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Current status and perspectives of accelerated carbonation processes on municipal waste combustion residues

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Abstract The increasing volumes of municipal solid waste produced worldwide are encouraging the development of processes to reduce the environmental impact of this waste stream. Combustion technology can facilitate volume reduction of up to 90%, with the inorganic contaminants being captured in furnace bottom ash, and fly ash/APC residues. The disposal or reuse of these residues is however governed by the potential release of constituent contaminants into the environment. Accelerated carbonation has been shown to have a potential for improving the chemical stability and leaching behaviour of both bottom ash and fly ash/APC residues. However, the efficacy of carbonation depends on whether the method of gas application is direct or indirect. Also important are the mineralogy, chemistry and physical properties of the fresh ash, the carbonation reaction conditions such as temperature, contact time, CO_2 partial pressure and relative humidity. This paper reviews the main issues pertaining to the application of accelerated carbonation to municipal waste combustion residues to elucidate the potential benefits on the stabilization of such residues and for reducing CO_2 emissions. In particular, the modification of ash properties that occur upon carbonation and the CO_2 sequestration potential possible under different conditions are discussed. Although accelerated carbonation is a developing technology, it could be introduced in new incinerator facilities as a “finishing step” for both ash treatment and reduction of CO_2 emissions.

Keywords Air pollution control (APC) residues · Bottom ashes (BA) · Carbonation · CO_2 · Incineration · Leaching

Introduction

Municipal solid waste (MSW) production is continuing to grow worldwide. To ensure that the environmental and economical impacts of increasing amounts of MSW can be sustained in the future, it is essential that integrated waste management strategies are adopted. In the EU, municipal solid waste has increased by 19% between 1995 and 2003, becoming

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the single fastest growing waste stream (Euractiv 2005). Most MSW is landfilled, but due to landfill space limitations and the introduction of the EU Landfill Directive (CEU 1999), alternative disposal routes are being adopted, such as recycling and incineration, although these may vary greatly from country to country (DEFRA 2006). Currently, for example, there are 17 municipal incinerators operating in England and Wales, which receive about 9% of the total municipal waste produced, and the number and capacity of these facilities is increasing, although it remains below the European average (17.3%), and in particular, is far lower than countries like France (27%) or Denmark (56%) (Dinsdale J. Environment Agency 2006).

In developing countries increasing waste production accompanies urbanization (Ahmed and Ali 2004). The World Bank estimates that solid waste production in the urban areas of East Asia alone will increase from 0.76 million t/day to approximately 1.8 million t/day within 25 years (Urban Age 1999). Incineration can reduce waste mass and volume by approximately 70 and 90% respectively, and facilitate the recovery of a considerable fraction of the energy bound in the waste (Hjelmar 1996).

The applicability and efficiency of incineration depends greatly on waste composition, including the non-biodegradable organic portion. The waste produced in developing countries generally has high moisture content and a low combustible fraction (e.g. paper and cardboard) due also to extensive scavenging (Ali 2003). In India for example, the majority of the waste is composed of vegetative matter (44%) and inert materials (42%) (Damodaran et al. 2003). Incineration though, can be also applied to sterilise MSW and infectious hospital waste (Ibànez et al. 2000).

The incineration of MSW is not a final treatment, since combustion and air pollution control (APC) residues are produced. The increasingly stringent limits on atmospheric emissions from waste incinerator facilities have produced a transfer of contaminants from gaseous emissions to the solid residues during combustion (Sabbas et al. 2003). Several treatment technologies have been proposed to reduce the environmental impact of disposed ash, including physical and chemical separation, thermal processing and solidification and/or stabilization. Accelerated carbonation has also been shown to improve the chemical stability and leaching behaviour of both bottom ash and APC residues.

The increase in atmospheric concentration of CO_2 is forcing the international community to develop technologies to capture this greenhouse gas (IPCC 2005). Mineral carbonation has been proposed as one of the options for the large-scale disposal of CO_2 (Huijgen and Comans 2003). The carbonation of alkaline residues, including combustion residues has been shown to be an effective way to sequestrate CO_2 (Lackner et al. 1995; Johnson 2000; Huijgen et al. 2005; Stolaroff et al. 2005; Fernández-Bertos et al. 2004a). This review discusses the main physical and chemical characteristics of incineration residues and their pacification through the application of accelerated carbonation. The process options for carbonation of MSW ash, the characteristic properties of carbonated ash and the potential for CO_2 sequestration by different carbonation processes are examined in detail in order to establish the state of the art for this emerging technology.

Carbonation process

Natural carbonation

Carbonation involves the uptake of CO_2 by alkaline materials. In the case of MSW ash residues, carbonation can occur naturally on prolonged contact with atmospheric CO_2. The weathering of MSW ash involves a complex series of chemical and mineralogical transformations including carbonation in addition to hydrolysis/hydration, dissociation/precipitation of hydroxides and salts of the main cations, formation of clay-like minerals from the glassy phase of the material, oxidation/reduction as well as formation of solid solutions.

The main macroscopic effects of natural carbonation of ash are the decrease in pH, a change in ash buffering capacity and the precipitation of calcite. Other possible effects include the precipitation of metal carbonates and the formation of new mineral phases (Huijgen and Comans 2006); all of these transformations contribute in influencing the leaching behaviour of MSW ash.

The relative importance of these ‘weathering’ effects depends on the initial chemical composition and mineralogical characteristics of the material and it will have an impact on its CO_2 uptake.

Accelerated carbonation

Natural carbonation reactions are generally quite slow and become significant in the longer-term. Accelerated carbonation has the potential to reduce the time required for complete carbonation down to timescales of hours or days. It has been applied as a treatment technique prior to reutilization or final disposal of MSW bottom ash (BA) with the purpose of producing a chemically stable material with improved leaching behaviour (Meima et al. 2002; Polettini and Pomi 2004; Van Gerven et al. 2005; Arickx et al. 2006; Rendek et al. 2006a).

In the case of APC residues, accelerated carbonation has been proposed as a possible CO_2 capture and storage (CCS) technology, due to the typically higher CO_2 uptake potential of these types of residues (Fernández-Bertos et al. 2004b; Baciocchi et al. 2006a; Li et al. 2006).

Mineral carbonation

Currently, CCS technologies have shown potential for ‘at source’ reduction of greenhouse gas emissions. In countries like China and India which are developing rapidly, the need to stabilize atmospheric CO_2 emissions will have to involve capture from point sources (or directly from the atmosphere) and subsequent storage in permanent, safe disposal sites (IPCC 2005). These sites could be geological formations, such as saline aquifers, oil reservoirs and coal seams, or oceans (Lackner 2002).

Carbonation of alkaline minerals mimics natural rock weathering and involves the permanent storage of CO_2 under the thermodynamically stable form of calcium or magnesium carbonates (IPCC 2005). This process is based on acid-base reactions in which an acid (H_2CO_3/H_2O) is neutralized by a solid base (alkaline minerals). Although oxides or hydroxides of alkaline or alkaline earth metals can be carbonated, calcium and magnesium silicate minerals are usually preferred, since they are available worldwide in large amounts.

Magnesium-rich silicates such as olivine, serpentine and talc can be found in ultramafic rocks such as dunites, peridotites and serpentinites, whereas one of the preferred calcium containing silicate is wollastonite (Huijgen and Comans 2003). These minerals are available worldwide and have the potential of sequestering the total amount of CO_2 emitted from the combustion of all the available fossil fuel reservoirs (Lackner 2002), which, according to updated calculations, would amount to approximately 8,000 Gtons (Ziock et al. 2000). CO_2 sequestration technology through mineral carbonation however, has not yet been developed at the full scale due to cost limitations; a recent study on mineral carbonation (O’Connor et al. 2005) assessed that a power plant equipped with a full CCS system with mineral carbonation would require between 60 and 180%, depending on the type of mineral selected for the process, more energy than a power plant with equivalent energy production without CCS.

An important aspect of mineral carbonation is the need to activate the surface of the mineral to increase its effective carbonation yield. This can be done by a variety of physical pre-treatment methods, including size reduction, magnetic separation, thermal treatment (to eliminate chemically-bound water) or steam activation (O’Connor et al. 2005). Chemical pre-treatment methods (Maroto-Valer et al. 2005) involving sulphuric acid were shown to be effective for serpentine as they increased the surface area from 8 to 330 m^2/g.

Upon activation, the mineral may be carbonated by two different routes:

(1) The *indirect route*, by which the alkaline metal is first extracted from the silicate matrix and then precipitated as carbonate. Metal dissolution is the rate-controlling step of the whole process and may be achieved by adding an acid, such as hydrochloric or acetic acid, to the reaction system (Park et al. 2003). Recently, the possibility of using high-pressure carbon dioxide to induce the extraction of magnesium from olivine minerals has also been proposed and successfully demonstrated through lab-scale dissolution experiments (Hänchen et al. 2006). However, irrespective of the type of process used for mineral dissolution, the acidic conditions required do not allow for quantitative precipitation of the alkaline metals in the carbonate form. The degree of supersaturation required for an efficient and effective

carbonate precipitation is so high that a pH shift to basic conditions is required. This is especially true when carbonation of Mg-bearing minerals is pursued, because magnesium carbonate formation is more difficult to achieve than calcium carbonate. This requires the addition of other amendments, such as NH_4OH (Park and Fan 2004), whose recycling is once again a critical issue.

Although these processes are generally characterized by high reaction rates and moderate operating conditions in terms of CO_2 pressure and temperature, the drawbacks discussed above have moved several authors (Lackner et al. 1995; Huijgen and Comans 2003; O'Connor et al. 2005) to investigate the direct carbonation route.

(2) The *direct carbonation* route, by which the reaction occurs either in the aqueous phase or at the gas-solid interface. In the aqueous process, carbonation occurs in a three-phase system (gas–water–solid medium), which considerably increases the reaction rate if compared to the direct gas–solid route. A recent study on aqueous mineral carbonation of wollastonite ($CaSiO_3$) (Huijgen et al. 2006) has found a maximum CO_2 conversion of 70% with a reaction time of 15 min at 200°C, 20 bar CO_2 partial pressure and particle size <38 μm. Carbonation through the aqueous route occurs mainly in three steps; as an example, in the case of $CaSiO_3$ the process involves: (1) the leaching of calcium from the wollastonite matrix (Eq. 1), (2) the contemporary dissolution of CO_2 and conversion of carbonate species to bicarbonates (Eq. 2) and (3) the formation of calcium carbonate (Eq. 3).

$$CaSiO_3(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2O(l) + SiO_2(s) \tag{1}$$

$$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq) \rightarrow HCO_3^-(aq) + H^+(aq) \tag{2}$$

$$Ca^{2+}(aq) + HCO_3^-(aq) \rightarrow CaCO_3(s) + H^+(aq) \tag{3}$$

The first step is considered rate-limiting for the whole carbonation reaction (O'Connor et al. 2005); enhancement though is found when specific surface area is increased or when additives such as NaCl or $NaHCO_3$ are used. In studying the kinetics of the process, Huijgen et al. (2006) identified two temperature regimes influencing the overall reaction rate. At temperatures below the optimum reaction temperature, they hypothesized that the reaction rate is limited by calcium leaching from $CaSiO_3$ (Eq. 1), due to the formation of a calcium depleted silicate rim on the mineral which limits Ca diffusion towards the water phase. At higher temperatures they found the nucleation and growth of calcite (Eq. 3) to be the rate-limiting step, due to reduced bicarbonate activity, resulting from the lower solubility of CO_2 at higher temperatures. CO_2 partial pressure was instead found to have an influence on the optimum reaction temperature. Similar results were also reported for Mg-containing silicates like olivine (O'Connor et al. 2005) concerning the influence of both reaction temperature and CO_2 partial pressure. Due to the relatively limited availability of wollastonite, work has focused mainly on the carbonation of Mg-bearing minerals, such as olivine or serpentine. In the case of olivine, the optimized conditions determined for aqueous carbonation are 180°C and 15 MPa (O'Connor et al. 2005) using 1 M NaCl and 0.64 M $NaHCO_3$. These conditions make the industrial implementation of this process economically unfeasible at present and at least until a better comprehension of the dissolution and precipitation mechanisms will allow for a tenfold costs reduction.

The direct gas–solid carbonation process may present the most straightforward route, as the carbonation reactions of calcium oxide and hydroxide (Eqs. 4 and 5) are rapid and completion can be achieved in minutes. Although $Mg(OH)_2$ carbonation is fast enough for industrial use, under dry conditions the rate of MgO is too slow for significant amounts of CO_2 to be sequestrated (Lackner et al. 1997).

$$Ca(OH)_2(s) \rightarrow CaO(s) + H_2O(g) \tag{4}$$

$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s) \tag{5}$$

In an early study, Bhatia and Perlmutter (1983) investigated the kinetics of the dry carbonation of lime in a modified TGA at different temperatures in a 100% CO_2 atmosphere and obtained a maximum calcium conversion of 70% at 500°C. The rate of the dehydroxylation (Eq. 4) and the carbonation (Eq. 5) reactions diminished in time as a thin layer of calcite, formed on the reagent material, acted as a barrier for both the outward diffusion of H_2O and the inward diffusion of CO_2 (Huijgen and Comans 2003).

Mineral carbonation of silicates like olivine (Eq. 6) requires a high CO_2 pressure to maintain a satisfactory reaction rate (Huijgen and Comans 2003).

$$Mg_2SiO_4(s) + 2CO_2(g) \rightarrow 2MgCO_3(s) + SiO_2 \qquad (6)$$

Accelerated carbonation of residues

One way of bypassing some of the drawbacks of accelerated carbonation of primary alkaline earth minerals is to use alkaline waste residues from thermal processes or from construction and demolition activities as a feedstock. As these materials are often associated with CO_2 point source emissions and tend to be chemically more unstable than geologically derived minerals (Huijgen et al. 2006), they require a lower degree of pre-treatment and less energy intensive operating conditions to enhance carbonation yields (Huijgen and Comans 2003; Huijgen et al. 2006). Furthermore, after stabilisation by accelerated carbonation, the leaching behaviour of alkaline waste materials such as incinerator bottom ash (Van Gerven et al. 2005), steel slag (Huijgen and Comans 2006) and APC incinerator residues (Baciocchi et al. 2006a, b,c) is improved, allowing for use in civil engineering applications or for safer final disposal to landfills.

Table 1 gives a list of the industrial residues that have been investigated. Accelerated carbonation has been applied to many of the solid residue streams produced from coal fired power stations, including pulverized fly ash (PFA) (Reddy et al. 1994; Johnson 2000), spent shale (Reddy et al. 1994), clean coal technology (CCT) ash (Tawfick et al. 1995), fluidized bed combustion (FBC) (Jia and Anthony 2000) and circulating fluidized bed combustion (CFBC) ashes (Anthony et al. 2002).

Slag produced as a by-product of steel manufacturing has also shown potential for CO_2 uptake, due to its high CaO content, including ground granulated blast furnace slag (GGBS) produced by the rapid cooling of molten slag (Johnson 2000) and stainless steel slag (SSG) (Johnson 2000; Huijgen et al. 2005; Stolaroff et al. 2005; Kodama et al. 2006).

The carbonation potential of several other types of combustion residues has also been investigated including de-inking ash, paper mill ash (Johnson 2000) and ash from MSW and special waste incineration.

The effects of carbonation on the mechanical properties of cement-based materials have been also extensively investigated primarily to study reinforced cement strength development and corrosion behaviour (see e.g. Papadakis et al. 1991; Johanneson and Utgenannt 2001; Short et al. 2001; Van Balen 2005). More recently, research has also focused on accelerated carbonation treatment of cement-bound waste to promote the stabilization degree and improve the leaching behaviour of the treated material (Lange et al. 1996; Bin-Shafique et al. 1998; Van Gerven et al. 2006). The CO_2 sequestration potential of concrete demolition waste has also been lately studied (Shtepenko et al. 2005; Stolaroff et al. 2005).

Accelerated carbonation of alkaline solid waste has been up to now primarily investigated through the direct aqueous route (see e.g. Fernández-Bertos et al. 2004b; Van Gerven et al. 2005; Huijgen and Comans 2006), or to a lower extent by means of the direct gas-solid

Table 1 Bulk composition of some of the calcium silicate containing waste residues examined for accelerated carbonation (weight % 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
GGBS	41.38	34.59	6.84	14.02	1.51
MSWI-b	22.62	10.32	1.61	5.30	0.95
MSWI-f	35.89	15.29	1.29	6.25	1.11
Deinking Ash	37.69	33.76	3.72	20.12	0.03
Stainless Steel Slag	46.66	27.92	9.75	2.91	1.22

reaction (Jia and Anthony 2000; Baciocchi et al. 2006a,b,c). In fact carbonation of residues does not generally require the extraction of alkaline metals from the solid matrix, since the main reactive species are Ca-containing silicates, oxides and hydroxides. These minerals, as earlier mentioned, behave differently from those containing Mg, as hydration, solvation and carbonation in the former case occur under the same operational conditions in a one stage operation.

The accelerated carbonation of waste materials of low solubility in which CaO is generally bound as a silicate is in most cases carried out in slurry-phase (L/S>1 w/w) (Stolaroff et al. 2005; Huijgen and Comans 2006; Kodama et al. 2006). Depending on residue composition, different operational parameters have been identified (Reddy et al. 1994; Tawfick et al. 1995; Fernández-Bertos et al. 2004a; Huijgen et al. 2005) and CO_2 uptake in materials with high contents of alkaline oxide silicates, such as steel slag, has shown to be influenced by operational parameters such as temperature and pressure, similarly to carbonation of minerals such as wollastonite; however, optimum operational conditions for the processing of residues were found to be less energy demanding (e.g., T= 150°C and p_{CO2} = 20 bar) (Huijgen et al. 2005).

Accelerated carbonation of MSWI BA

MSWI BA can be characterized as a heterogeneous mixture of slag, ferrous and non ferrous metals, ceramics and other non-combustible materials (IAWG 1995). Excluding oversized material (>10 cm), particle size is generally quite uniform and BA can be classified as well gradated sand and gravel. Porosity and specific surface area are very high, due to the expelling of gas from the material in a molten state, whereas moisture contents can vary quite considerably depending on quenching procedures.

BA is alkaline in nature, with pH values ranging from 9.5 to 11.5, and contains alkaline and alkaline earth elements and metal oxides which form hydroxides during hydrolysis. The elemental composition of BA depends primarily on the composition of the feed stock and on the type, capacity and operational temperature of the furnace. The major elements (>10 g/kg) in MSWI BA are O, Si, Fe, Ca, Al, Na, K, Mg and C. Trace elements commonly detected in BA include Ba, Cr, Sn, Ni, Mn, V, Co and Sb (Hjelmar 1996). The more volatile trace elements (Cd, Hg, As, Pb and Zn) are generally present in relatively low concentrations in BA and are rather concentrated in fly ash and APC residues, although a recent study on metal distribution in Japanese ash residues reported that two thirds of the total waste content of Pb and Zn were found in BA (Jung et al. 2004).

Mineralogical studies indicate that the main crystalline phases of BA are silicates (quartz, gehlenite, augite, etc.), sulphates (mainly anhydrite, ettringite and gypsum), carbonates (calcite, metal carbonates), to a lower degree metal oxides and hydroxides (magnetite, hematite, etc.) and chlorides (Kirby and Rimstidt 1993; IAWG 1995; Eusden et al. 1999; Speiser et al. 2000). The overall solubility of BA is relatively low when compared to the other residue streams and is mostly due to calcium and sodium salts, i.e. NaCl, $CaCl_2$ and $CaSO_4$ (IAWG 1995). BA is typically classified as a non-hazardous waste according to the European Waste Catalogue, and has therefore a high recycling potential. It is currently being used as an aggregate substitute in road bases and bituminous pavements in several European countries (e.g., The Netherlands, Denmark) (IAWG 1995). BA has potential to be used in concrete bricks to replace sand and gravel but its wider use is controlled by the leaching of heavy metals, which must not exceed regulatory limits.

The carbonation of BA has been investigated to produce mineralogical changes similar to those occurring as a result of natural weathering and to induce a related reduction in trace metal mobility (Meima et al. 2002; Polettini and Pomi 2004; Van Gerven et al. 2005). Recent studies have also focused on the principal carbonation mechanisms and controlling operating parameters, such as temperature, CO_2 partial pressure, water content, residence time as well as particle size (Fernández-Bertos et al. 2004b; Rendek et al. 2006a). Rendek et al. showed that, due to the presence of unburned organic material, microbial activity can be detected in MSWI BA and they hypothesized that atmospheric CO_2 augmented by the CO_2 produced during biodegradation processes might account for the stabilization of BA during carbonation (Rendek et al. 2006b).

Table 2 gives a summary of the operating conditions for accelerated carbonation as applied in the examined literature studies. The exclusively adopted carbonation route was the direct aqueous process,

Table 2 Summary of operating conditions for accelerated carbonation of MSWI BA

Material type	Carbonation conditions					
	CO_2 conc.	Pressure	Temperature	Duration	Water content	Reference
MSWI BA	10% vol.	atmospheric	50°C	1 h, 2 h, 3 h, 6 h, 1 d, 2 d, 3 d, 1 w, 2 w , 3 w, 4 w	natural moisture content (initial)	Arickx et al. 2006
MSWI BA	100% vol.	not specified (slight overpressure)	Ambient	20 min, 40 min, 1 h, 3 h, 6 h	not specified	Bodénan et al. 2000
MSWI BA	100% vol.	atmospheric	Ambient	not specified	not specified	Bone et al. 2003
MSWI BA	20% vol.	not specified	37°C	2 h, 6 h, 1 d, 7 d	6.4%	Cornelis et al. 2006
MSWI BA	20% vol. (CO_2-enriched air)	atmospheric	not specified	24 h	not specified	Dijkstra et al. 2006
MSWI BA	100% vol. (R.H. 65%)	3 bar	Ambient	0–400 min	0–60 %.	Fernández-Bertos et al. 2004b)
MSWI BA	0.03% (atmospheric air)	atmospheric	Ambient	3–4 d	slurry phase (L/S 5)	Meima et al. 2002
MSWI BA	100% vol. (water-saturated CO_2 flow)	atmospheric	Ambient	24 h, 48 h	not specified	Polettini and Pomi 2004
MSWI BA	100% vol.	atmospheric	Ambient	24 h, 48 h	slurry phase (L/S 10)	Polettini et al. 2005
MSWI BA	100% vol.	2, 3, 5, 7, 11, 17 bar	Ambient	0–180 min	5–25% (initial)	Rendek et al. 2006a
MSWI BA	100% vol.	atmospheric	Ambient	27 d (+49 d)	natural moisture content (initial)	Todorovic and Ecke 2006
MSWI BA	10% vol., 20% vol.	not specified	30°C, 37°C, 50°C	1 h, 2 h, 3 h, 1 d, 2 d, 3 d, 6 d/7 d,	2.3%, 6%, 13%, 25%, 37%, 50% (initial)	Van Gerven et al. 2005
MSWI BA	0.03% (atmospheric air)	atmospheric	40°C	1 h, 2 h, 3 h, 1 d, 2 d, 3 d, 6 d/7 d	6% (initial)	Van Gerven et al. 2005

however different water contents were used, with values of the water-to-solids ratio either in the low range (typically 0.05–0.6 w/w), or in the range corresponding to slurry-phase conditions (typically 5–20 w/w). Other operating parameters were typically: pressure from atmospheric to 17 bar, temperature between ambient and 50°C, CO_2 percentage from 0.03 to 100% with residence times from a few hours to a few weeks.

Pre-treatment of materials consisted mainly of drying, sieving and grinding. Generally only the size fraction from 0.1 to 4 mm was investigated, since presumably larger particles are typically less reactive towards CO_2 on account of chemical composition (lower CaO and higher SiO_2 content) (Speiser et al. 2000; Rendek et al. 2006a) and lower specific surface area.

The mechanisms involved in the carbonation of MSWI BA have not been completely elucidated; however on the basis of the mineralogical characteristics of ash prior to and after accelerated carbonation, it is possible to hypothesise the reactive phases involved and their carbonation pathways.

Speiser et al. (2000) studied the mineralogical composition of deposited MSWI BA and argued that hydrated calcium silicate may form as a result of the reaction between $Ca(OH)_2$ and SiO_2. A number of other potential reactive phases for carbonation, including olivine, wollastonite, feldspar and dicalcium silicate were also detected (Kirby and Rimstidt 1993; Eusden et al. 1999; Fernández-Bertos et al. 2004b). XRD analyses of carbonated MSWI BA (Fernández-Bertos et al. 2004b; Polettini and Pomi 2004) showed an increase in the amount of calcite and quartz, a decrease in corundum and the disappearance of ettringite upon carbonation. The formation of quartz as a result of carbonation can be explained by the dissolution of calcium silicate and consequent precipitation of calcite, thus increasing the availability of silicate ions, which form quartz or amorphous aluminosilicates (Meima et al. 2002).

The fate of Al-containing minerals as a result of the decreased pH of carbonated BA was discussed by Zevenbergen and Comans (1994). Under the pH conditions pertaining, Al can be precipitated into a number of mineral phases, which may include amorphous Al (hydr)oxides, with lower amounts of aluminosilicate minerals (Meima et al. 2002). The dissolution of ettringite upon carbonation has been observed by several authors (Zevenbergen and Comans 1994; Meima and Comans 1997; Meima et al. 2002; Polettini and Pomi 2004) and may result in increased sulphate leaching (Bodénan et al. 2000; Polettini and Pomi 2004). However, the fate of sulphates during the carbonation process has not been fully explained. Fernández-Bertos et al. (2004b) reported an increase in gypsum detected during XRD analyses; Meima et al. (2002) did not find any evidence of gypsum precipitation in carbonated BA and Polettini and Pomi (2004) showed a decrease in the amount of anhydrite in accelerated carbonated BA.

A number of workers have focused on the effects of accelerated carbonation on the leaching of trace metals from bottom ash. In general the multiple reaction mechanisms occurring during carbonation are accompanied by surface interactions between trace contaminants and neo-formation minerals and these will impact on the mobility of trace metals. The specific properties of individual trace metals, their solubility curves, and behaviour as a function of pH and Eh conditions and their affinity for such minerals as calcite and Al and Fe (hydr) oxides are important.

The fate of major elements during accelerated carbonation is of particular relevance in that the chemistry of major species of BA has been shown to be capable of affecting the behaviour of trace contaminants in fresh, naturally weathered and accelerated aged BA (Zevenbergen and Comans 1994; Meima and Comans 1997, 1999). Ca leaching at alkaline pH values has generally been found to decrease for carbonated BA as a result of solubility control by calcite (Zevenbergen and Comans 1994; Meima and Comans 1997, 1999; Bone et al. 2003; Polettini and Pomi 2004; Polettini et al. 2005), which is less soluble than ettringite and portlandite.

Carbonation has also been variously reported to result in increasing the amount of amorphous Al (hydr) oxides (Dijkstra et al. 2006) or to have little effect (Cornelis et al. 2006). The same investigators found no appreciable effect of carbonation on precipitation of Fe (hydr) oxides.

Among the heavy metals which are immobilised by accelerated carbonation, Pb and Zn are particularly relevant. A strong reduction in both Pb and Zn release from carbonated BA has been reported by Fernández-Bertos et al. (2004b). Zn released from two BA samples during the EN 12457 leaching at L/S 10 decreased from around 10 mg kg^{-1} to less than 1 mg kg^{-1}, while the release of Pb from the same samples decreased from initial values of about 50 and 100 mg kg^{-1} to less than 1 mg kg^{-1}. A significant decrease in Zn and Pb leaching, by one and two orders of magnitude respectively, was observed by Bone et al. (2003) under the same leach testing conditions, by Arickx et al. (2006) using the EN 12457-2 and NEN 7343 (column test) leaching procedures, and by Bodénan et al. (2000) using the NF X31-210 test (L/S 10 deionized water leaching in three steps each 16 h-long). In studies on slurry-phase carbonation of BA, Polettini et al. (2005) measured Pb leachate concentrations in the EN 12457 L/S 2 and L/S 10 eluates below 50 μg kg^{-1}, while Zn concentrations were below 0.4 mg kg^{-1} as opposed to 0.9 mg kg^{-1} in the fresh BA. Leaching as a function of pH showed that the reduction in Zn was pH dependent, whereas for Pb, this resulted from a modified leaching curve, as compared to that of the fresh material. Geochemical modelling indicated strong undersaturation in eluates for both $Pb(OH)_2$ and Pb carbonate species, and the authors concluded that, as a consequence of slurry-phase carbonation, Pb was probably sorbed onto newly precipitated phases. Different results for Pb and Zn release were obtained by Van Gerven et al. (2005) in L/S 10, 24-h deionized water leaching tests. Carbonation did not affect Pb release, while Zn leaching increased with carbonation time. The application of the NEN 7345 diffusion leaching test on two accelerated carbonated BA samples by Todorovic and Ecke (2006) showed mobilization of both Pb and Zn.

The leaching behaviour of Cu is affected by accelerated carbonation, with most literature indicating immobilisation, although with different leaching characteristics. Van Gerven et al. (2005) measured a change in Cu leaching (EN 12457, L/S 10) from about 3.3 mg kg^{-1} for untreated BA to between 1.0 and 2.0 mg kg^{-1} at the end of the carbonation period (7 days), while the reduction found by Arickx et al. (2006) was from about 29 mg kg^{-1} to about 8 mg kg^{-1}. Meima et al. (2002) found that Cu concentrations in BA suspensions were reduced by about 50% upon carbonation. Similar shaped leaching curves for Cu were found by Van Gerven et al. (2005) and Meima et al. (2002) (see Fig. 1a and b), with a poor pH dependency of Cu release from carbonated BA. In other work, Arickx et al. (2006) indicated a stronger pH dependent leaching for Cu in 4-week old carbonated BA, with a one order of magnitude decrease in Cu concentration at the point of minimum solubility if compared to the untreated material (see Fig. 1c)); however, in the acidic pH range, the leaching from fresh and carbonated BA were coincident. In their study, Meima et al. (2002) also analyzed the composition of the precipitates formed during carbonation of filtered BA leachates and concluded that the reduction in Cu leaching was due to the precipitation of amorphous Al species, that typically display a very high affinity for this metal.

The findings by Polettini and Pomi (2004) and Polettini et al. (2005) indicated a very similar pH dependence of Cu leaching for fresh and carbonated BA (using both direct and slurry-phase carbonation) for pH values below the natural pH of the carbonated material (pH 8.3) (see Fig. 1d)). Since the natural pH of fresh bottom ash was around 10 units (i.e., already in the range of minimum solubility), the reduction to about 8.5 as a consequence of carbonation resulted in an enhanced Cu release, although there may be other mechanisms potentially controlling Cu leaching in the pH range 8.5–10. Further indications on the mechanisms of Cu release from carbonated BA were provided by Dijkstra et al. (2006), who observed similar shapes of the leaching curves for the untreated and carbonated material in the acidic to neutral pH range, while a consistently lower Cu leaching from carbonated BA between pH 7.5 and 10, thus confirming the results obtained by Arickx et al. (2006).

Speciation modelling calculations involving Cu complexation by Fe and Al (hydr) oxides and humic substances, showed that at pH>7 the leaching of Cu is controlled by sorption on humic acids and that the positive effect of carbonation on Cu release in the alkaline pH range is mainly related to the change in leaching of such species, augmented by an enhanced adsorption onto Fe/Al (hydr)oxides (Dijkstra et al. 2006).

A contrasting Cu leaching behaviour of BAs from different incineration plants was found by Todorovic and Ecke (2006), who reported both the effects of mobilization and immobilization of Cu as a result of carbonation.

In the absence of detailed information about the mineralogy of BA prior and after the carbonation treatment, the inconsistencies in the literature cannot be explained. However, the different initial composition of the materials investigated may be important, as are the particular carbonation process conditions (Van Gerven et al. 2005) which were found to result in decreased Cu leaching by 2–3 times, as compared to carbonation with atmospheric air.

The leaching behaviour of typical oxyanion-forming metals such as Cr has been investigated by several workers. Bone et al. (2003) report that, while Cr leaching from fresh BA was in the order of 1–10 μg l^{-1}, Cr concentrations in the eluate from carbonated BA ranged from 10 to 100 μg l^{-1}. A mobilization effect of Cr was also indicated by Van Gerven et al. (2005), although the maximum release appeared to occur after 6 h of carbonation, and for longer treatment durations Cr leaching was shown to decrease again. A similar result was obtained by Polettini et al. (2005) for slurry-phase carbonation of BA, where Cr leaching was found to increase by two to three times after the application of the process, although the mobilization effect was reduced by prolonged carbonation times. Rendek et al. (2006a), however, reported immobilization of Cr, with a decrease in leachate concentration (deionized water, L/S 10, 24 h) from 0.022 to 0.005 mg l^{-1}, whereas Arickx et al. (2006) reported a very weak or even absent Cr immobilization effect of carbonation.

An attempt to explain the mechanisms of Cr leaching from carbonated as opposed to fresh BA was given by Van Gerven et al. (2005) in their study on pH-dependent Cr leaching. They found that in the pH range 8–11.5 leached Cr was lower for carbonated than for untreated BA. This was linked to the acidic pH range resulting from carbonation which leads to

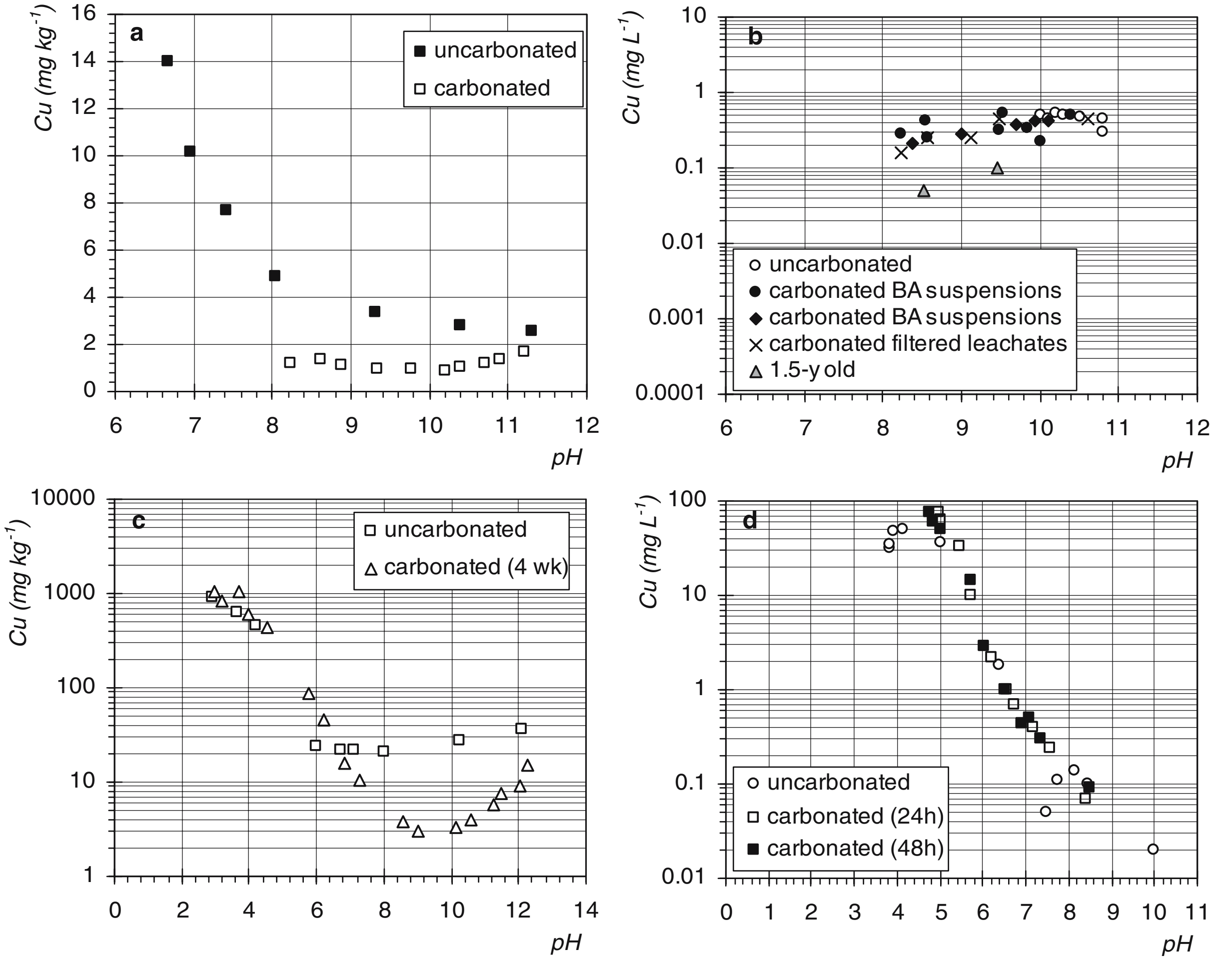


Fig. 1 Cu leaching from carbonated BA as a function of pH reported in different literature studies: **a** Van Gerven et al. (2005); **b** Meima et al. (2002) (*empty circle* uncarbonated BA; *filled diamond* carbonated BA suspensions; *filled circle* carbonated filtered BA leachates, *times sign* 1.5-y old BA); **c** Arickx et al. (2006); **d** Polettini et al. (2005)

sorption of anionic species including chromates onto the surface of Al and Fe (hydr)oxides precipitates in BA. The influence of the operating conditions on Cr leaching showed that an increase in CO_2 concentration yielded higher Cr release, while an increase in treatment temperature improved Cr leaching (Van Gerven et al. 2005).

The other oxyanionic metals Mo and Sb were shown to be affected by carbonation in different ways. Van Gerven et al. (2005) found that while Mo leaching remained approximately constant during carbonation and appeared not to be appreciably affected by changes in pH (as also reported by Meima et al. 2002 and Bone et al. 2003), Sb was mobilized, with eluate concentrations increasing by a factor from three to two as the carbonation degree increased. Conversely, the study by Todorovic and Ecke (2006) indicated a slight reduction in Sb release during diffusion leaching of carbonated BA.

The pH-dependent leaching behaviour of Mo (see Fig. 2) was investigated by Van Gerven et al. (2005) and Dijkstra et al. (2006) and showed a large decrease in Mo release from carbonated BA between pH 6 and 10, with the positive effect of carbonation in the pH range 8–11 being associated to increased amounts of Fe and Al (hydr)oxides as a result of carbonation.

The leaching behaviour of Sb was studied in detail by Cornelis et al. (2006). In untreated BA, Sb can be incorporated in ettringite formed after quenching. The effect of carbonation on the dissolution of ettringite was thought to cause the mobilization of Sb, whose solution concentrations become controlled by calcium antimonate, $Ca[Sb(OH)_6]_2$, at pH>9. The same authors noted that in the pH range 6–8.6 Sb solubility was likely

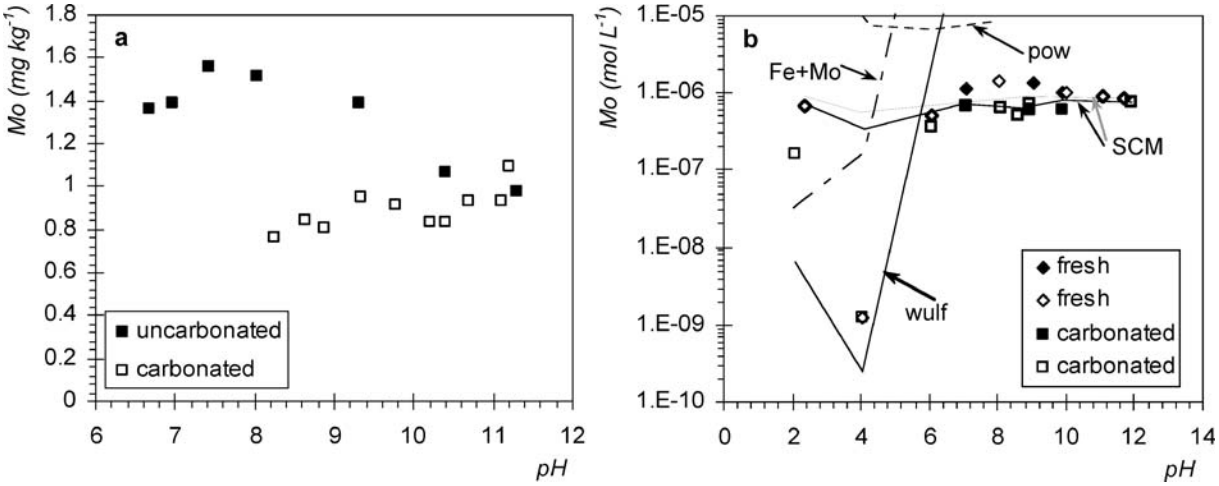


Fig. 2 Mo leaching from carbonated BA as a function of pH as reported by: **a** Van Gerven et al. (2005); **b** Dijkstra et al. (2006) (*filled square* fresh BA; *filled diamond* carbonated BA; *Fe+Mo* ferrihydrite + $Fe_2MoO_{4(s)}$, *SCM* complexation to Fe/Al (hydr) oxides, *pow* powellite, *wulf* wulfemite)

controlled by sorption onto amorphous Fe (hydr) oxides for both untreated and carbonated BA.

Dijkstra et al. (2006) investigated the fate of organic matter during carbonation. They indicated a consistent reduction in DOC leachate concentration over a wide pH range. The speciation of organic matter in the eluates showed a strong decrease in concentrations of fulvic acids over the entire pH range investigated (2–12). Since the total amount of fulvic acids was not shown to be affected by carbonation and the degradation process of such substances has been shown to occur within timeframes of thousands of years (Petterson et al. 1994) it was hypothesized that adsorption onto the active surfaces of BA (presumably Fe and Al (hydr) oxides) could be the reason for decreased release of fulvic acids. Modelling studies using tentative equilibrium constants values for the surface complexation reactions involving fulvic acids with Fe (hydr) oxides indicated that the assumption was reasonable.

The sequestration potential of accelerated carbonation of BA is influenced by the main operational parameters governing the carbonation process. CO_2 uptake potential is generally measured as the weight gain in treated BA after oven-drying, or as the decrease in CO_2 partial pressure in the reactor. Because of the possibility of hydration reactions occurring (Van Balen 2005), TG is an appropriate method to quantify the increase in the calcium carbonate content of the material upon carbonation. Due to the metastability of many mineral phases in BA, the temperature range at which calcium carbonate decomposes can be quite wide (600–900°C) leading to inaccuracies in calcium content calculations. Therefore, coupling TG devices with gas chromatographic measurements of the CO_2 evolved could provide advantages (Baciocchi et al. 2006b). For BA, maximum values of weight gain upon carbonation w/w dry weight range from around 3% to 6.5% (Johnson 2000; Fernández-Bertos et al. 2004b; Rendek et al. 2006a), but these are dependant on particle size and the source of BA.

The mechanisms involved in the carbonation of BA are not yet well known, due to the material's complex chemistry and mineralogy. However, it is likely that more than one alkaline oxide-containing mineral (including Ca and Mg silicates) reacts with CO_2 in addition to calcium hydroxide. Most of the studies hitherto reported have considered a simplified approach for the carbonation of $Ca(OH)_2$ via the aqueous route (Arickx et al. 2006; Rendek et al. 2006a).

The rate limiting steps of the carbonation reaction involve the dissolution of calcium from the solid matrix into the liquid phase and the diffusion of CO_2 into the pore system. Arickx et al. (2006) proposed a model for the diffusion of CO_2 from air to a porous solid and the reaction with Ca^{2+} in the liquid phase to calculate the change in pH occurring after accelerated carbonation (assuming pH control by the dissolution of $Ca(OH)_2$).

The kinetics of CO_2 uptake is generally characterized by two reaction steps: (1) a first steep increase in the rate of CO_2 uptake with time, followed by (2) a decrease in the rate until an approximately constant value of CO_2 uptake is attained (Fernández-Bertos et al. 2004b; Van Gerven et al. 2005; Rendek et al. 2006a). Huijgen et al. (2005) observed this trend for steel slag and assumed that the first reaction stage may involve 'faster' reacting minerals such as $Ca(OH)_2$; whereas the second stage may involve other, less reactive, minerals. Similar phenomena could occur during BA carbonation and the degree of carbonation achieved (or process efficiency) should be calculated as the conversion to calcium carbonate of all Ca-reacting species found in the feed-stock, although it should be recognised that some uncertainty remains.

Fernández-Bertos et al. (2004b) found that, under specified reaction conditions, 75% of the carbonation reaction took place in the first 2.5 h and therefore they selected this time interval as the optimum reaction time. However, the main process-related parameters were found to be: sample water content and particle size, temperature and the partial pressure of CO_2.

Particle size has been pointed out as an important process parameter, since Ca content is often enriched in fine fractions. Rendek et al. (2006a) found that 4 mm-sieved material had double the CO_2 uptake when compared to the unsieved material. Fernández-Bertos et al. (2004b) found similar results but related the higher CO_2 uptake to the increased surface area of the smaller particles, indicating 710 μm as the optimal size fraction for carbonation (weight gain around 3% w/w).

The efficacy of accelerated carbonation via aqueous-based processes is dependent upon the water content employed. As water content increases, a critical liquid to solid ratio, characteristic of the material, is reached and then carbon dioxide uptake diminishes. Although water is necessary to hydrate and solvate CO_2 and Ca^{2+}, when it exceeds the pore capacity of a material it forms an inter-granular film and hinders CO_2 diffusion. For BA carbonation, optimum L/S values of 0.18 and 0.3–0.4 have been reported (Rendek et al. 2006a; Fernández-Bertos et al. 2004b, respectively).

The effect of other process parameters such as temperature and CO_2 partial pressure has not been extensively examined up to now; however Rendek et al. (2006a) noted that the time required for complete carbonation to be achieved decreased from over 2 days to 3.5 h when the partial pressure of CO_2 increased from 2 to 17 bar.

Van Gerven et al. (2005) have studied the influence of process parameters on leaching behaviour and found that an increase in CO_2 from atmospheric levels to 20% decreased Cu leaching, but increased for example, Cr and Sb leaching. Whereas, increasing temperature from ambient levels to 50°C reduced or stabilized the leaching of contaminants from the material. They also concluded that moisture contents of 13 and 25% gave the lowest leaching concentrations.

Authors agree (Van Gerven et al. 2005; Baciocchi et al. 2006c; Rendek et al. 2006a) that the CO_2 uptake potential of BA produced in a MSW incinerator could reduce CO_2 emissions by only 0.4–1% (0.4, 0.5 and 0.5–1% respectively). However, with the primary aim of accelerating BA natural weathering, incinerator stack gas emissions, which normally contain around 10% CO_2, could be blown into BA stockpiles (Steketee et al. 2006) or supplied in a counter-current mode (Arickx et al. 2006) or in a closed reactor with mixing equipment (Sakita et al. 2006) to BA. One of the main problems that occurs when stack gas is carbonated via the aqueous process (temperatures ranging from ambient to approximately 50°C) is, as reported by Arickx et al. (2006), the condensation of the water contained in the gas which leads to the soaking of the BA media and hence to a reduction in process efficiency. Sakita et al. (2006) solved this problem by using a heat exchanger to decrease the water content of the stack gas prior to carbonation.

Accelerated carbonation of APC residues

Solid residues generated from flue gas treatment are a heterogeneous mixture of excess sorbent material injected into the stack gas (mainly activated carbon and lime) and flue gas condensation and reaction products and, when not captured upstream, combustion fly ash. Fly ash particles are generally larger (40–200 μm) than treatment sorbent particles (10–40 μm). The particle size is usually lower for semi-dry scrubber systems involving fabric filters (IAWG 1995).

The porosity of APC ash is very high when excess amounts of activated carbon are injected into the stack gas as during, for example, hazardous waste incineration. The pH of residues from dry and semi-dry APC systems is typically >12, due to the excess of lime. APC ash is typically characterized by a high buffering capacity.

The major elements found in APC residues are Ca, Cl, Si, Al, Na, K, S, Mg, Fe, O. High levels of volatile elements, such as Cd, As, Hg, Pb and Zn, may be present (Hjelmar 1996) together with soluble salts (mainly chloride and sulphate salts), therefore APC residues are classified as hazardous waste according to the European Waste Catalogue.

Calcium and chloride containing compounds make up around 75–95% w/w APC residue, whereas the remaining species are H_2O, organic carbon, iron oxides, silicates and quartz. The main crystalline phases detected by XRD are $Ca(OH)_2$, $CaSO_4$, silicates and alluminosilicates, carbonates (calcite, metal carbonates) and salts (mainly NaCl, KCl, CaClOH and Na_2SO_4) (IAWG 1995; Bodénan and Deniard 2003; Fernández-Bertos et al. 2004b). Mineralogical investigations have shown that CaClOH is the main crystalline calcium and chloride containing phase (Bodénan and Deniard 2003). This is regardless of the type of flue gas treatment process, filtration mode and specific surface of the Ca-based sorbent and shows that, in both dry and semi-dry systems $Ca(OH)_2$ does not react completely with HCl; and explains why $CaCl_2$ is generally not readily detected (Bodénan and Deniard 2003; Li et al. 2006).

A high soluble salt content (30–40% w/w) is found in APC residues from dry and semi-dry acid gas scrubbing, which contain readily soluble salts (Hjelmar 1996) and thus require careful management to limit their environmental impact during final disposal, including physical/chemical separation, thermal processing and solidification and/or stabilization (Sabbas et al. 2003).

The application of accelerated carbonation to APC residues before landfilling may also be beneficial as carbonation has been shown to decrease the pH of alkaline materials to values corresponding to minimum solubility levels of specific metals and within defined regulatory limits ($pH<9.5$) (Ecke 2003; Fernández-Bertos et al. 2004a). Furthermore, APC residues can have a high content of CO_2-reactive minerals (see Table 1) such as $Ca(OH)_2$ and CaClOH and therefore may have a useful CO_2 uptake potential (Fernández-Bertos et al. 2004b; Baciocchi et al. 2006a,b).

The accelerated carbonation of APC residues has been investigated via the aqueous route similarly to BA, with water contents ranging from 5 to 60% w/w (Johnson 2000; Bone et al. 2003; Ecke 2003; Fernández-Bertos et al. 2004a) and also via the direct gas–solid route (Baciocchi et al. 2006a,b). The high soluble salts content of APC residues mean that slurry-phase carbonation is not considered viable. Table 3 summarises the operating conditions adopted for the accelerated carbonation of MSWI APC residues; as it can be noted operating parameters varied quite considerably. For aqueous-based experiments, ambient temperature and pressure at or slightly above atmospheric levels, as well as raised CO_2 partial pressures were generally used. For the dry route, CO_2 partial pressures typical of flue gas and temperatures ranging from 300 to 500°C were adopted. Residence time depended on the aims of the investigation, varying from a few minutes (for assessing process kinetics) to a few weeks, when the long-term effects of carbonation were being studied. APC ash was not normally pre-treated in any way.

The main reacting species in APC residues ($Ca(OH)_2$ and CaClOH) were degraded during carbonation (Fernández-Bertos et al. 2004b; Li et al. 2006). During progressive carbonation TGA analysis showed an increase in sample weight loss in the temperature range corresponding to calcite decomposition (500–850°C) (Baciocchi et al. 2006b; see Fig. 3). Li et al. (2006) detected Si–Al–Ca compounds, including gehlenite, braunite and larnite in carbonated APC residues, which could indicate that hydration of the samples could have been occurring at the same time as carbonation.

As a result of a higher content of CO_2-reactive mineral species in APC residues, physical changes were more evident than for BA carbonated under similar conditions. Particle size increased due to particle agglomeration, while porosity, tortuosity and total pore size decreased probably due to $CaCO_3$ precipitation into pore space (Fernández-Bertos et al. 2004b). Microstructural analysis also revealed notable differences in the morphology of carbonated and non-carbonated APC ash samples (Fernández-Bertos et al. 2004b). Figure 4 shows a complex microstructure where the size and shape of individual grains are variable, whereas in carbonated APC ash (Fig. 5) grains are larger and pore space is lower. The morphology of carbonated APC is more regular and "rounded out," typical of calcium carbonate particles.

The changes in the physical, chemical and mineralogical properties of carbonated APC residues may influence leaching behaviour. Studies on the stabilisation of APC residues by carbonation have in fact

Table 3 Summary of operating conditions for accelerated carbonation of MSWI APC residues

Material type	Carbonation conditions					
	CO_2 conc.	Pressure	Temperature	Duration	Water content	Reference
MSWI APC residue	0.03% (atmospheric air)	atmospheric	Ambient	2–4 w	not specified	Astrup et al. 2005
MSWI APC residue	0.03% (atmospheric air)	atmospheric	Ambient	4 w	not specified	Astrup et al. 2006a, 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. (70% R.H.)	3 bar	Ambient	not specified	30%	Li et al. 2006

recorded the modification of leaching properties upon carbonation (Ecke 2003; Fernández-Bertos et al. 2004b).

In regard to the mechanisms controlling the leaching of trace metals from carbonated APC residues, the behaviour of major cations can help to understand the processes governing solution chemistry and pH conditions (Astrup et al. 2006b); for this reason, elements such as Al, Ca, Si, as well as S, have been investigated (Bone et al. 2003; Astrup et al. 2006a; Baciocchi et al. 2006a).

A comparison of the results obtained reveals that the change in contaminant leaching can be affected by the L/S ratio (which is a parameter that provides a measure of the leaching timeframe). It is also well established that pH is a key parameter determining metal release, so by evaluating pH dependent leaching properties, the processes controlling leaching at various pH values, as well as the potential solubility-controlling phases for each contaminant of interest, can be elucidated.

Accelerated carbonation induces mineralogical change in APC residues. For example, hydroxides conversion into carbonates results in a consequent lowering of pH which affects the solubility and leachability of many elements and enhances the acid neutralization capacity of the material. Thus, carbonation is likely to promote the retention of metals which are mainly mobilized at high pHs and to lead to a faster release of metals leached at moderate or low pHs (Astrup et al. 2006b).

Accelerated carbonation was found to reduce the release of Zn and Pb during the EN 12457 leaching test (Bone et al. 2003; Fernández-Bertos et al. 2004b; Baciocchi et al. 2006a). Zn release from APC residues was equal to 100 mg kg^{-1} (Baciocchi et al. 2006a) and 20–100 mg kg^{-1} (Fernández-Bertos et al. 2004b) before carbonation, while it decreased to 10 mg kg^{-1} (Baciocchi et al. 2006a) and to below 2 mg kg^{-1} (Fernández-Bertos et al. 2004b) after carbonation. In the case of Pb, EN 12457 leaching test results indicated that, while Pb leachate concentrations ranged from 100 to 1,000 mg kg^{-1} for fresh APC ashes, these were reduced by two or three orders of magnitude to, in some cases, below 1 mg kg^{-1} after carbonation (Fernández-Bertos et al. 2004b; Baciocchi et al. 2006a).

Geochemical modeling (Astrup et al. 2006a) revealed that the U-shaped pH-dependency for Zn could not be attributed to smithsonite ($ZnCO_3$), which

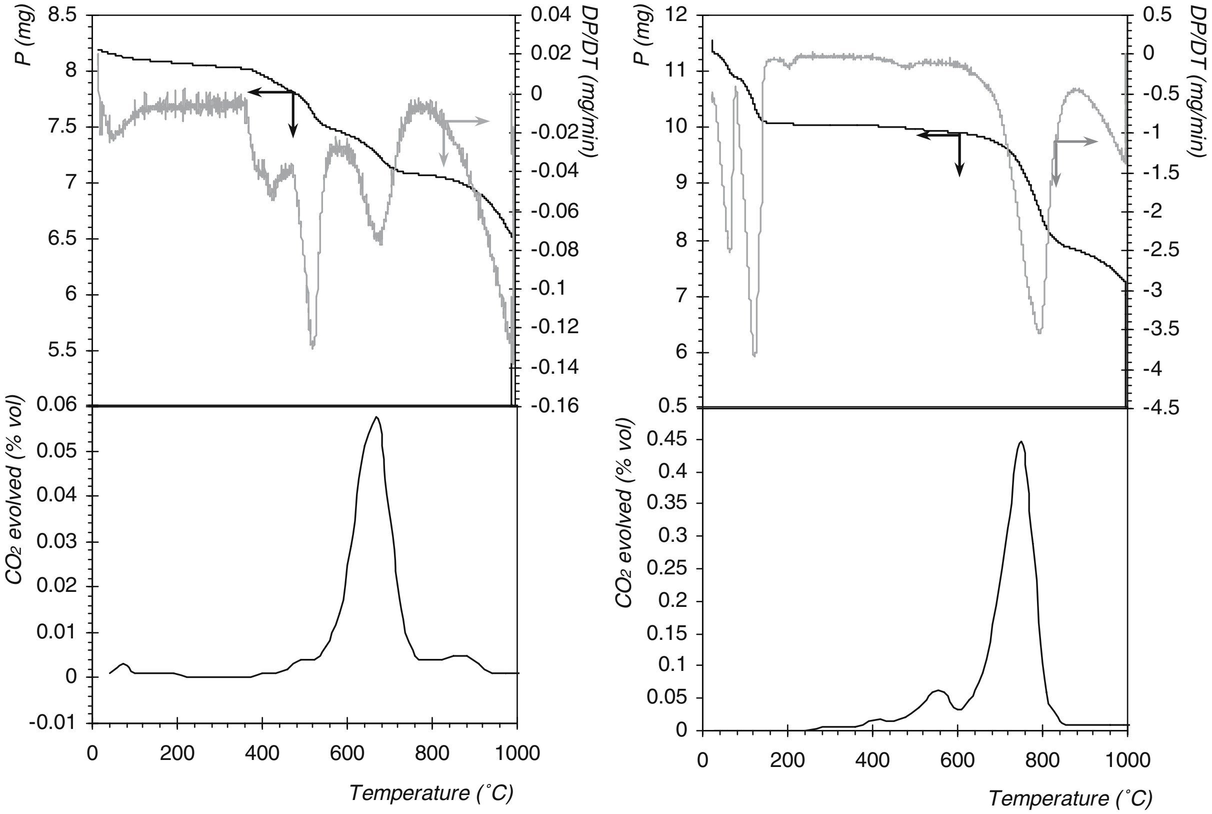
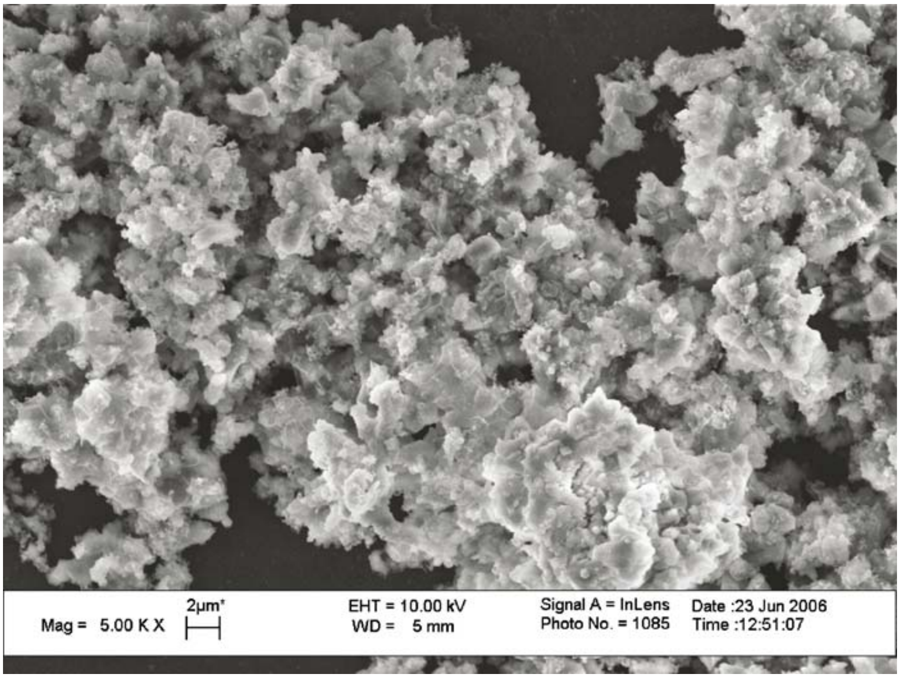


Fig. 3 TGA/DTG results (*top*) and CO_2 evolved (*bottom*); **a** as received fly ash; **b** fly ash treated in CO_2 flux at 400°C (Baciocchi et al. 2006b)

Fig. 4 SEM picture of a sample of non-carbonated APC residues



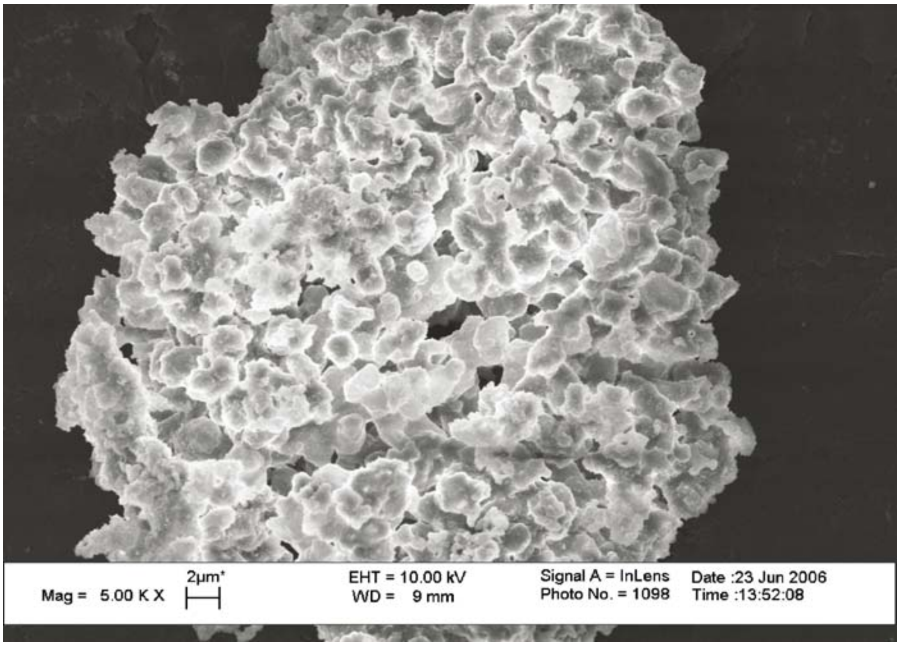


Fig. 5 SEM picture of a sample of APC residues carbonated for 1.5 h 100% CO_2 (73% RH) with operational conditions set at 30°C and 3 bar CO_2 partial pressure

was undersaturated by more than one order of magnitude in the eluate, for both fresh and carbonated APC residues. A similar behaviour was observed for lead, even though cerrusite ($PbCO_3$) appeared to act as a solubility controlling mineral in the pH range 6–12.

For Cu, the shape of the leaching curve was not modified by carbonation. The possibility that copper carbonate (malachite) precipitated in the eluates of carbonated APC ash was indicated. During EN 12457 leaching, Cu was reduced from approximately 0.6 $mg \cdot l^{-1}$ for fresh ash to below 0.2 $mg \cdot l^{-1}$ for carbonated ash (Baciocchi et al. 2006a), although in this case Cu release was ascribed to the reduction of pH towards the range of minimum solubility.

Cr leaching is more complex when compared to other metals in the case of both fresh and carbonated APC ashes; this may be explained considering mechanisms other than solubility control (Astrup et al. 2006a). The decrease in Cr concentration observed at high pH values can be due to hexavalent chromium incorporation into low-solubility minerals, such as ettringite and $Ba(S, Cr)O_4$ (Astrup et al. 2006a). At pH values in the range 4.5–8.5, lower chromium leaching might be explained by the reduction of Cr (VI) to the less soluble form of Cr(III) by the Al(0) present in the APC ash (Astrup et al. 2005).

The CO_2 uptake potential of APC residues is considerably greater than that of other MSW combustion residues. Values ranging from 7% (Fernández-Bertos et al. 2004b) to 12–13% (Johnson 2000; Baciocchi et al. 2006a) have been reported. Differences in values, however, probably depend on the carbonation conditions used in each study and the incineration facilities from which the APC residues were collected.

The mechanisms governing APC carbonation are more straightforward than those for BA carbonation, since in the former case the reactive species are almost entirely composed of portlandite and CaClOH. The kinetics of CO_2 uptake for APC residues show the same trend as for BA, though with higher weight gains, which are related to higher lime contents, specific surface areas and microporosity (Fernández-Bertos et al. 2004b). During carbonation of APC residues via the aqueous route, water content, particle size, temperature, CO_2 partial pressure and concentration are important. Fernández-Bertos et al. (2004b) selected the 212 μm size fraction and L/S ratios of 0.2–0.3 w/w as the optimal values.

Fernández-Bertos et al. (2006) studied the influence of CO_2 concentration and temperature on CO_2 uptake in APC residues and showed that as the % CO_2 increased, higher CO_2 uptakes were recorded, although the conversion achieved at a 50% v/v CO_2 was only 5% lower than that measured for a 100% CO_2 v/v. Thus, during industrial-scale carbonation at combustion facilities, CO_2 could be directly sequestered from the flue gas, reducing the operational costs and complexity of the system. An increase in carbonation reaction temperature was shown to have a dual effect on the carbonation of APC residues. Initially it enhanced the kinetics of the carbonation reaction, while later it reduced the final conversion values (Fernández-Bertos et al. 2006). Initially this could be related to an increase in Ca^{2+} dissolution from residues at higher temperatures, followed by a reduction in CO_2 solubility/diffusion as a layer of reaction product is formed.

Ecke (2003) studied the influence of temperature, water content, CO_2 partial pressure and reaction time on the leaching behaviour of APC residues using multivariate data analysis and a two-level factorial design. The results showed that at high CO_2 concentrations and long treatment times, the stabilization of APC residues (in terms of lower pH and Pb and Zn leaching) was enhanced. Temperature and sample water content instead, were found to exert minor influence on the process (Ecke 2003).

Baciocchi et al. (2006b) have shown that the main mechanisms governing dry carbonation of $Ca(OH)_2$ apply to the gas–solid carbonation of APC residues. In similarity with the aqueous route process, the kinetics of gas–solid carbonation was found to consist of two distinct stages: (1) the rapid conversion of calcium to carbonate and (2) a much lower rate phase involving diffusion of CO_2 into the porous material (see Fig. 5). The first stage was described by Bhatia and Perlmutter (1983) as being characteristic of a kinetic control regime, whereas the second one was linked to the reduction of the global process rate by the diffusion of CO_2 through the product layer.

To further investigate the kinetics of carbonation in the first stage of the reaction and to obtain kinetic parameters, Baciocchi et al. (2006b) used the random pore model (Bhatia and Perlmutter 1983) to correlate the reaction behaviour of the material with the internal pore structure. From their results they concluded that the process could be fast enough to enable fluidized bed processing of APC directly using flue gases. The formation of carbonate increased with temperature, although the conversion at 450 and 500°C was approximately 60% over 6 h (see Fig. 6).

The results reported so far in the literature indicate CO_2 uptake potentials of 120 g CO_2 per kg of APC residues for the gas–solid carbonation route (Baciocchi et al. 2006a) and lower values via the aqueous carbonation route (Ecke 2003). The sequestration potential of APC residues indicates that carbonation technology is a technically viable option to reduce CO_2 emissions from point sources, such as waste incinerators or power plants. Although Baciocchi et al. (2006a) have calculated that the use of all the APC residues annually produced from the existing plants in the EU would have the same CO_2 sequestration capacity as one of the largest pilot-scale CO_2 geological storage facilities running today (IPCC 2005).

Comparison between MSWI bottom ash and APC residue carbonation

On the basis of literature results, it appears that accelerated carbonation can be applied to different types of MSWI residues with different purposes.

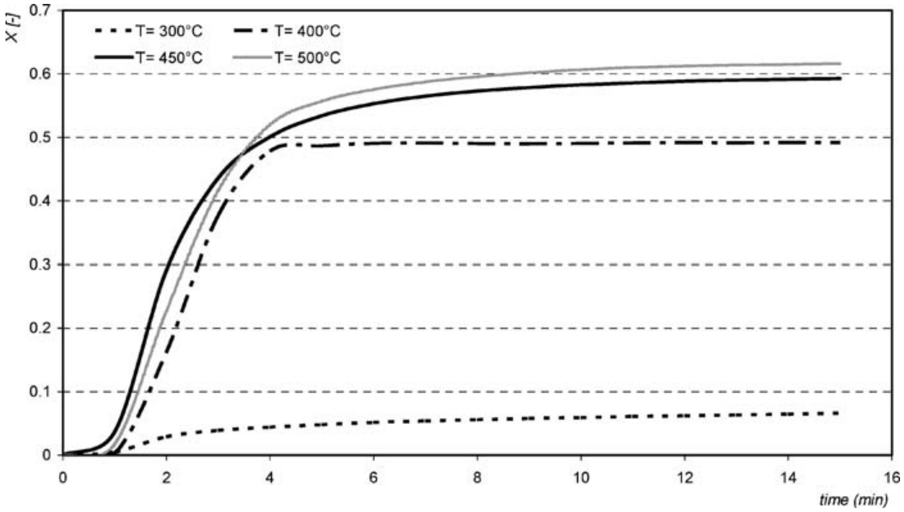


Fig. 6 Carbonation kinetics of APC residues at different operating temperatures under a 10% vol. CO_2 flux in Argon, with X indicating calcium conversion into carbonate (Baciocchi et al. 2006b)

For APC residues, the high contents of readily reactive calcium hydroxides make carbonation potentially suitable for CO_2 sequestration purposes, with possible integration of the carbonation process with waste combustion in order to reduce the net CO_2 emissions of incinerator facilities. However, due to the relatively low amounts of such residues as compared to the original waste, a still limited reduction in CO_2 emissions can be anticipated.

In the case of MSWI bottom ash, typical Ca and Mg contents are not high enough to render CO_2 sequestration through accelerated carbonation a viable option. For bottom ash, the application of accelerated carbonation is thereby applied with the aim to attain a chemically stable structure with improved leaching behaviour.

Concerning the release of contaminants from carbonated MSWI residues, leaching mechanisms have been found to be different for APC residues as compared to bottom ash, depending on the different role played by major components towards the stabilization of trace contaminants. The higher Al and Si content in bottom ash, as compared to the other solid residues, accounts for the formation of larger amounts of mineral phases which likely possess sorption capacity towards trace contaminants, implying generally higher contaminant immobilization efficiencies. The higher organic matter contents in bottom ash as compared to APC residues can also account for a different effect of accelerated carbonation on the mobility of such metals as Cu and Pb which can be complexed by dissolved organic carbon.

Conclusions

MSW incinerator residues can be carbonated and stabilized to reduce the leaching of specific metals (particularly Pb and Zn). Although the mechanisms for trace metal leaching from carbonated MSWI residues still need to be elucidated, literature studies seem to indicate a reduction in metal cations mobility (particularly Pb, Zn and Cu) and a possible mobilization effect on oxyanionic metals including Cr and Sb. However, the type and extent of the effects of accelerated carbonation on metal release are strongly related both to the mineralogical characteristics of the original residues and to the degree of carbonation attained, so that no general and univocal conclusion on leaching can be derived.

Concerning the contribution of accelerated carbonation to CO_2 sequestration, a reduction in carbon dioxide emissions to the atmosphere can also be achieved if the solid residues are used for the capture of CO_2 from stack gases.

The carbonation of pure compounds, such as alkaline and alkaline earth oxides and hydroxides, is a well known process and the reaction mechanisms and variables involved have all been investigated. However, this review has shown that heterogeneous materials such MSWI ash can also be carbonated using both aqueous and gas–solid carbonation routes, but more work is required to fully understand the mechanisms involved in the carbonation process of such materials, before this type of technology can be applied on an industrial scale. Further effort is required to model the kinetics of ash carbonation to account for the different reaction stages identified, to elucidate optimal processing conditions, and to model the leaching behaviour of ash processed under different carbonation conditions.

These efforts should be focussed on validating accelerated carbonation as a best demonstrable technology by determining the optimal processing conditions of MSWI ash with carbon dioxide gas and characterising carbonated ash performance during reuse and under ultimate disposal conditions.

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