means of the ANC test, by mixing several sub-samples of dry material with distilled water containing pre-selected amounts of acid (HNO_3) at a L/S = 10 l/kg and stirring the suspension for 48 h (UNI CEN/TS 15364).

The Cu, Zn, Pb, Cr, Sb and Mo partition in APC ash was investigated by performing the four-step sequential extraction procedure proposed by the Standards, Measurements and Testing Program of the European Union (Bruder-Hubscher *et al.*, 2001). Details of the method are given in Chapter 3.

Carbonate content was performed by a thermogravimetric analyser, in air atmosphere (Stanton Redford, model STA 780) equipped with a Pt/Rd crucible ($V = 135$ mm^3, $D = 6$ mm) at a heating rate of 15 °C/min. Calcimetry determination was performed by placing 0.5 g of APC subsample in a Dietrich-Fruehling apparatus, and adding 10 ml of HCl 1:1 v/v.

Diffractometric analyses were performed using a RIGAKU device, with Cu-Kα radiation (copper tube operated at 30 kV and 30 mA).

The effect of carbonation on metals mobility (Pb, Zn, Cr, Cu, Mo and Sb) was assessed by performing the EN 12457-2 test on the untreated and carbonated APC ash, as well as through the above mentioned ANC test. After filtration of suspension at 3 – 5 μm, the metals concentration in the solution was measured with ICP-OES spectrometry (Varian, model 710 ES).

The applied accelerated carbonation treatment consisted of a single step aqueous-route process carried out at ambient conditions (20 °C and atmospheric pressure). The treatment was performed into an open vessel, by blowing CO_2 through the continuously mixed APC ash slurry (L/S = 2.5 l/kg). The slurry was homogenized by both gas bubbling and a magnetic stirrer. With the aim of studying the evolution of the carbonation process, in terms of both pH decrease and effects on metals mobility, the pH value was continuously monitored and the input of CO_2 was stopped when pH reached prefixed values in the range between 13.17 (pH of fresh APC ash) and 8.22 (final pH attained during carbonation); APC slurry samples were collected at the end of each carbonation step in order to perform the leaching tests and pH control (at 24 hours).

In the following, carbonated $APC_{10.7}$, for instance, indicates APC ash carbonated until pH 10.7 was reached. All the samples were immediately dried at 105 °C and stored in closed bottles to arrest ageing reactions. The time required to reach the final pH of 8.22 was about 3 hours.

4.3 Results and discussion

In this section the effects of the accelerated carbonation treatment on chemical and mineralogical properties are discussed as well as the effect produced by treatment on the metals mobility. In the Section 4.3.3 the results concerning the CO_2 uptake of APC residue are reported.

4.3.1 Effects of accelerated carbonation treatment on chemical and mineralogical properties

The results of the APC ash preliminary characterization are reported in Table 4.1. Calcium and chloride are the main constituents, but a significant metal concentration was also assessed, in agreement with other studies reported in the literature (Baciocchi *et al.*, 2009;

Wang *et al.*, 2010). In figure 4.1, the XRD analysis displayed *portlandite*, $Ca(OH)_2$, as the main mineral phase, high amounts of NaCl, KCl, Ca(OH)Cl, and Na_2SO_4 crystalline phases and a little amount of $CaCO_3$, indicating a partial degree of natural carbonation of the fresh material. The Ca(OH)Cl compound is probably formed during neutralization reaction of acid gas flue which contains HCl, with lime, as reported by Wang *et al.* (2010). The XRD performed on the carbonated APC ash showed the disappearance of the $Ca(OH)_2$ and Ca(OH)Cl peaks, whilst the calcite peak was more evident, consistent with the applied carbonation process. The TC content increased after the complete carbonation treatment from 2.22 % to 6.93 %, presumably due to the carbonates produced during the process.

Table 4.1. Total elements content (mg/kg dry wt.), water content, LOI, TC (% wt.) assessed for the fresh APC ash residues. SD = standard deviation (*n* = 3).

Elements	Concentration	Elements	Concentration
Na	20,233±1256	Zn	4,372±497
K	41,178±2238	Cu	441±26
Ca	308,069±9144	Ni	86.87±6
Mg	29,243±988	Cd	112±4
Fe	1,946±92	Pb	2,176±101
Mn	170±16	Sb	434±18
Al	6625±61	Mo	8.28
Si	30,002±756	Cr	74.04±11

Chemical-physical property	Concentration	Anion	Concentration
LOI (%)	29.11±0.21	Sulphate	157±89
Water content (%)	2.52±0.47	Chloride	104,118±1352
TC (%)	2.22±0.02		

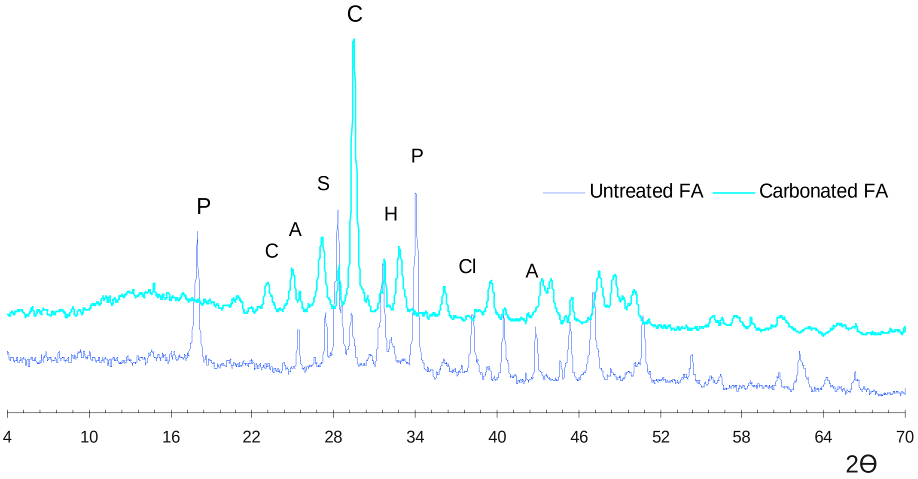


Figure 4.1. Diffractometric analysis performed on untreated and carbonated APC ash. (P = portlandite, C = calcite, H = halite (NaCl), S = sylvite (KCl), A = anhydrite ($CaSO_4$), Cl = Ca(OH)Cl).

The acid titration curves obtained for both the fresh APC ash and the same residue after the last step of the carbonation treatment (carbonated $APC_{8.2}$), are depicted in Figure 4.2. It can be observed that the buffering capacity of the APC was altered after the treatment. The shape of the curve, related to the fresh APC, evidences a plateau at pH around 12, corresponding to the presence of calcium hydroxides buffering systems (Baciocchi *et al.*, 2007). Due to the decrease in the free oxides and hydroxides content and the subsequent precipitation of calcite induced by carbonation, the ANC curve, after the treatment, a significant buffering capacity between neutral and alkaline values, as pointed out by the wide plateau at pH around 7 - 8.

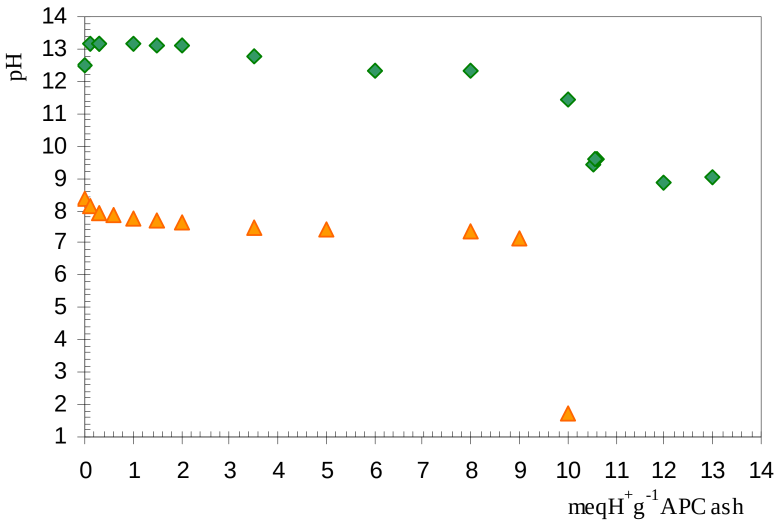


Figure 4.2. ANC curves obtained for the fresh APC (▲) and carbonated $APC_{8.2}$ (▲) material.

As far as the effect of carbonation on the mobility of metals was concerned, Figure 4.3 reports the release of Pb, Zn, Cu, Cr, Mo and Sb as resulted from the leaching tests performed on the APC ash at different stages of carbonation, as a function of the pH reached at each considered step. The leaching from fresh APC, as resulted from ANC test, is also reported.

4.3.2 Effect of accelerated carbonation treatment on metal leaching

As for the observed leaching trends, it can be assessed that the leachability from both fresh APC ash and carbonated APC ash was largely controlled by the solution pH. Leaching of Pb, Zn and Cu was characterized by a V-shaped release curve, typical of amphoteric metals. A certain degree of pH dependency was observed also for Cr leaching (increased mobility at higher pH values) and Sb (increased mobility at lower pH values). As far as Mo leaching was concerned, the data did not seem to follow a clear trend, thus any dependence from pH can not be underlined.

When comparing the leaching behaviour of fresh and carbonated APC ash, it can be stated that the release from the carbonated material was generally lower than that from the fresh APC ash, with the only exception of Sb. Indeed, the leaching trends at the different pH investigates indicated a higher mobility of Pb, Zn, Cu and Cr from fresh APC ash as compared with the carbonated one. The positive effect of the carbonation can be noticed especially when comparing the release from the fresh APC ash with that from the carbonated one till a pH of 10.5 - 10.7. As a result of the carbonation treatment, the amount of Pb released was reduced by 4 orders of magnitude, the release of Zn and Cu of 2 orders of magnitude, whilst the mobility of Cr and Mo was reduced of one order of magnitude. Conversely, at the same level of carbonation, the negative effect on Sb mobility corresponded to an increase of two orders of magnitude.

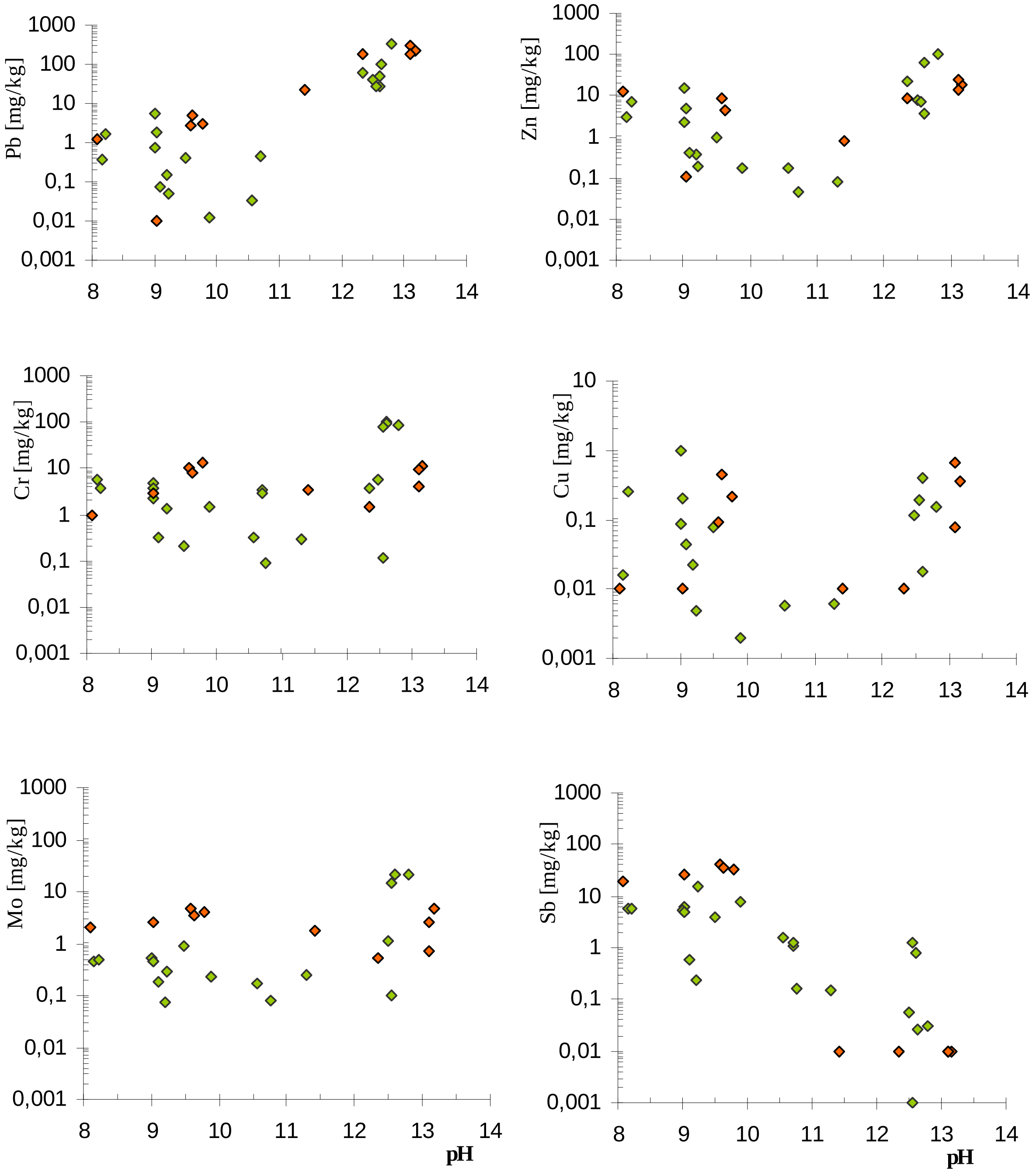


Figure 4.3 Metal release vs. pH in EN 12457-2 leaching test performed on treated APC ash at different stages of carbonation (◆) and metal release vs. pH in ANC test performed on fresh APC ash (◆).

Based on the demobilization effect assessed for Pb, Zn, Cu, Cr and Mo, the optimum final pH for the carbonation treatment was estimated to be close to 10.5. These results are consistent with the study of Wang *et al*. (2010), who found the best effect of carbonation, in terms of reduction of metal mobilization, at pH of 9 - 10. As observed in Table 4.2, if the overall performance of the treatment is evaluated in view of final disposal, it can be concluded that accelerated carbonation was effective; in fact, as far as only metals and oxyanions are considered, fresh APC ash is classified as a hazardous waste, whilst carbonated $APC_{10.5}$ would be allowed for disposal in landfills for non-hazardous waste. However, it has to be emphasized that leaching of chloride and sulphate, which are also critical species for APC ash in view of landfilling, was not affected by carbonation treatment (Table 4.2), thus the residue should be still considered a hazardous waste, with respect to the release limit of chloride obtained by EN 12457-2 test.

The positive effect exerted by carbonation on the Pb, Zn, Cu, Cr and Mo leaching could be related with the chemical and mineralogical transformations induced by carbonation (Meima *et al*., 2002; Fernández-Bertos *et al*., 2004; Van Gerven *et al*, 2005): i) carbonation originates a pH decrease to values at which several metals exhibit their minimum solubility; ii) both carbonation and pH decrease cause the conversion of metal oxides and/or hydroxides to metal carbonates, that are less soluble; iii) an additional retention mechanism is based on the affinity of some metals with calcite, thus to possible sorption onto $CaCO_3$ and/or co precipitation into newly formed minerals. The higher release observed for Sb after carbonation could be explained taking into account its oxyanion nature: often Sb in high temperature solids is incorporated in ettringite-like minerals and/or Ca antimoniate, which dissolve upon carbonation (Van Gerven *et al*., 2005; Baciocchi *et al*., 2009); however, it has to be underlined that the mineralogical characterization on the fresh material did not evidence presence of such mineral phases, at least above the XRD detection limit.

Table 4.2. Comparison between the release in EN 12457-2 test on both fresh APC ash and treated APC ash ($APC_{10.7}$ and $APC_{8.2}$) and the release limit as derived from the Italian landfill acceptance criteria (Italian Ministerial Decree 27/09/2010).

Element	Concentration (mg/kg)			Limit concentration (mg/kg)		
	Untr. APC	$APC_{10.7}$	$APC_{8.2}$	HW	n-HW	IW
Pb	228	0.03	1.59	50	10	0.5
Zn	18.13	0.05	3.05	200	50	4.0
Cr	9.36	0.09	3.58	70	10	0.5
Cu	0.65	0.01	0.26	100	50	2.0
Mo	4.6	0.08	0.51	30	10	0.5
Sb	0.01	0.17	5.81	5.0	0.7	0.06
Cl	104,118	112,400	98,491	25,000	25,000	800

The results of the metal partitioning assessed for both the fresh APC ash and the carbonated $APC_{10.7}$ are reported in Figure 4.4.

As far as the fresh APC ash was concerned, all the elements of interest were extracted mainly under oxidizing conditions (step 3: metals bound to organic matter and sulphides). Copper was also present in the reducible fraction (step 2; 35 % by weigh of total element) and a relevant amount of Pb was found to be bound to the soluble, exchangeable and carbonate fraction (step 1; 24 % by weigh of total element). In the case of Sb, a negligible amount was found to be bound to the soluble, exchangeable and carbonate fraction (0.5 % by weight of total element), exhibiting a low mobility under natural/acid conditions. As shown in figure 4.4, the carbonation treatment did not affect the elements distribution in the residual fraction, whilst the influence on the other fractions was of different extent depending on the element under concern. Lead and Cr amounts bound to the soluble, exchangeable and carbonate fraction decreased with benefit for the oxidizable fraction, while it increased for Zn, Mo and Sb, to detriment of the oxidizable fraction. The evolution of the soluble, exchangeable and carbonate fraction during carbonation is of particular interest (Figure 4.5), for most of the mobility of metals is related to this fraction. However, the mobility assessed through the EN 12457-2 leaching test takes into account only the soluble fraction, so that data are not directly comparable. The Pb and Cr reduced mobility assessed by performing the EN 12457-2 test could be explained also by the SE data, hypothesizing an increased affinity of these metals to organic matter and sulphides after the carbonation treatment. Ferrari *et al.* (2002) reported that the organic matter in APC ash is composed mainly by elemental carbon and not-extractable organic carbon which are water insoluble.

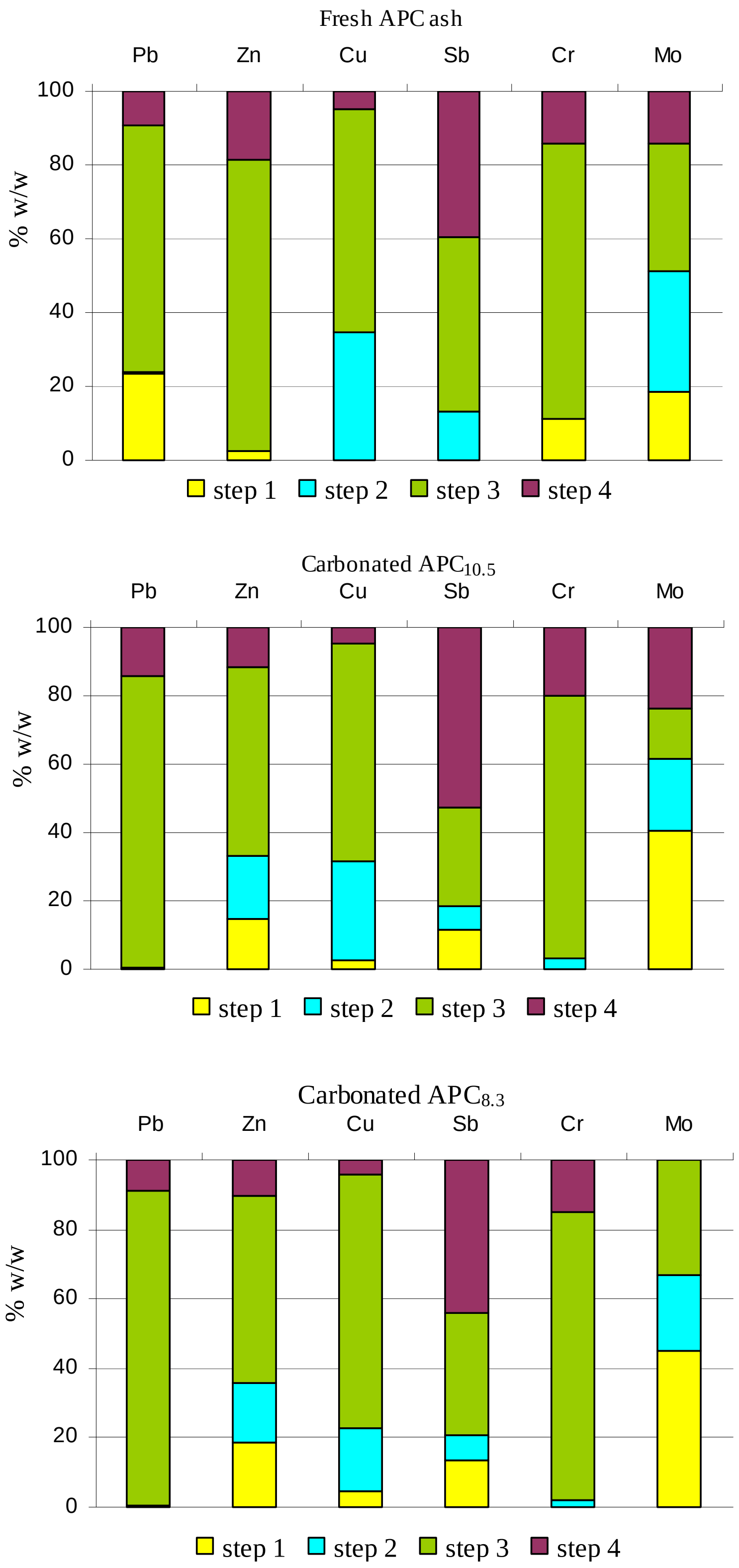


Figure 4.4. Elements partitioning assessed by the sequential extraction procedure applied to the fresh APC ash and the carbonated $APC_{10.7}$ and $APC_{8.3}$ ash.

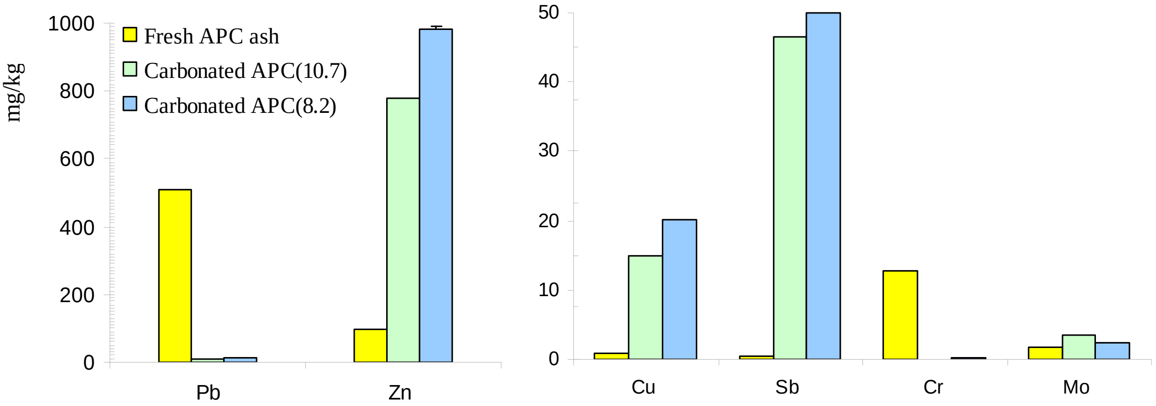
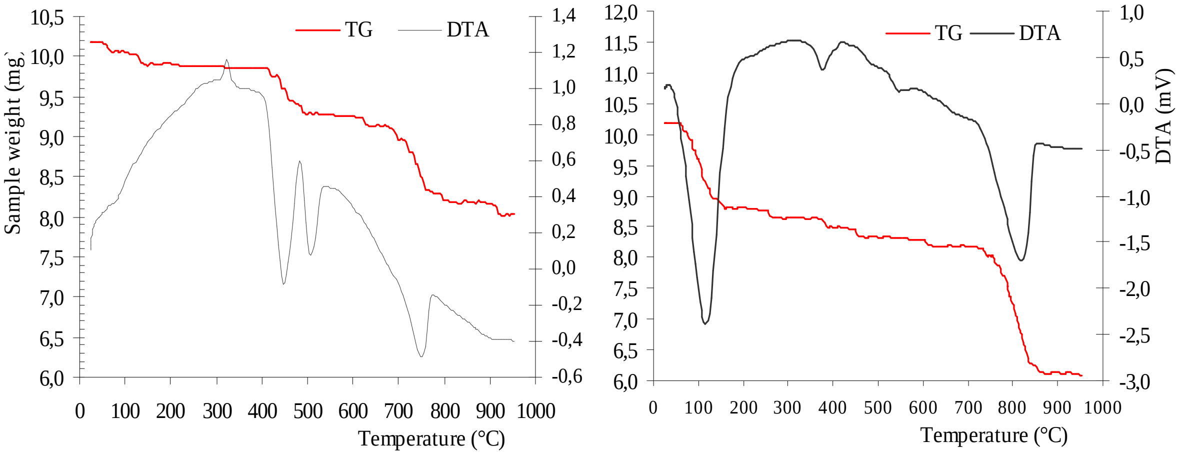


Figure 4.5. Soluble, exchangeable and acid soluble fraction in fresh and in carbonated APC ash.

As far as Zn and Cu were concerned, given the reduced mobility assessed after the treatment, the increase of the soluble, exchangeable and carbonate fraction should be interpreted in terms of increase of the carbonate one, which is less soluble than (hydr)oxides present in fresh APC (Wang *et al.*, 2010). As for Mo, a significant increase of the amount bound to the soluble, exchangeable and carbonate fraction was assessed after the carbonation, consistent with the data presented by Wang (Wang *et al.*, 2010), whilst the amount bound to both reducible and oxidizable fractions decreased. As for Sb, the SE showed an increase of element bound to the soluble, exchangeable and carbonate fraction, probably due to sorbing onto neo forming $CaCO_3$ (Johnson *et al.*, 2005).

4.3.3 Carbon dioxide sequestration capacity

The CO_2 sequestration potential of APC ash was evaluated by both calcimetry and TG analyses. As it is well known, during the TG analysis the weight loss that occurs in the range of 650° – 850 °C could be directly linked to the carbonate decomposition. As reported in Figure 4.6, for the fresh APC ash the TG/DTA curves showed three steps of weight loss (Figure 4.6 a): a first one between 300°- 400 °C, associated to organic matter oxidation; the second one between 400° – 500 °C caused by $Ca(OH)_2$ decomposition; a third one, at 750 °C, related to $CaCO_3$ and NaCl decomposition.



a) b)

Figure 4.6. TG/DTA results on fresh (a) and carbonated (b) APC ash.

In the carbonated APC ash (Figure 4.6 b), water hydration and gypsum dehydration loss were evident in both TG and DTA curves at a temperature close to 100 °C; the oxidation of organic matter occurred in a range between 200° – 450 °C, and finally at 850 °C the loss of weight was due to $CaCO_3$ decomposition. The CO_2 uptake was evaluated by the percent loss weight at 600° – 850 °C, before and after accelerated carbonation, with respect to the initial weight. The amount of CO_2 sequestrated by the residues, on the basis of TG/DTA, was estimated by calculating the difference, after and before treatment, of the weight loss in the range of 700° – 900 °C, with respect to the initial weight of APC residue, taking into account the weight increase upon carbonation. Calcimetry results agreed with the data obtained from TG analyses, with an estimated CO_2 uptake of about 200 g/kg. This result is consistent with several other experiences (Huijgen and Comas, 2005; Baciocchi *et al.*, 2007, Costa *et al.*, 2007), where a maximum CO_2 uptake of as much as 250 g/kg is reported, but using high pressures (3 bar) and different temperature values (30° – 50 °C).

The maximum theoretical sequestrating capacity was also estimated by assuming that 1 mol of CaO (molecular weight 56) reacts with 1 mol of CO_2 (molecular weight 44) (Kodama *et al.*, 2008). Finally, on the basis of the CO_2 emission factors available for the WtE plant, the reduction of CO_2 emissions potentially achievable was evaluated (Table 4.3).

Table 4.3. CO_2 sequestration capacity of the APC ash and reduction of the CO_2 emissions achievable at the WtE plant.

Residue	CO_2 uptake (kg CO_2/ kg residue)	Maximum theor. CO_2 uptake (kg CO_2/ kg residue)	Plant Emission factors (kgCO_2/ kg residue)	Reduction of CO_2 emissions * (%)	Maximum Reduction of CO_2 emissions ** (%)
MSW combustion APC ash	0.20	0.39	39.26	0.51	0.99

*Calculated on the basis of the measured uptake

** Calculated on the basis of the maximum theoretical uptake

The measured CO_2 uptake was in general quite lower than the maximum theoretical value, indicating that by adopting appropriate operating conditions and/or using chemical/physical pre-treatments the storage potential of the residue could be increased. As far as the effective storage potential of the ash is concerned, it can be stressed that despite the high CO_2 uptake (0.51 % by weigh of residue), the APC residues showed a low reduction of CO_2 emission (0.99 % by weigh of residue), due to the little amounts of APC ash generated at the WtE plant, if compared with the emission of the plant itself.

4.4 Conclusions

The study presents the assessed effects of an aqueous phase accelerated carbonation treatment performed on MSW combustion APC ash at different final pHs values. The treatment was able to modify some important properties of APC ash, such the mineralogy, the metals partitioning and mobility. As far as the metals mobility was concerned, carbonation proved to be effective in reducing the release of Pb, Zn, Cr, Cu and Mo, with an optimal final pH, identified on the basis of the demobilization effect, close to 10.5. Nevertheless, along the whole studied pH range (13.17 < pH < 8.22), a mobilization effect was noticed for Sb. On the basis of the experimental findings, it could be assessed that the accelerated carbonation treatment exerted a positive effect on the mobility of several elements, but the combination with other process (e.g. sorbent adding) might be necessary to immobilise Sb. Moreover, it has to be underlined that the carbonation treatment does not modify the chloride mobility, thus the carbonated residue should still be classified as hazardous waste. To this regard, an additional washing treatment could be appropriated to remove salts from the material, especially if performed after a carbonation step.

As far as the CO_2 sequestration capacity of APC ash is concerned, the CO_2 uptake evaluated during the accelerated carbonation treatment showed that the residue could be suitable for CO_2 storage, even if the quantity of APC ash produced by incineration plants is relatively low if compared with the WtE plants CO_2 emissions.

Accelerated carbonation treatment can be considered as potentially viable option in order to improve the environmental behaviour of APC ash and reduce CO_2 emissions from Waste to Energy plants.

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Chapter 5. Stabilization of MSW combustion APC ash by a combined carbonation and washing treatment

5.1 Introduction

The main problem related to the disposal or reuse of MSW combustion APC ash is represented by the potential release of metals and soluble salts (e.g. chlorides and sulphates), dioxins and heavy metals (Chang and Wey, 2006; Chang and Li, 1998; Hinton and Lane, 1991).

Several treatments have been proposed to reduce the potential risk of environmental contamination, such as melting, cement solidification, calcination and chemical extraction, as well as the water washing and the acid washing. In particular, the acid washing and the possibility to recover heavy metals have been explored by Van der Bruggen *et al*., (1998). Some of the minerals contained in APC ash, such as SiO_2 and CaO, can be used as raw material in cement production (Nakamura *et al*., 2007).

Mineral phases such as halite, sylvite and Ca(OH)Cl detected in APC ash are the main components containing chlorides (Bodenan and Deniard, 2003) and their high solubility leads to high chlorides concentration in leachate.

The water washing treatment implies the use of a large amount of water to remove leachable compounds and it might increase the treatment costs, because wastewater obtained must be treated, before discharge. Chimenos *et al*. (2005) investigated the best washing parameters (L/S ratio, mixing time and stirring speed) to reduce chlorides content in APC ash and as a result the optimum L/S ratio was found at 3 l/kg and the mixing time was close to 1 hour. Afterward, by using the mentioned conditions and by adding small amounts of $MgSO_4$, a counter-current process with two washing-steps, was applied to APC ash. The treatment was based on the pH decrease, till to a range 9 – 10; in this pH range, heavy metal hydroxides show minimum solubility. The process applied has shown a dual benefit: (i) a chlorides reduction in APC residue, (ii) the production of a wastewater which is less contaminated by heavy metals.

Recently**,** Zhu *et al*. (2009) have proposed a new recycling system, consisting in "washing, calcinating and changing/converting" (WCCB system) of washed fly ash into cement raw material with bottom ash. The proposed method is based on water washing of

APC ash residue to get rid of chlorides and, after that, the ash is not discharged outside of the system, but it is fed back into the thermal process. Subsequently, APC ash and BA residues are removed together and sent to cement industries.

In another study, Zhu *et al*. (2010) discussed the chlorides behaviour during washing treatment, by considering the chemical differences between water soluble chlorides (e.g. NaCl, KCl, and $CaCl_2$) and insoluble Friedel's salt (general formula $[Ca_2Al(OH)_6Cl]*2H_2O$). The experimental study compared the effects of a single washing treatment to those of the double washing; the outcome was that the double washing process was more effective in removing the soluble chlorides fraction than the single washing.

During the washing process, others elements dissolve in water, such as heavy metals; thus, with the aim of reducing the leaching of hazardous elements, carbonation process might be adopted on APC ash, before the washing treatment (Wang *et al*., 2010). In this case, the application of both treatments might reduce the environmental impact of APC ash and allow a better management of residue in view of the recycling and/or the final disposal.

The present chapter focuses on the application of a single water washing treatment on fresh and carbonated MSW combustion APC ash in order to achieve a reduction of chlorides content in residue and obtain a wastewater with a small content of hazardous metals. The aim of the preliminary tests carried out in this section was to verify the best operating conditions to be adopted for the combined treatment.

5.2 Materials and methods

Municipal solid waste combustion APC samples were collected at a WtE plant in Cagliari, Sardinia. The samples were homogenized in order to produce representative laboratory subsamples to be used for accelerated carbonation treatment, water washing experiments as well as preliminary leaching tests.

5.2.1 Leaching test

The effect of carbonation on metals mobility (Pb, Zn, Cr, Cu, Mo and Sb) was assessed by performing the EN 12457-2 test on the untreated and carbonated APC. After filtration of suspension at 3 – 5 μm, pH was assessed and the metals concentration in the solution was measured with ICP-OES spectrometry (Varian, model 710 ES).

5.2.2 Carbonation treatment

The applied accelerated carbonation treatment consisted of a single step aqueous-route process carried out at ambient conditions (20 °C and atmospheric pressure). The treatment was performed into an open vessel, by blowing CO_2 (2 bar) through the continuously mixed APC ash slurry (L/S = 2.5 l/kg). The slurry was homogenized by both gas bubbling and a magnetic stirrer. With the aim of studying the evolution of the carbonation process, in terms of both pH decrease and effects on metals mobility, the pH value was continuously monitored and the input of CO_2 was stopped when pH reached prefixed values between 9.0 – 10.0; APC slurry samples were collected at the end of each carbonation step in order to perform the EN 12457-2 leaching tests and to control the pH of residue (after 24 hours). In the following, carbonated $APC_{10.7}$, for instance, indicates APC ash carbonated until pH 10.7 was reached. All the samples were immediately dried at 40 °C and stored in closed bottles to arrest ageing reactions. The time required to reach the final pH of 8.22 was 2 - 3 hours.

5.2.3 Water washing treatment

During the washing experiments, carried out using distilled water and by performing a single washing step, the influence of operating parameters such as washing time and L/S ratio were tested. The release of chloride and heavy metals (Pb, Cu, Zn, Cr, Mo and Sb) from the APC ash were in fact measured by varying the washing time (1, 15, 30 min and 1, 2 hour) and the liquid-solid ratio (L/S = 2.5, 5, 7, 10 l/kg). Twenty grams of untreated and carbonated APC ash ($9.00 < pH < 10.50$) were put in contact with distilled water to reach the prefixed L/S ratio. The flasks were stirred for two hours and in a magnetic shaker at room temperature. After 1, 15, 30 60 and 120 minutes a sample of slurry phase was collected and filtered at 2 – 3 μm; the filtered solution was analysed for chlorides and elements of interest (Pb, Zn, Cu, Cr, Mo and Sb), respectively by IC and ICP-OES.

5.3 Results and discussion

As previously mentioned, the carbonation process was performed in order to reach different carbonation levels and thus different final pH values for the treated materials. When performing the washing experiments, the initial pH of fresh residue and the carbonated ones were respectively (12.95 ± 0.03), (10.47 ± 0.03), (9.00 ± 0.04) and (9.60 ± 0.04).

During the washing experiments, chloride concentration in solution was not affected by the mixing time (results not reported). In Figure 5.1 the chloride concentration in water solution as a function of L/S ratio is reported. By increasing the L/S ratio, the chloride concentration decreased; the anion release from fresh APC ash was (124 ± 2.87) g/kg for all the L/S values studied; after carbonation treatment the release from $APC_{10.47}$ and $APC_{9.00}$ ashes was respectively (127 ± 2.36) g/kg, and (99.00 ± 3.27) g/kg and it was independent from the L/S ratio used. Li *et al*. (2007) found a little reduction in sulphates and chlorides release after carbonation; it might be explained by assuming that after the treatment $Ca(OH)Cl$, which is a highly water soluble phase contained in fresh residue, is carbonated and chloride could be immobilised in a new insoluble form.

The optimum L/S ratio was found close to 2.5 l/kg. Zhu *et al.* (2009) found that a L/S ratio close to 3 and a mixing time of 5 minutes were sufficient to remove chloride from APC residue, according to data obtained in this work. In fact, the chloride ions are present mostly in halite and sylvite phases, which are highly soluble.

In Figure 5.2 the metal release from fresh and carbonated $APC_{9.00}$ during the water washing treatment (L/S= 10 l/kg) applied on fresh and carbonated APC ash is shown. The role of accelerated carbonation as stabilization treatment is evident, with the exception of Sb and Cu; nevertheless, the final pH was not the optimum to immobilize most of metals (see Figure 4.3 of Chapter 4). In the case of fresh residue, the Zn, Cr, Pb and Mo release in water seemed to be independent by the washing time; in carbonated APC ash, it appeared to be modified in the first 30 minutes. After that period of time, the metal release was steady.

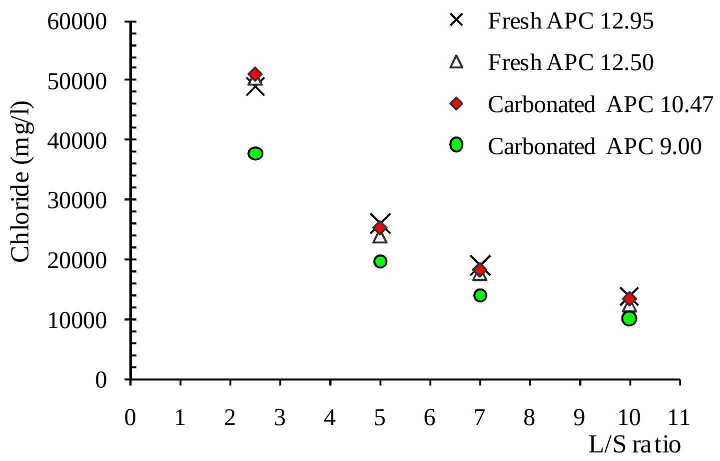

Figure 5.1. Chloride concentration (mg/l) in water washing tests as function of L/S ratio.

Table 5.1. Chloride release (mg/kg) in washing tests on fresh and carbonated $APC_{10.47}$ ash as function of L/S ratio and mixing time.

L/S ratio (l/kg)	Time (min)	$APC_{12.45}$ (mg/kg)	$APC_{10.47}$ (mg/kg)
2.5	0	127493	127493
	120	126230	130345
5	0	119150	119150
	120	119930	134965
7	0	122836	122836
	120	123354	134554
10	0	122810	122810
	120	123180	148580

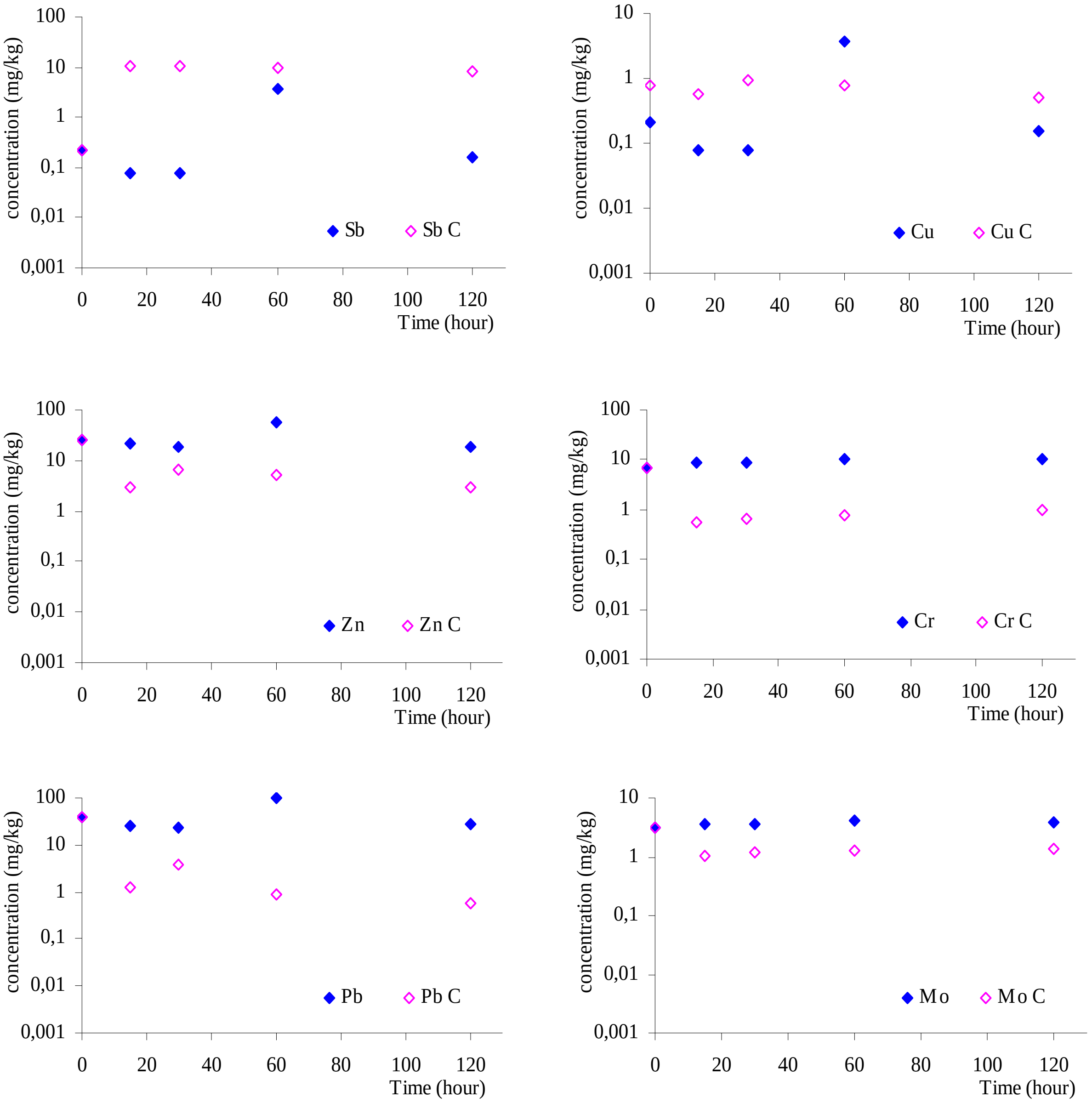

Figure 5.2. Metal release during washing experiments from fresh and carbonated (C) APC$_{9.00}$ ash as function of time at L/S= 10 l/kg.

A preliminary carbonation-water washing combined test was carried out on fresh, carbonated and carbonated-washed APC ash at final pH= 9.60 (APC$_{9.60}$ and APC$_{9.60}$ + W). The procedure consisted in mixing the dry residue (40 °C) with water (L/S ratio = 10 l/kg) for 15 min. The suspension was filtered at 2 – 3 μm and the solid residue was dried at 40 °C for 24 hours. Leaching test EN 12457-2 was performed on solid residue. The metal mobility in carbonated APC$_{9.60}$ was generally reduced, with respect to it from fresh residue.

Table 5.2 reports the metal release obtained by leaching test EN 12457-2 performed on fresh APC, carbonated APC till pH= 9.60 ($APC_{9.60}$) and finally carbonated APC after washing treatment ($APC_{9.60}$ + W). In carbonated $APC_{9.60}$ ash the Sb and Cr release increased. In fresh APC residue the metals release exceeded the Italian limits for the deposit it in non-hazardous waste landfill, whilst the, chloride release even exceeded the Italian limits for the deposit it in hazardous landfill. Sulphate release was, on the contrary, below the limits for both fresh and carbonated ash (results not shown).

After carbonation treatment performed till a final pH of 9.60, the Pb and Zn release showed a decrease of 2 and 1 order of magnitude. Copper and Mo release seemed to be fairly constant. In the case of Sb and Cr the release increased. The extent of release was influenced by the degree of carbonation attained; according to the results discussed in Chapter 4, the carbonated APC ash at pH= 9.60 showed in fact a metal release higher with respect to that obtained at pH close to 10.5. The leaching of chloride did not decrease in response to carbonation.

After the washing step, the release of chloride was strongly reduced (2 orders of magnitudes). The pH reached was 8.80. Unfortunately, as results of the washing treatment, a strong, further increase of the Sb release was noticed.

On the basis of the preliminary test conducted on a possible combined carbonation-washing treatment, if the overall performance of the process is evaluated in view of final disposal, i.e. by comparing the metal release evaluated during EN 12457 leaching test with the Italian limits for landfill disposal (Table 5.2), it can be concluded that the combination of the two treatments was not effective in improving the environmental behaviour of the APC ash. Indeed, even if chloride release would allow for a waste declassification, the increase of Sb release entailed the waste to be still considered hazardous. Since the Sb release is strongly influenced by the degree of carbonation attained, a further investigation is needed in order to optimize the carbonation step and thus to assess the feasibility of the combined treatment.

Table 5.2. Results of EN 12457-2 leaching test on untreated $APC_{12.95}$, carbonated APC ash to final pH of 9.00 ($APC_{9.00}$) and carbonated APC ash after washing ($APC_{9.00}$ + W), and comparison with the release limit as foreseen by the Italian landfill acceptance criteria (Italian Ministerial Decree 27/09/2010).

Element	Untreated $APC_{12.95}$	Carbonated $APC_{9.60}$	Carbonated $APC_{9.60}$ + W	HW	n-HW	IW
Sb	0.12 ± nd	0.68 ± 0.06	7.81 ± 0.00	5.0	0.7	0.06
Pb	24.2 ± 5.52	0.35 ± 0.28	0.47 ± 0.24	50	10	0.5
Cu	0.48 ± 0.06	0.18 ± 0.06	0.21 ± 0.02	100	50	2.0
Zn	15.04 ± 2.37	2.76 ± 1.72	2.13 ± 0.66	200	50	4.0
Cr	7.76 ± 0.18	13.23 ± 0.21	6.35 ± 0.08	70	10	0.5
Mo	2.07 ± 0.06	2.20 ± 0.02	1.16 ± 0.00	30	10	0.5
Cl	136,485 ± 2,580	103,839 ± 13,167	9708 ± nd	25,000	25,000	800

HW = hazardous waste; n-HW = non-hazardous waste; IW = inert waste.

5.4 Conclusions

The water washing treatment performed on fresh APC ash allows the remove of chloride and metals. When the treatment was applied on fresh and carbonated MSW combustion APC ash, the release of chlorides was independent of the L/S ratio and mixing time. According to the results, and taking into account the need of using the minimum volume of water, a L/S ratio close to 2.5 l/kg and a mixing time of 1 – 15 minutes were selected as optimal operating conditions in order to achieve the chlorides reduction in the residue under concern.

The treatments of accelerated carbonation and washing sequentially applied aimed to obtain first the stabilization of metals in the solid matrix and subsequently the removal of soluble salt only, with the advantage of preventing/reducing the leaching of metals into a wastewater that would need to be treated.

The preliminary set of experiments carried out by performing the combined treatment (carbonation step at pH = 9.60 and washing step) has shown a general reduced release of both metals and chloride if compared to the fresh material, with the exception of Sb.

In particular, since the Sb mobility is strongly influenced by the extent of carbonation, it implies that the first step of the combined process should be opportunely performed in order to obtain the declassification of the APC residue from Hazardous to a Non Hazardous waste. Further investigation should be devoted to this aim.

5.7 References

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Chapter 6. Conclusions

The main objectives of this doctoral thesis were to: (i) investigate the effects of the direct aqueous accelerated carbonation process, applied on BA, its particle size fractions and APC ash residues, in order to gain new insight on the chemical and mineralogical changes for each type of material; (ii) evaluate the CO_2 sequestration capacity of residues under investigation; (iii) evaluate the effect of a carbonation and washing combined treatment applied on APC ash in terms of chlorides and metal release.

The carbonation treatment applied on MSW combustion BA and APC ash may represent a pre-treatment stage prior to either recycling or landfilling options. The process can stabilize the leaching behaviour of these alkaline combustion residues and is an effective way to sequestrate CO_2. With regard to the findings of the research activity carried out by applying the accelerated carbonation on BA and on its particle fractions (see Chapter 3), it appears that the treatment is able to modify some important macroscopic properties of BA, such as pH, buffering capacity and mineralogy. The pH decrease observed during carbonation was stronger for the BA fine particle size fractions than for the coarser ones, the final value being 8.20 vs. 9.50, and the difference being probably due to the higher quartz content in the latter. The BA buffering capacity doubled at pH 8, mirroring the results of other studies. Concerning the effect of the treatment in terms of metal mobility, the leaching of Pb and Cu was reduced, whilst increased the Mo one and no significant reduction was noticed for Zn and Cr. The sequential extraction procedure applied on BA improved the understanding of the results obtained by the leaching tests. In particular, the behaviour of metals partition in the soluble, exchangeable and acid soluble fraction (first step of procedure) is linked to the metal leached out in EN 12457-2 leaching test. The results of sequential extraction were consistent with the metal release measured in the leaching test. Considering the single size fractions, the effects on Pb (decrease) and Mo (increase) mobility were fairly homogenous for all the size fractions, whilst the overall positive effect on Cu mobility seemed to depend mainly on the particles having size < 1.0 mm. The effect of carbonation on Cr mobility seemed to be negative for fractions having particle size < 1.0; furthermore the finest fractions represent a small percentage of the total mass of residue. As far as the whole BA is concerned, the experimental findings suggest that the carbonation treatment may exert different effects on the mobility of the different metals. Furthermore, as far as each single metal is considered, different effects were noticed when the treatment was applied to different particle size fractions. Therefore, in order to achieve an overall positive effect in terms of reduction of metal mobility, the combined application of accelerated carbonation with other processes seems advisable. To this regard, the use of sorbent additives, eventually characterized by low cost, such as the red mud derived Bauxol, might be a possible solution in order to immobilize oxyanion elements (e.g. Mo or Sb).

As far as the capacity of capturing the CO_2 is concerned, the results obtained that the extent of CO_2 uptake varied largely depending on the individual BA size fraction investigated. The results obtained underlined that the CO_2 uptake is higher for the smaller BA particles. In the fine fractions, the CO_2 uptake was about 5 - 9 % by weigh of residue (class A, B and C), while for the coarse fractions, it was 3 - 4 %. This result can be explained by considering the high ratio of Ca/Si measured in the finest fractions (about 2 - 3); in fact a part of glass and ceramic materials rich in SiO_2 do not react with the CO_2. The CO_2 uptake measured for the different particle size fractions of BA was compared to the CO_2 emitted during the thermal process to evaluate the potential reduction of CO_2 emissions that could be achieved by applying the carbonation treatment on the residues under concern. The CO_2 uptake measured was higher in the fractions with $0 < D < 1.00$ mm (class A-B-C-D) and by considering the relative composition of BA, the sequestration capacity was estimated close to 3 % by weigh of residue. The combustion process of 1 ton of MSW produces approximately 600 Nm^3 of CO_2 and 250 kg of BA, thus the amount of the CO_2 emitted, potentially sequestered by mineral carbonation of the combustion residue, might be no more than ~ 0.5 % by weight of the residue. This feature could be improved, for instance applying the process to the fractions which exhibited the highest potential for CO_2 capture.

The results obtained by applying the accelerated carbonation on MSW combustion APC ash show that the treatment may be able to modify the residue mineralogical characteristics as well as the metal partitioning and mobility. The induced mineralogical changes, such as the conversion of hydroxides into carbonates, results in a lower pH which can affect the solubility and leachability of many elements. Indeed, the carbonation treatment applied on APC ash proved to be effective in reducing the release of Pb, Zn, Cr, Cu and Mo, with an optimal final pH, identified on the basis of the demobilization effect, close to 10.5. Lead and Zn release decreased respectively of 4 and 3 orders of magnitude, whereas Cu, Cr and Mo release exhibited a less significant decrease. It is worth to underline also that, along the whole studied pH range ($13.17 < pH < 8.22$), a significant increase of the Sb mobilization was noticed (2 orders of magnitude). On the basis of these experimental findings, for the APC residues also it could be assessed that, though the accelerated carbonation treatment exerted an immobilizing effect on most of the elements, the combination with other processes (e.g. sorbent adding) might be advisable to reduce the Sb mobility. Moreover, it has to be underlined that the carbonation treatment does not exert any effect on chloride mobility, so that the carbonated residue should still be classified as hazardous waste. To this regard, an additional washing treatment could be appropriated to remove salts from the material, especially if it is performed after the carbonation stage. In Chapter 5, the results of a preliminary water washing treatment applied on fresh and carbonated MSW combustion APC ash are reported. The preliminary tests carried out indicated that the water washing process was able to remove the soluble chlorides. A L/S ratio of 2.5 l/kg and a mixing time of 15 minutes were selected as optimal operating conditions.

The combined carbonation-water washing treatment was able to produce a solid residue characterized by a lower metals and chloride release, while Sb was mobilised; the compliance test performed on carbonated-washed APC ash did not allowed to classify the residue as a non-hazardous waste.

Since it is known that the final pH of the carbonated residues affects considerably the release of metals and oxyanions, further studies are needed in order to select the best carbonation conditions able to better immobilize the oxyanions (e.g. Sb and Cr). In this way, the subsequent washing step would allow to remove chlorides and thus to classify the APC ash as a non-hazardous waste.

As far as the CO_2 sequestration capacity of APC ash is concerned, the CO_2 uptake evaluated during the accelerated carbonation was 20 % by weight of the residue. Therefore the residue could be suitable for a significant CO_2 storage, although it has to be taken into account that the quantity of APC residue produced by incineration plants is relatively low if compared with the associated CO_2 emissions (~ 30 kg of APC ash/1 ton of waste combusted).

BA and APC ash showed different CO_2 uptakes, depending on both the materials properties (e.g. size fraction, mineralogy) and the specific treatment conditions adopted. The highest CO_2 storage potential was shown by the APC ash (0.20 kg_{CO2}/kg residue), whilst the lower one was assessed for the BA coarser fractions (0 – 0.020 kg_{CO2}/kg). The measured CO_2 uptakes were in general quite lower than the maximum theoretical values, indicating that by adopting appropriate operating conditions and/or using chemical/physical pre treatments the storage potential of the different residues could be significantly increased. As far as the effective storage potential of the different residues is concerned, it can be observed that the APC ash showed the lowest reduction of CO_2 emissions (0.99 %); as mentioned before, this is due to the scarce amounts of APC ash generated at the plant site if compared with the emission of the plant itself. Conversely, the feasibility of an accelerated carbonation treatment proved to be higher in the case of BA which could exhibit a potential for CO_2 sequestering of 3.82 % of the related emissions.

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