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Characterization and treatment options of residues from waste-to-energy plants

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To my angel and my two princes:
my father, Nicola and Niccolò

Abstract

Bottom ash (BA) is the residue produced in greatest amount from incineration of municipal solid waste (MSW). Several countries allow the use of BA for civil engineering applications, as road construction, embankment, pavement, aggregate, filler for concrete, asphalt, or low-cost tiles. In these cases, leaching of heavy metals is a major issue and can limit the feasibility of these reuse options.

In order to comply with limits set by law for leaching of heavy metals, several options are available for treating MSW combustion residues: solidification, stabilization, vitrification, classification by granulometric size particles and ageing or weathering. The choice of the treatment depends on site specific conditions, utilization or disposal objectives and law requirements. When an ash treatment method must be chosen, much attention must be payed to investment and operating costs.

The main objective of this doctoral thesis was to investigate the effect of size separation and weathering as pre-treatments applied to different residues from waste incineration plants. The following materials were chosen for the experimental activities:

- BA from MSW grate furnace combustion plants;
- BA from wood waste grate furnace combustion plants;
- vitrified residues from refuse derived fuel (RDF) high-temperature gasification plants.

Size separation was applied to BA from two high temperature RDF gasification plants. These residues were analysed for the following parameters: grain size distribution, specific gravity, compaction behaviour, hydraulic conductivity, water content and chemical composition. Besides, leaching characteristics were also investigated by means of the EN 12457-2 batch leaching test, the TS 14429 Acid Neutralization Capacity (ANC) test and the Availability Test (NEN 7371). Results of the analytical investigations showed marked differences between the two investigated BA. In one case the levels of heavy metals were always below the Italian regulatory limits for either reuse or disposal as inert waste and a there was a uniform contaminant distribution above the different grain size classes. In the other case Cu,

Cr and Ni were above the limits set for reuse. Moreover, the finest fractions appeared to be more contaminated in Cu and Ni and a size separation pre-treatment could be considered as a viable solution to reduce their content in BA. On the other hand, Cr was more or less evenly distributed in all the grain size classes, making the size separation pre-treatment not effective for this metal.

As regards weathering treatment of BA from MSW and wood waste grate furnace combustion plants, the residues were analysed at different steps of treatment and characterized for their chemical and mineralogical composition, volume stability and both short term as well as long term leaching behaviour. Pb, Zn and Cu were the heavy metals to be released in greatest amount. After 12 weeks of treatment the concentration of leached Zn fell significantly in both cases, while for Pb it was possible to observe a concentration decrease only for biomass. Lead concentrations seemed to be independent from the BA pH and undersaturated with respect to lead hydroxide ($Pb(OH)_2$), anglesite ($PbSO_4$) and cerrusite ($PbCO_3$). Leaching of Cu was well described by complexation processes with dissolved organic carbon.

ANC test permitted to carry out analysis of the weathering process, with particular reference to mineralogical transformation and behaviour of heavy metals.

The treatment resulted to be effective to comply with law limits concerning volume stability.

As regards the effects of natural weathering on RDF high-temperature gasification residues, the study was conducted on a single BA sample and with reference to different grain size fractions. Significant results were obtained for the leaching of amphoteric elements such as Zn and Pb, while for oxyanion forming elements, such as Cr, it did not exert beneficial effects. Leaching of Cu appeared to be not affected by weathering. Cr and Cu resulted to be the most critical elements in view of recycling or disposal as inert waste.

Abstract

Le bottom ash (BA) rappresentano il residuo solido prodotto in maggior quantità dagli impianti di trattamento termico dei rifiuti. Molti paesi europei consentono il riutilizzo di questi materiali nell'industria dei materiali da costruzione, in quella siderurgica e nel settore di sottofondi stradali.

A causa del rischio legato al possibile rilascio di specie contaminanti, le scorie possono porre problemi una volta reimmesse nell'ambiente. Tali materiali, pertanto, prima di essere posti in discarica o proposti per un eventuale recupero, possono necessitare di un idoneo pretrattamento. I trattamenti più semplici e più comunemente utilizzati sono la separazione dimensionale, la rimozione dei metalli magnetici e non magnetici e la maturazione. Fra i trattamenti più avanzati ci sono, invece, i processi di stabilizzazione/solidificazione e quelli termici di vetrificazione, fusione e sinterizzazione. La scelta del trattamento dipende da condizioni sito-specifiche, dagli obiettivi di recupero e dai limiti normativi. In ogni caso, nella scelta del pre-trattamento è necessario porre particolare attenzione ai costi sia operativi che di investimento.

Il principale obiettivo della presente tesi di dottorato è stato quello di valutare l'effetto dei pre-trattamenti di separazione dimensionale e maturazione (o *weathering*) applicati a residui da processi di incenerimento di rifiuti. In particolare sono stati considerati i seguenti materiali:

- BA da impianti di incenerimento a griglia di RSU;
- BA da impianti di incenerimento a griglia di biomasse;
- Residui vetrificati da impianti di gassificazione ad alta temperatura di combustibile da rifiuti (RDF).

Il trattamento di separazione dimensionale è stato applicato a due campioni di BA provenienti da due diversi impianti di gassificazione di RDF ad alta temperatura. I residui sono stati caratterizzati con riferimento ai seguenti parametri: distribuzione granulometrica, peso specifico dei costituenti solidi, caratteristiche di compattazione, permeabilità, contenuto d'acqua e composizione chimica. Il comportamento a lisciviazione è stato valutato mediante il test di cessione EN 12457-2, il test per la determinazione della Capacità di Neutralizzazione Acida (ANC) secondo la metodica

TS 14429 ed il test di Availability (NEN 7371). I risultati della indagini analitiche hanno evidenziato delle marcate differenze fra i due materiali considerati. In un caso le concentrazioni dei metalli pesanti negli eluati sono sempre risultate inferiori rispetto ai limiti imposti dalla normativa per il recupero o il conferimento in discarica per rifiuti inerti ed i contaminanti sono risultati uniformemente distribuiti fra le differenti classi granulometriche. Per l'altro materiale analizzato, le concentrazioni di Cu, Cr e Ni sono risultate superiori rispetto ai limiti fissati per il recupero. Tuttavia, per lo stesso campione, i risultati sperimentali hanno evidenziato una maggiore concentrazione di Cu e Ni nelle frazioni più fini. Di conseguenza il pre-trattamento di separazione dimensionale potrebbe dimostrarsi efficiente nel ridurre il contenuto di tali metalli nel residuo. Dall'altra parte, invece, il Cr è risultato presente in maniera pressoché uniforme in tutte le classi granulometriche, rendendo quindi la separazione dimensionale non idonea per la sua rimozione.

Per quanto riguarda il trattamento di weathering di BA da impianti di incenerimento di RSU e biomasse, i residui sono stati analizzati a successivi steps di trattamento e caratterizzati in termini di composizione chimica e mineralogica, stabilità volumetrica e tendenza a lisciviazione sia a breve che a lungo termine. I metalli risultati più critici sono stati Pb, Zn e Cu. Dopo 12 settimane di trattamento, la concentrazione di Zn è diminuita in maniera significativa per tutti i materiali considerati, mentre per il Pb si è osservata una lieve diminuzione solo per le BA da biomasse. Le concentrazioni di Pb negli eluati si sono rivelate indipendenti dal pH ed inferiori rispetto alle concentrazioni di saturazione fissate da idrossido di piombo ($Pb(OH)_2$), anglesite ($PbSO_4$) e currusite ($PbCO_3$). Il comportamento a lisciviazione del Cu è risultato strettamente correlato a fenomeni di complessazione con il carbonio organico disciolto.

Il test ANC ha permesso di condurre una analisi maggiormente dettagliata del processo di weathering, con particolare riferimento alla correlazione fra trasformazioni di carattere mineralogico e comportamento a lisciviazione dei metalli pesanti.

Il trattamento, infine, si è dimostrato efficace nel garantire ai materiali una adeguata stabilità volumetrica.

Per quanto riguarda l'effetto del weathering applicato a residui da processi di

gassificazione ad alta temperatura di RDF, la ricerca è stata condotta su un singolo campione, facendo riferimento alle diverse classi granulometriche. Il trattamento si è dimostrato efficace nel ridurre la tendenza a lisciviazione dei metalli anfoteri quali Zn e Pb, mentre non ha avuto effetti benefici sul comportamento dei metalli che tendono a formare ossianioni, fra cui il Cr. La tendenza a lisciviazione del Cu non è apparsa influenzata dal processo di maturazione. Alla fine del trattamento Cu e Cr sono risultati i metalli più critici per il recupero o il conferimento in discarica per inerti del materiale oggetto di studio.

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Introduction: Aims and contents of this thesis

Today integrated waste management represents an increasing problem for both developed and emerging countries, particularly where the population density is high. After recovery of recyclable materials, most municipal solid waste (MSW) is currently landfilled. This contributes to related problems due to lack of available land, environment protection issues and health concerns.

Under the framework of integrated waste management, thermal treatment represents a valid option for reducing the amount of waste to be landfilled, at the same time allowing for waste hygienization. It allows a waste volume reduction which can reach up to 90%; but it also produces by-products (bottom and fly ashes) in amount of about 33 wt% of the incinerated waste. Bottom ash (BA) represents about 80% by weight of total solid waste generated in incineration facilities. It shows a complex mineralogical composition consisting, mainly, of silicates, oxides and carbonates, as well as secondary phases like amorphous glass phases, iron metals and feldspars and trace substances as metals, alloys, sulphates and salts.

BA is generally disposed in landfills, although several European Countries have developed regulations aimed at encouraging its utilization in construction applications rather than its final disposal. In Italy there is no specific legislation for BA reuse and valorisation; the only reuse option that is currently being adopted is its use as secondary raw material in cement production. However, in other EU countries (e.g. Germany, the Netherlands, France and Denmark), about 50% or more of stockpiled MSW incineration BA is used as secondary building material or for other similar purposes, in road sub-bases and the construction of embankments, wind and noise barriers and other civil engineering applications.

MSW incineration residues disposal in landfills, as well as its reuse as secondary building material, are strictly controlled, e.g. some countries do not landfill the ash unless it is properly treated. Costs related to bottom ash and fly ash treatment must be added to the entire process cost.

Solidification, stabilization, vitrification, classification by granulometric size particles and ageing or weathering are some of the currently available methods for treating MSW incineration residues.

In EU countries, mainly in Germany, the weathering of BA for estimated period of 1-3 months before its final disposal or its eventual reutilization is the most commonly employed method due to its low investment and operating costs.

Most of the high-temperature solids contained in incinerator BA are, in fact, metastable under atmospheric conditions because they are formed at high temperatures in the combustion chamber and then cooled rapidly via a quench tank. Therefore, under ambient conditions, and especially during the first three months of weathering, they undergo further mineralogical processes such as the hydrolysis of oxides of Ca, Al, Na, and K, dissolution/precipitation of hydroxides and salts of these cations, carbonation, and formation of clay-like minerals from glasses. Chemical and mineralogical changes caused by such processes greatly affect metal solubility as well as speciation.

Short term natural ageing on MSW and wood waste incinerator BA was investigated during a six months research period carried out at the Institute for Technical Chemistry – Thermal Waste Treatment in the Forschungszentrum Karlsruhe (since October 2009 KIT) (Germany). The aim of this study was to investigate the effect of a short-period natural weathering treatment on physical, mineralogical and chemical properties of BA. In particular, the samples were analysed at different steps of treatment (fresh, 4 weeks and 12 weeks aged) and characterized for their chemical and mineralogical composition, volume stability and both short as well as long term leaching behaviour of main elements and heavy metals.

Vitrification of BA is a treatment technique (mainly used in Japan) that gains some advantages over other treatment options; namely, it leads to a volume reduction, a destruction of >95% of dioxins (as toxicity equivalent, TEQ) and, compared to nontreated residues, molten MSW incinerator ashes have a much lower potential to mobilize metals. In particular, melting of BA at high temperature reduces the availability of Cr, Cu, Zn and Pb for leaching as the formation of glassy material decreases the surface area and entraps the metals within the amorphous glassy matrix. Hence, the utilization of vitrified BA is expected to decrease the environmental drawbacks. Vitrification, however, is a very energy consuming process due to the high temperatures required; therefore, related costs can be significant and impair its advantages. A promising alternative to the cost of vitrification is represented by new generation MSW incinerators, which provide energy by using waste as a fuel and where by-products are not subsequently vitrified because of the high temperatures involved during waste combustion, i.e., 1600°C.

The experimental study investigated the characteristics of BA from two high temperature RDF gasification plants.

Firstly, the behaviour of the different particle size fractions were evaluated, with the aim of assessing suitability to be reused. The materials were characterized for both technical and environmental parameters, with particular reference to leaching behaviour. Finally, the utilization of size separation as a pre-treatment was discussed.

Secondly, the effects of the application of short term natural weathering to RDF gasification BA were investigated, in particular paying attention to the relationship between pH values ad the leaching behaviour of the main trace elements. The study was still carried out with reference to different grain size classes.

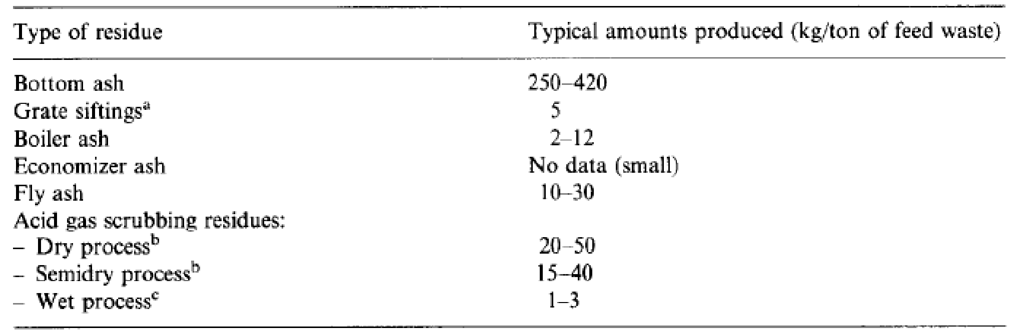
The present thesis is structured as follows: in Chapter 1 a general overview on MSW incineration residues and treatment options in view of disposal or recycling is presented. Chapter 2 presents the results of the first study carried out on BA from high temperature gasification plants. The results of the physical and chemical characterization and an assessment of size separation as a pre-treatment are reported. In chapter 3 the results of natural weathering of MSW and wood waste incineration residues are presented, whereas Chapter 4 reports the main findings of the application of the same treatment on vitrified residues. Finally, in Chapter 5 the most interesting results achieved in this study are summarized and perspectives on future developments are proposed.

Chapter 1: MSWI residues and treatment options

1.1 MSWI residues characteristics

From waste-to-energy conversion of municipal solid waste, in which high standards of emission control are reached, solid residues remain, including bottom ash (BA), fly ash (FA) and air pollution control (APC) residues that need to be dealt with in an environmentally acceptable manner (van der Sloot, 2001). In fact, as a result of the incineration process, different solid and liquid residual materials as well as gaseous effluents are generated and approximately one-fourth of the waste mass on a wet basis remains as solids. The volume of residues corresponds to one-tenth of the initial waste volume (Sabbas et al., 2003). Advanced air pollution control measures in incinerators shift constituents of concern from air emissions to solid residues, which potentially may lead to soil and water pollution. The evaluation of the environmental quality of such residues is necessary before decisions can be taken on the utilization, treatment or disposal of the residues (van der Sloot et al., 2001; Li et al., 2004).

The quality of the residues from waste-to-energy conversion is very diverse, as has been detailed in the International Ash Working Group’s (IAWG) book “Municipal Solid Waste Incinerator (MSWI) Residues”. The amount of each residue produced at an incinerator depends on several factors, such as feed waste composition, incinerator technology and operation and air pollution control system technology and operation (Hjelmar, 1996). Some typical amounts of MSWI residues produced are reported in Table 1.



Type of residue	Typical amounts produced (kg/ton of feed waste)
Bottom ash	250–420
Grate siftings[a]	5
Boiler ash	2–12
Economizer ash	No data (small)
Fly ash	10–30
Acid gas scrubbing residues:	
– Dry process[b]	20–50
– Semidry process[b]	15–40
– Wet process[c]	1–3

Table 1: Typical amounts of residues produced per metric ton of waste incinerated. Notes: [a]Only data from one incinerator; [b]including 10-30 kg fly ash; [c]Dry weight of sludge from wastewater treatment; the process also produces 0.3-0.5m^3 of treated wastewater containing 8-15 kg of calcium and sodium chloride. Fly ash is precollected separately (Hjelmar, 1996).

With reference to MSWI by grate combustion, typical residues are:

Bottom ash, which consists primarily of coarse non combustible materials and unburned organic matter collected at the outlet of the combustion chamber in a quenching/cooling tank (Sabbas et al., 2003).

BA consists mainly of silicates, oxides and carbonates. Secondary phases occurring are amorphous glass phases, several iron minerals and feldspars. Accessory and trace substances detected include metals, alloys as well as a great variety of sulphates (Pfrang-Stotz et al., 1997, Freyssinet et al., 2002).

The matrix elements of MSWI bottom ash are comparable in concentration with igneous rocks, the main components (>10g/kg) being O, Si, Ca, Al, Fe, 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), instead, are generally present in relatively low concentrations in BA and are rather concentrated in fly ash and air pollution control (APC) residues. The trace metal and soluble salt concentrations are approximately 10-100 times the average composition of the earth’s crust. In addition, residual organic components make up 1-2% of the MSWI bottom ash material (Johnson et al., 1995).

Mineralogical studies have found that MSWI bottom ash is composed of equal amounts of fine ash material and melted components, of which half have crystallized, small quantities of metallic components, ceramic and stones. The main crystalline phases of BA were found to be silicates (quartz, gehlenite, augite, etc.), sulphates (mainly anhydrite, ettringite and gypsum), carbonates (calcite, metal carbonates), to a lower degree metal oxides and hydroxides (magnetite, haematite, etc.) and chlorides (Kirby and Rimstidt, 1993; IAWG, 1995; Speiser et al., 2000).

Up to 20% of bottom ash has a particle size of > 10 cm, consisting of ferrous and non-ferrous metals, slags, and construction-type materials. The fraction < 10 cm is somewhat uniform with up to 10% fines <200mm. This latter fraction resembles well graded sand and gravel (Wiles et al., 1996). In Fig. 1 different granular fractions of BA are depicted.

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 (generally from 15 to 25%), depending on quenching procedures. With optimum moisture content of approximately 16%, the bottom ash can be compacted to proctor densities of 1600kg/m^3, resulting in hydraulic conductivity of 10^{-6}cm/s or less. Such hydraulic conductivities can play an important role in the management and utilization of these residues (Wiles, 1996).

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 (Costa, 2009).

0/6 mm fraction

6/12.5 mm fraction

12.5/20 mm fraction

Fig.1: Different granular fractions of MSWI bottom ash (Becquart et al., 2009).

Grate siftings are the fine material that drops through openings in the grate into the air plenums (Niessen, 2002). Grate siftings are usually combined with bottom ash, so that in most cases it is not possible to separate the two waste streams. Grate siftings comprise approximately 1%-3% by weight of the bottom ash. This fraction, however, contributes a significant fraction of the elemental Pb, Al, Cu and Zn to the bottom ash of mass burn systems (Wiles et al., 1996). The ranges of these elements in the grate siftings of mass burn systems have been reported as Pb (5600-34000 mg/kg), Al (38000-63000 mg/kg), Cu (2400-25000 mg/kg) and Zn (2450-5300 mg/kg). These metals are largely present in their elemental form and may enter into redox reactions, generating H_2 and causing swelling. Investigations have indicated that the grate siftings contain almost 50% of the lead in the residues considered available for leaching (Wiles, 1996).

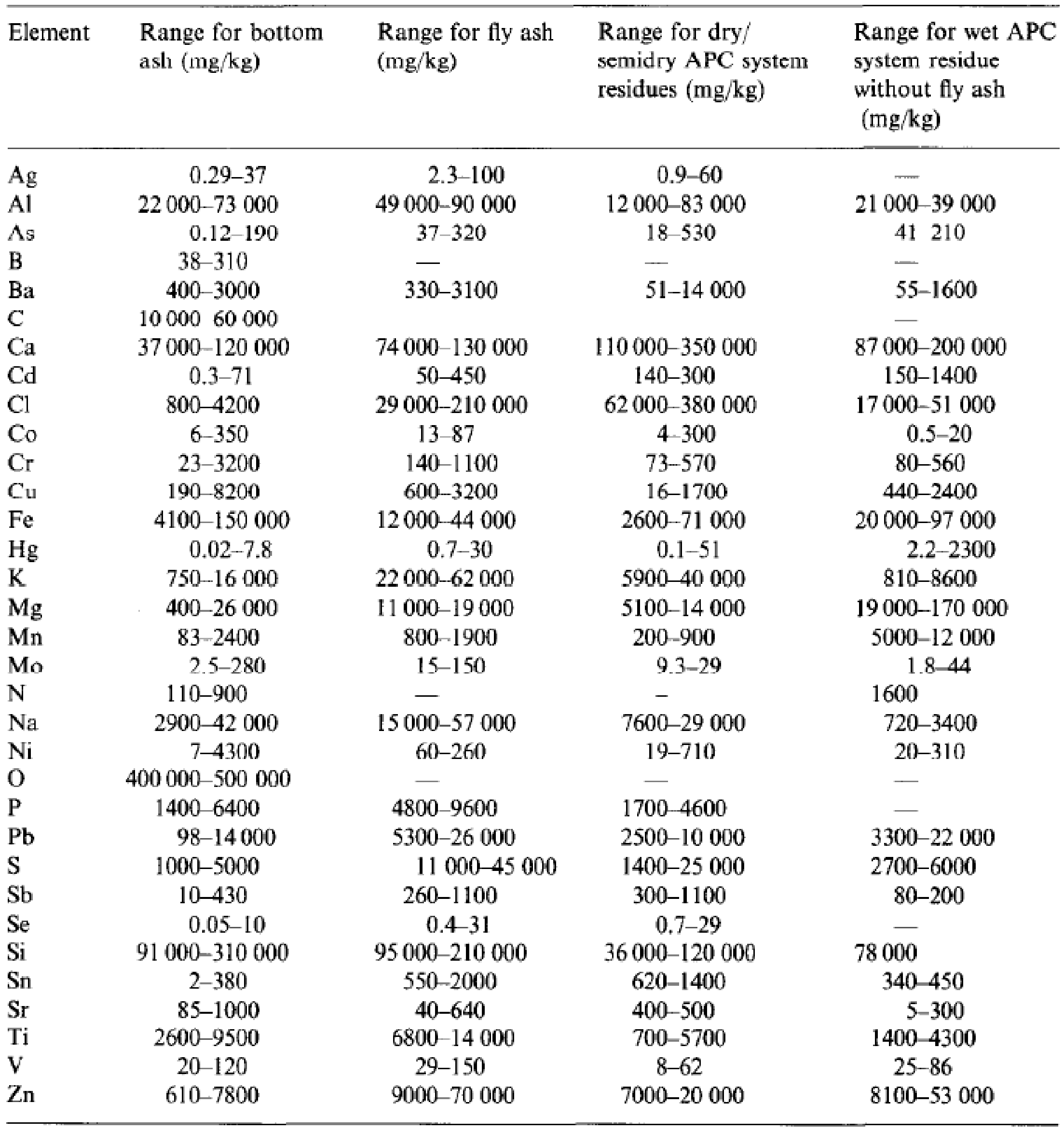
Boiler and economizer ash, which represent the coarse fraction of the particulate carried over by the flue gases from the combustion chamber and collected at the heat recovery section. This stream may constitute up to 10% by mass of the original waste on a wet basis (Sabbas et al., 2003).

Fly ash is the finely divided particles entrained in the gases that originate from waste combustion. They may be recovered separately from the gas stream by a combination of precipitators and cyclones, but are now more typically incorporated into the APC residues. The amount of fly ash produced by an MSW incinerator is in the order of 1-3% of the waste input mass on a wet basis (Sabbas et al., 2003; Li et al., 2004).

Fly ash from MSW incineration (MSWI) is a complex mixture of various minerals. Spherical particles are common in fly ash, associated with aggregates of polycrystalline, amorphous and glassy material (Wan etal., 2006). The spherical particles are composed of complex calcium, sodium and potassium aluminosilicates, whilst the associated amorphous and crystalline material is enriched in the more volatile heavy metals. In such a complex system, the leachability of heavy metals is complicated and confusing because of the difficulty of identifying the exact chemical species of the heavy metals (Wan et al., 2006).

Air Pollution Control (APC) residues, these are produced by dry and semi-dry scrubber systems that involve the injection of an alkaline powder or slurry to remove acid gases, particulate and flue gas condensation/reaction products. Fabric filters in baghouses are used after the scrubber systems to remove fine particulates (baghouse filter dust). APC residues also include the solid phase generated by wet scrubber systems (scrubber sludge). They are a mixture of fly ash, carbon and lime. APC residues are usually in the range of 2% to 5% of the original waste on a wet basis (Li et al., 2004).

Due to the volatilization and subsequent condensation as well as concentration phenomena acting during combustion, fly ash and APC residues bear high concentrations of heavy metals, salts as well as organic micro-pollutants (Sabbas et al., 2003).



Element	Range for bottom ash (mg/kg)	Range for fly ash (mg/kg)	Range for dry/semidry APC system residues (mg/kg)	Range for wet APC system residue without fly ash (mg/kg)
Ag	0.29–37	2.3–100	0.9–60	—
Al	22 000–73 000	49 000–90 000	12 000–83 000	21 000–39 000
As	0.12–190	37–320	18–530	41–210
B	38–310	—	—	—
Ba	400–3000	330–3100	51–14 000	55–1600
C	10 000–60 000			—
Ca	37 000–120 000	74 000–130 000	110 000–350 000	87 000–200 000
Cd	0.3–71	50–450	140–300	150–1400
Cl	800–4200	29 000–210 000	62 000–380 000	17 000–51 000
Co	6–350	13–87	4–300	0.5–20
Cr	23–3200	140–1100	73–570	80–560
Cu	190–8200	600–3200	16–1700	440–2400
Fe	4100–150 000	12 000–44 000	2600–71 000	20 000–97 000
Hg	0.02–7.8	0.7–30	0.1–51	2.2–2300
K	750–16 000	22 000–62 000	5900–40 000	810–8600
Mg	400–26 000	11 000–19 000	5100–14 000	19 000–170 000
Mn	83–2400	800–1900	200–900	5000–12 000
Mo	2.5–280	15–150	9.3–29	1.8–44
N	110–900	—	–	1600
Na	2900–42 000	15 000–57 000	7600–29 000	720–3400
Ni	7–4300	60–260	19–710	20–310
O	400 000–500 000	—	—	—
P	1400–6400	4800–9600	1700–4600	—
Pb	98–14 000	5300–26 000	2500–10 000	3300–22 000
S	1000–5000	11 000–45 000	1400–25 000	2700–6000
Sb	10–430	260–1100	300–1100	80–200
Se	0.05–10	0.4–31	0.7–29	—
Si	91 000–310 000	95 000–210 000	36 000–120 000	78 000
Sn	2–380	550–2000	620–1400	340–450
Sr	85–1000	40–640	400–500	5–300
Ti	2600–9500	6800–14 000	700–5700	1400–4300
V	20–120	29–150	8–62	25–86
Zn	610–7800	9000–70 000	7000–20 000	8100–53 000

Table 2: Elemental composition of bottom ash from all types of incinerators and fly ash, dry/semidry, and wet APC systems residues from mass burn incinerators (Wiles, 1996)

The major elemental constituents in APC residues are O, Si, Ca, Al, Cl, Na, K, S and Fe. Zn, Mg and Pb are often found in concentrations exceeding 10000 mg/kg, while Hg is usually found in concentrations below 10 mg/kg. Other trace elements (i.e., Cu, Sb, Cd, Sr, Ni, As, Ag, Co, V, Mo and Se) are present in concentrations below 1000 mg/kg (Wiles, 1996).

The total organic content (TOC) is generally below 10000 mg/kg for all types of APC residues. The pH for dry/semidry APC system residues typically exceeds 12, while wet scrubber sludges have pH values around 10.5. The excess lime in the dry/semidry system result in higher buffering capacities compared to electrostatic precipitator (ESP) fly ash and wet sludge (Wiles, 1996).

Table 2 provides the range of constituents found in bottom ash, fly ash and wet and dry APC system residues from many facilities. In the following chapters only bottom ash will be considered.

1.2 Chemical behaviour of bottom ash after disposal or reuse

When BA is landfilled or reused, it undergoes a number of processes, which will cause a set of modifications in the waste matrix at the micro-structural level. The main effect is the production of leachate, but also related phenomena such as gas production and temperature development must be taken into account (Sabbas et al., 2003).

In the following section the above mentioned effects will be discussed.

1.2.1 Leachate production

Since incineration residues are produced by high temperature processes, they are thermodynamically unstable under ambient conditions. This renders incineration residues highly reactive, especially under wet conditions. After discharging from the combustion chamber via a quench, bottom ash undergoes further mineralogical processes, affecting their physico-chemical characteristics as well as their leaching behaviour, as long as thermodynamic equilibrium conditions with the surrounding environment are attained. The specific environmental conditions influence and change the leaching behaviour and contaminant release for such materials during utilization or final land disposal (Pfrang-Stotz, 1997; Sabbas et al., 2003).

Management practices for incineration residues are very different in different jurisdictions. In Italy there is no specific legislation for waste incineration BA reuse and valorisation; the only reuse option that is currently being adopted is its use as secondary raw material in cement production (Rocca et al., 2009). Landfill disposal is the most commonly used method, however, several European Countries have recently developed regulations aimed at encouraging its utilization in construction applications. In North America, e.g., most of the MSWI residues currently produced are landfilled, while in Denmark, France, Germany and the Netherlands significant quantities of the BA from the MSWIs are actually been utilized for road construction and similar purposes (Hjelmar, 1996).

Different studies demonstrated the suitability of reusing these residues for civil engineering applications, as road construction, embankment, pavement, aggregate, filler for concrete, asphalt, or low-cost tiles (Forteza et al., 2004; Vegas et al., 2008; Ferraris et al., 2009; Rocca et al., 2009). This necessitates a judgement on the short and long-term environmental acceptability of such utilization scenarios. In addition to the environmental aspects, the new material will have to meet technical specifications similar to those of natural materials traditionally used for the same purposes (van der Sloot et al., 2001).

If utilization is not possible due to regulatory constraints or to other reasons (such as sufficient source of natural raw materials), these residues have to be disposed in an environmentally acceptable and economically sustainable way (Sabbas et al., 2003).

Whether BA is reused or landfilled, a fundamental knowledge of MSWI characteristics is essential. As reported by Rendek et al. (2007), several parameters have the potential to influence the physical and chemical nature of this residue:

- Municipal solid waste stream: MSW is a complex and very variable fuel. The feed stream to incineration plants varies from one plant to another. The main type of waste supplied to the municipal incineration plants is household waste, but various types of industrial waste streams can also be added, depending on the industrial activities in the surrounding area.
- Combustion technology: Many types of grates and combustion chambers have been designed and developed. Depending on combustion parameters, bottom ash still contains a fraction of residual organic matter and unburned particles. This organic carbon represents a potential source of microbial activity. Biodegradation processes and organic carbon leaching could then influence the long-term behaviour of bottom ash in a landfill or during reuse.
- Weathering reactions: Bottom ash is usually stored for several months before being reused and storage conditions are variable. During storage, the reactivity of bottom ash is significantly reduced by the carbonation of lime, which is locally accompanied by solidification of the bottom ash.

As leaching of contaminants from MSWI residues may occur during the temporary storage, treatment or reuse as well as during the final disposal of the material, the following aspects should be investigated: the leaching behaviour of contaminants, the environmental conditions that may occur in any of the above mentioned scenarios, as well as their variation over time. Thus, the following items should be considered:

- residue characteristics, in terms of physical and mechanical properties, particle size distribution, acid neutralization capacity, concentration of contaminants, availability of contaminants for leaching, leaching mechanisms, controlling factors, and their variation over time due to the weathering reactions;
- characteristics of the application site in terms of dimensions and material properties;
- hydrological conditions of the application site;
- mitigation effects due to leachate/soil interactions and to dilution.

The extent of the impact depends on the rate at which leaching occurs and on the type and concentration of the dissolved species. The following elements must be considered as hazardous contaminants potentially leachable from MSWI residues: As, Al, B, Ba, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Zn, Br^-, Cl^-, CN^-, F^-, NH_4^+, NO_3^-, NO_2^-, SO_4^{2-} (Sabbas et al., 2003).

The distinction between the short and the long-term leaching behaviour appears as a key factor. The long term leachability of the MSWI residues is the most important factor in the assessment of the potential hazards associated with landfilling or use in construction (Johnson et al., 1996). The commonly used laboratory leaching tests provide data on the potential leaching characteristics under specified conditions. Samples are ground or sieved and generally equilibrated for up to 24h under a variety of solid/liquid ratios (1-20) and pH values. Leach tests at low pH values (pH 3-5) are employed to determine leaching potential. Other tests are used to assess the influence of physical parameters such as permeability. However, mobilization of constituents from inorganic wastes into the leaching medium is the result of the interaction between chemical and physical factors, that cannot be discerned from a single leaching test. Hence, long-term behaviour can be predicted only on the basis of a synthesis information on leaching principles, leaching tests results, field measurements, simulation of mineral changes and speciation (Johnson et al., 1996;

Sabbas et al., 2003). Chemical factors include waste composition and mineralogy, temperature, pH, redox potential and the presence of ligands, while physical factors are represented by specific surface area, particle size, L/S ratio, porosity, hydraulic conductivity. Some physical factors also affect the percolation pattern (advection, diffusion) and hence the modes of contact between leachate and waste, which can be caused by leachate flowing around the waste, leachate flowing through the waste or by a combination of the two (Johnson et al., 1996, Sabbas et al., 2003).

The process and factors relevant to leaching can also vary depending on the contaminant under concern; in particular, for MSWI residues different groups of contaminants can be identified, including metal ions, amphoteric metals, oxyanionic species as well as salts, which display typical leaching patterns (Sabbas et al., 2003). The total content of such contaminants can even be considerably different for the various residues from waste incineration. However, the risk associated with the presence of potentially hazardous constituents in waste materials, with respect to their mobility and ecotoxicological significance, are determined by their leaching potential rather than their total content (Kosson et al., 2002; Dijkstra et al., 2006), so by their *availability for leaching*. It represents a function of the total content of contaminants in the waste itself.

When a fluid flows through a loosely packed granular waste material, the amount of contaminants released is dictated by solubility constraints, so that the leaching process is referred to as being solubility-controlled. In the case of very soluble mineral phases, which can completely dissolve as a result of contact with the fluid, leaching is generally defined as availability-controlled (Sabbas et al., 2003).

As far as the environmental impact assessment related to leaching of contaminants out of the MSWI residues is concerned, availability as opposed to the total concentration of contaminants in the solid matrix provides an estimation of the maximum amount of contaminants that in theory could be leached over a 1000- to 10000- year timeframe (with the exception of highly soluble salts, for which the maximum leachable amount can be attained within shorter periods, typically a couple of years) (Sabbas et al., 2003).

The geochemistry of MSWI residues is characterized by their basic properties. Leachate composition is the result of reaction between the various mineral phases in the waste and the leaching fluid, with calcium compounds playing a major role in controlling solution chemistry (Dijkstra et al., 2006; Meima and Comans, 1997a). Moreover, the interaction between heavy metals and cement minerals must also be taken into account (Johnson et al., 1996, Sabbas et al., 2003).

The leachability of strongly soluble species (e.g., alkali salts) is almost pH-independent, whereas for a number of contaminants a clear pH-dependence can be observed. The influence of pH on the leaching of contaminants is strongly related to the nature of the particular contaminant under concern as well as the mineral phase(s) in which this is bound (Sabbas et al., 2003).

Three main typical leaching behaviours for solubility-controlled leaching have been identified:

- Cation-forming species and non-amphoteric metal ions (e.g. Cd) see Fig.2a)
- Amphoteric metals (including Al, Pb, Zn) see Fig. 2b) and
- Oxyanion-forming elements (e.g. As, Cr, Mo, V, B, Sb), see Fig. 2c)

The concentration of cation-forming species and non-amphoteric metal ions displays fairly constant high values at $pH<4$, and decreases strongly up to pH 8 to 9, remaining approximately constant or slightly increasing for higher pH values. Amphoteric metals exhibit increased solubility under both strongly acidic and strongly alkaline conditions, resulting in a V-shaped solubility curve. For oxyanion-forming elements usually solubility decreases in alkaline ranges ($pH>10$).

In particular, interest in the leaching behaviour of As, Cr, Mo, Sb, Se, V and W has been growing over the last years because they are often found in relatively high concentrations in leachates compared to the cationic species due to their high solubility. Most of these elements are redox sensitive and some oxidation states can form oxyanions (negatively charged species containing O) in solution, forming a range of different species depending both on pH and redox potential (Cornelis et al., 2008).

Our interest concerns above all oxidised species (As^{V}, As^{III}, Cr^{VI}, Se^{IV}, Se^{VI}, Sb^{V}, Mo^{VI}, V^{V}, W^{VI}) because they are found more frequently in waste leachates, whereas elements occurring in their elemental state as well as many hydroxides and oxides formed by reduced species at high pH (Cr^{III}, Sb^{III}, V^{III}, V^{IV}) are only slightly soluble (Cornelis et al., 2008).

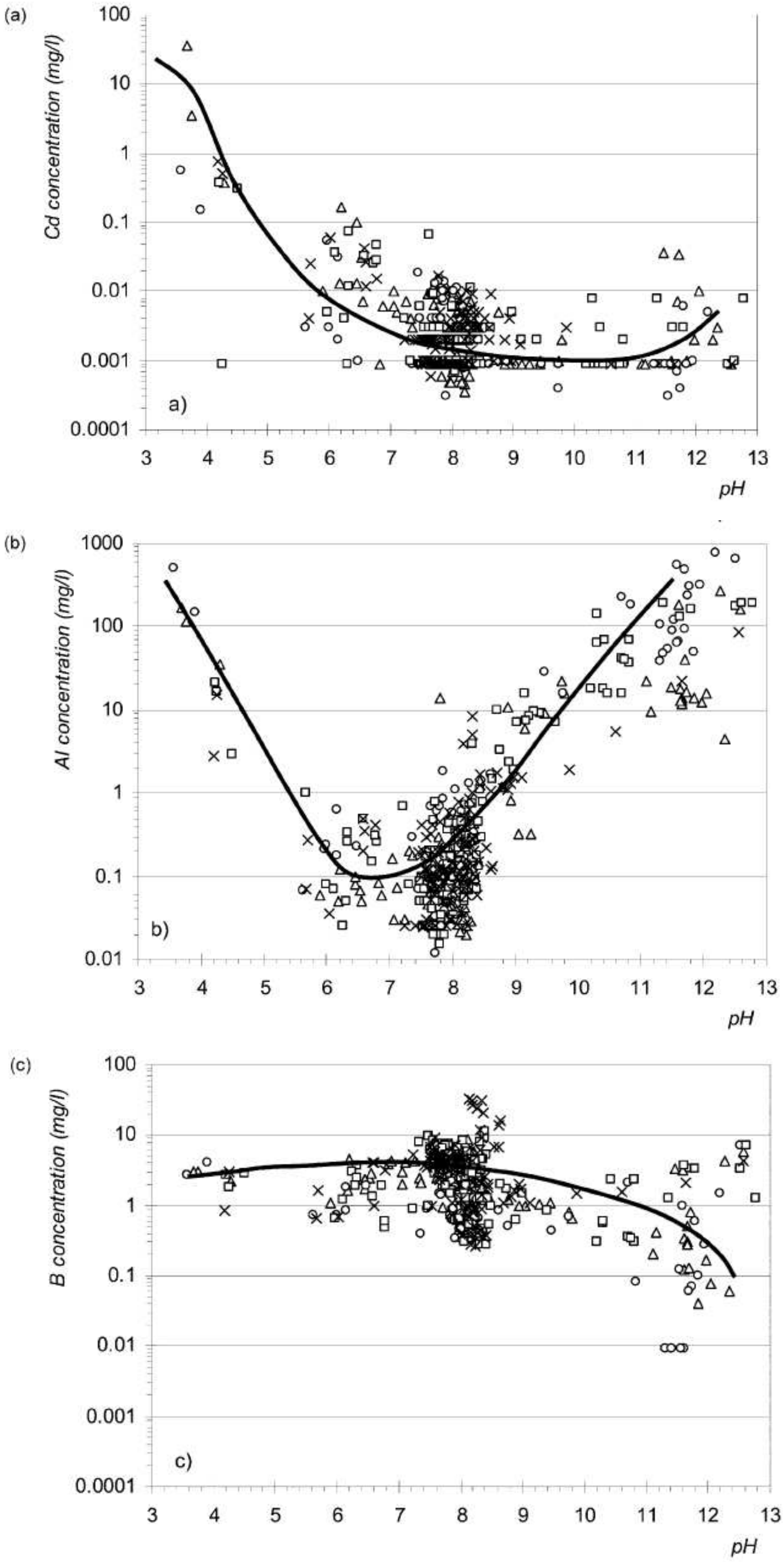


Fig. 2: Cd (a), Al (b) and B (c) concentration in eluates and leachate samples of fresh and aged samples (Sabbas et al., 2003).

While nearly all As and Sb is reduced at temperatures >500° to volatile gaseous states that escape from bottom ash, Cr^{III} and V^{V} are known to be highly involatile and reaction with metal oxides, without oxidation, lowers their volatility even further (Paoletti, 2002; Cornelis et al., 2008). Volatile V^{IV} compounds are oxidised at temperature > 370°C, whereas Cr^{III} is relatively resistant to oxidation (Paoletti, 2002). Only a very small amount is oxidised to metal chromates at temperature <850°C in the presence of metal oxides (Paoletti et al., 2002) or volatilised as hexavalent $CrO_2Cl_{2(g)}$ or $CrO_2(OH)^{2-}{}_{(g)}$ (Chen et al., 1998). Cr^{III} compounds, however, are sparingly soluble and hence, predominantly Cr^{VI} is found in bottom ash leachates (Kersten et al., 1998). Although they are sometimes found in waste, solid oxides of As^{V}, As^{III}, Cr^{VI}, Se^{IV}, Se^{VI}, Sb^{V}, Mo^{VI}, V^{V} and W^{VI} are generally not relevant in the context of leaching due to their relatively high solubility. Since Ca^{2+} will often be the most important multivalent cation in solution, particular attention should be given to Ca metalates but possibly also to Ba and Pb metalates because they have relatively low solubility products (Cornelis et al. 2008).

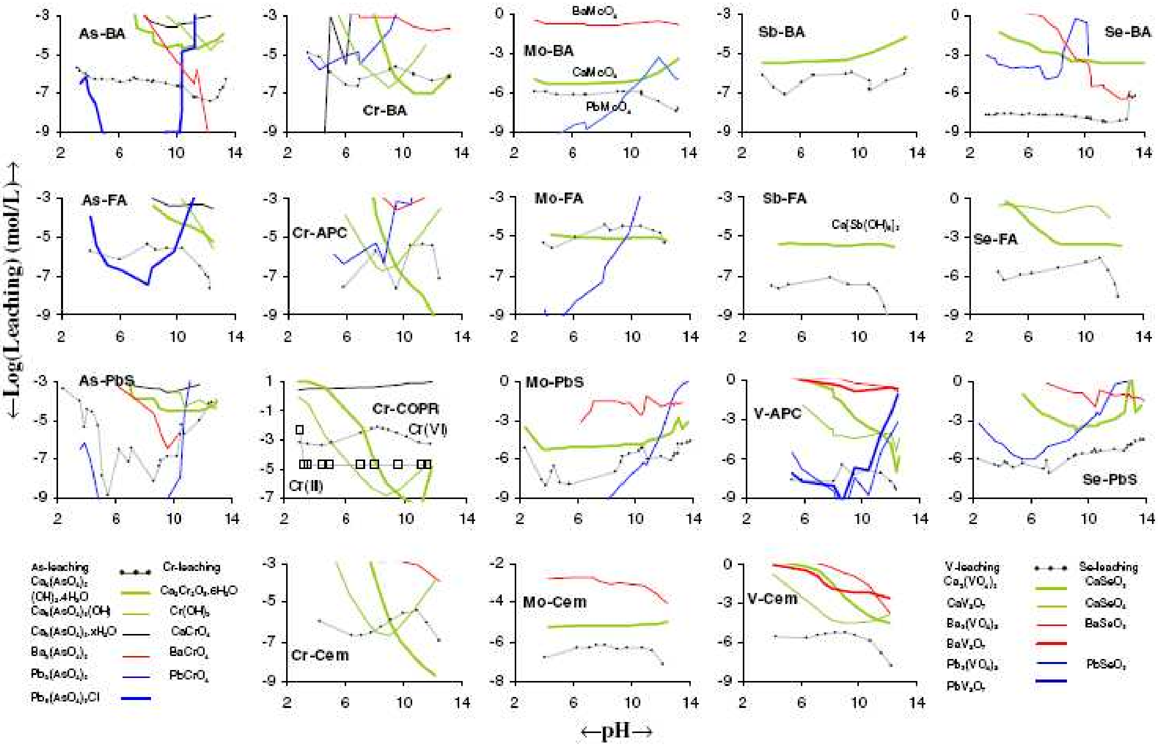


Fig. 3: pH-dependent leaching behaviour of oxyanion forming elements in MSWI BA, coal fly ash (FA), MSWI air pollution control residues (APC), Pb slag (PbS); Chromite ore processing residue (COPR) and OPC-mortar (Cornelis et al., 2008).

With reference to Fig. 3, although wastes with different characteristics are considered, the oxyanion forming elements still exhibit similarities in their general leaching trend. For example, a leaching minimum is found around pH 12 and sometimes also a second one at pH<6. It can be seen that most Ca and Ba metalates exhibit a minimum in leaching at alkaline pH whereas Pb metalates are more soluble in alkaline situations (Cornelis et al., 2008).

It should be emphasized that the shape of the actual solubility curve is the result of complex competing chemical equilibria where common ion effects can significantly alter the theoretical concentration calculated for pure aqueous solutions (Sabbas et al., 2003).

Depending on the specific leaching behaviour, critical pH regions can be identified where minimum and maximum solubility for the individual contaminants is attained. In the light of this, a matter of major concern is to predict the pH conditions which are likely to occur at the application site. These depend on the characteristics of the leaching fluid as well as on the properties of the waste. Probably the most relevant waste property affecting the pH of the leachate is represented by the acid or base neutralization capacity (ANC/BNC). The acid neutralizing capacity (and factors affecting this parameter) is thus one of the most important intrinsic properties of MSWI bottom ash with regard to trace metal mobility (Johnson et al., 1995; Johnson et al., 1996, Sabbas et al., 2003).

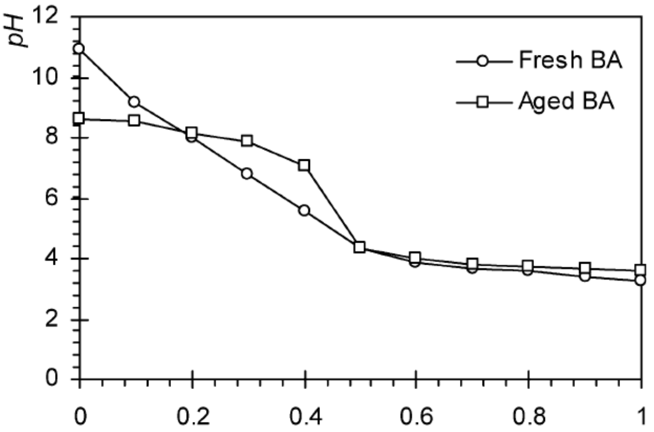


Fig.4: Acid neutralization capacity of MSWI bottom ash (Polettini et al., 2001).

ANC and BNC are measures of the ability of a system to neutralize the influence of acids or bases. In the case of MSWI residues, which are most often basic in their nature, alkalinity of the material is the relevant parameter, so that ANC is the appropriate measure of neutralization capacity (Sabbas et al., 2003).

The ANC test is a leaching procedure that is able to provide informations on the buffering capacity of a given material, its phase composition, as well as its leaching behaviour under different environmental conditions. In particular, the ANC test allows the resistance to acidification to be investigated and the presence of solid phases that are stable to be determined (Giampaolo et al., 2002). The buffering capacity of the material affects the evolution of the pH of the leachate over time, thus allowing the expected pH range for the application site to be estimated. Fig. 4 depicts the ANC of two samples of BA from Italian municipal solid waste incinerators.

In the case of alkaline MSWI residues, the reduction in the buffering capacity of the material over time is related to the depletion of alkalinity, which occurs as a consequence of progressive leaching. At the time of disposal, MSWI residues will display their maximum alkalinity level. The level will decrease as the material comes into contact with the leachate and dissolved alkalinity is removed from the system by the leachate. As a consequence, the residual alkalinity at any time will depend on the initial alkalinity of the material, the dissolution of alkalinity at various pH values in the leaching scenarios and the infiltration through the application site (Sabbas et al., 2003).

On the other hand, dissolved alkalinity depends on the solubility of a number of minerals ($Ca(OH)_2$, $CaCO_3$, etc.) and thus on the leaching system pH. The pH in turn is dependent on the system's ability to buffer the infiltrating leachate, i.e. on the amount of residual alkalinity in the system itself (Sabbas et al, 2003).

Acid neutralization capacity allows for the evaluation of the environmental behaviour of MSWI residues, in that ANC data can be transformed in order to estimate the time required for the pH to drop from the "inherent" pH of the material to critical values for contaminants release. Such time-related information can be gathered on the basis of the size of the application site, hydrological and hydrogeological conditions, leachate composition, and leachate flow towards soils and groundwater (Sabbas et al., 2003).

Other than pH, the amount of leachate that comes into contact with a given amount of waste, usually expressed through the so-called liquid-to-solid (L/S) ratio, also affects the leaching behaviour, especially in the case of solubility-controlled leaching. The L/S ratio is the result of climatic conditions, hydrology and hydrogeology of the application site, as well as the physical characteristics of the waste material (Sabbas et al., 2003).

Solubility controlled leaching is characterized by an approximately linear dependence of cumulative release on the L/S ratio. In some cases the linear trend of cumulative release of a given element as a function of L/S can be altered by the presence of other species. Delayed release is observed when a sparingly soluble phase controlling solubility is present and is depleted after a relatively short period (Sabbas et al., 2003).

On the other hand, for availability controlled leaching the amount of contaminants released into the solution is at its maximum level due to the high contaminants solubility and is not dependent on solution pH. At a given L/S ratio, the transition from solubility-controlled to availability-controlled leaching is evidenced by a constant concentration in solution with decreasing pH. Availability-controlled leaching results in rapid washout of the soluble constituents at low L/S ratios, so that the available amount often is attained at L/S values of 1 to 2; for higher L/S ratios, the cumulative release remains at this maximum (Sabbas et al., 2003).

From V and Mo leachability as a function of pH and as a function of contact time, further conclusions can be drawn with respect to mechanism of release, which in turn can be used to guide activities to improve ash quality and in assessing short- and long-term environmental impact (Fig.5). Mo is leached as molybdate (oxyanion) and its mobile fraction is almost completely washed out within L/S=2 l/kg. Molybdenum is therefore an example of availability controlled leaching. When the percolation test data are plotted in the pH dependence graph (test carried out at L/S=10 l/kg) the cumulative leached amounts approach the pH stat curve (determined at L/S=10 l/kg) at the relevant pH from L/S=2 l/kg onwards. Obviously, when concentration data from the column test at low L/S are plotted in comparison to the pH dependence curve, greater concentrations are observed from the column test. However, this is also relevant information, as it will indicate what concentration may be expected in leachate in the short-term or even long-term, depending on the level of infiltration (van der Sloot et al., 2001)

In the case of V, solubility controls release, which is reflected by the horizontal line in the plot of concentration in percolate versus L/S and the slope of about 1 (dotted line in the middle figure in Fig. 5) in the cumulative release versus L/S curve (van der Sloot et al., 2001).

Irrespective of the mechanism controlling leaching, additional factors, including the presence of sorbing/complexing agents, redox reactions and the occurrence of processes causing mineralogical changes over time (e.g. due to ageing/weathering) can also affect the extent of contaminant release, as qualitatively illustrated in Fig. 6.

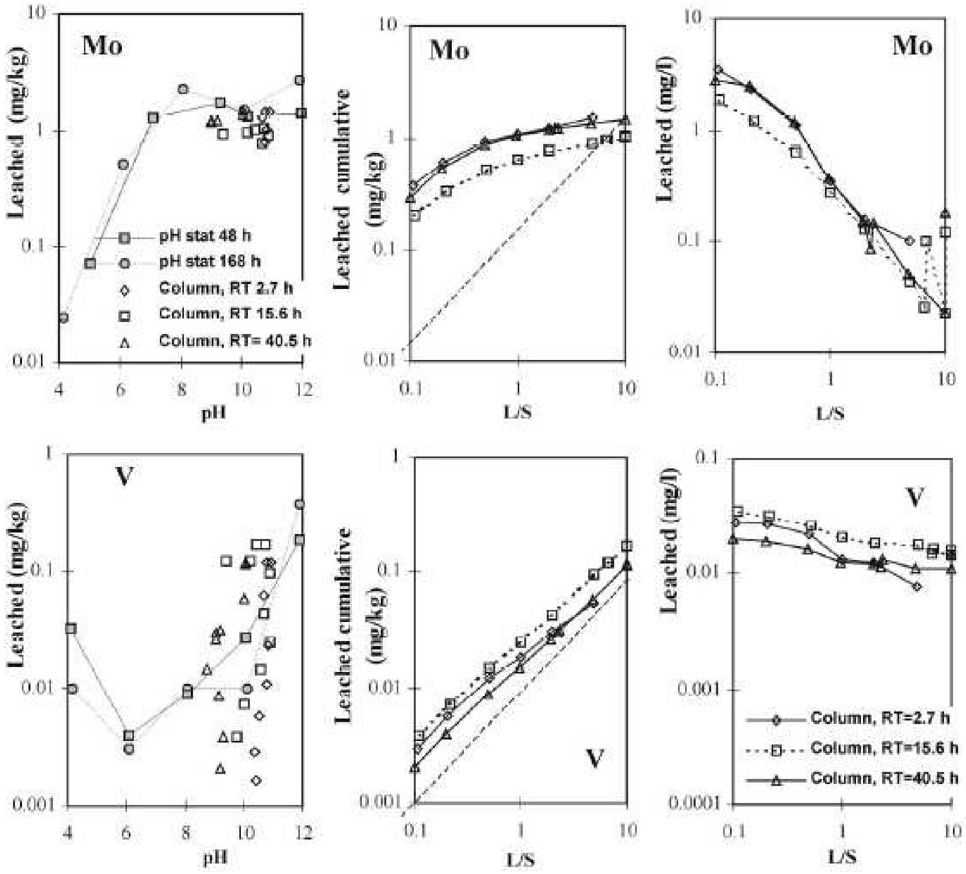


Fig.5: Leaching of V and Mo from MSWI bottom ash in a pH dependence test (left) and in percolation test (middle: cumulative release and right: eluate concentrations). Dotted line in middle graph points at solubility control (van der Sloot et al., 2001).

By the formation of complexes total metal ion concentrations can be enhanced by orders of magnitude. The effect can be quantified if all complexes are known. This means that anions such as Cl^- , SO_4^{2-}, CO_3^{2-}, HCO_3^-, OH^- and organic ligands have to be known in order to determine heavy metals cation concentrations (Johnson et al., 1995).

Mechanisms that limit solubility are associated with the solid phase. These include surface adsorption, cation exchange and incorporation into solid phases as solid solution. Quantification of these processes can only be determined by a knowledge of the solid phase. The concentration of available sorption sites, the cation exchange capacity or the type and composition of solid solutions have to be known if the influence of the heavy metals concentration is to be determined. Only the precipitation of pure solid phases is independent of solid phase composition. In the case of heavy metals cations, hydroxides and carbonates are the most commonly assumed solid phases. Though other phases may be thermodynamically more stable, kinetics factors involved in the precipitation also play an important role (Johnson et al., 1995).

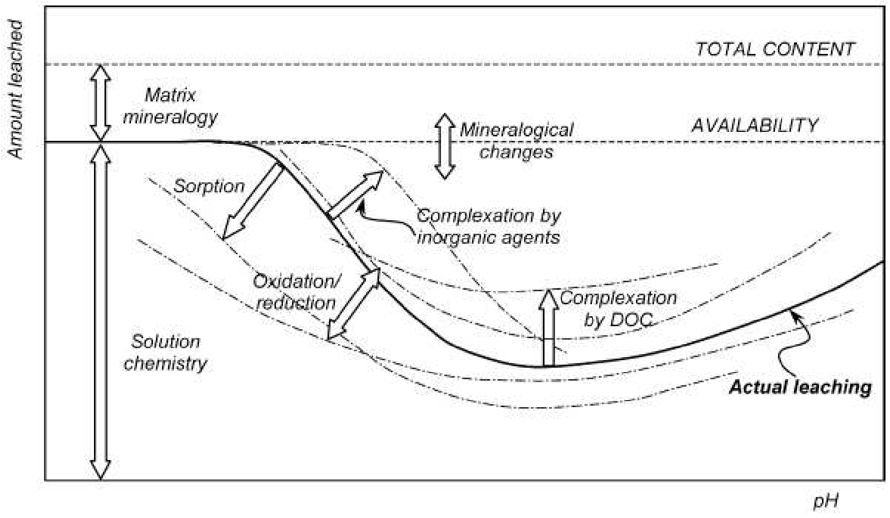


Fig.6: Influence of different processes on contaminant solubility as a function of pH (Sabbas et al., 2003).

Among the processes capable of altering the leaching behaviour of the material, sorption includes different mechanisms of adsorption, ion exchange, surface complexation and electrostatic attraction of ions at the surface. During weathering of less stable phases, new minerals with high surface area are formed. For instance, oxidation of iron in MSWI bottom ash leads to the formation of iron oxides, goethite

(FeOOH) and hydrous ferric hydroxide $[Fe(OH)_3]_n$, (often termed HFO). The resulting finely grained phases are able to sorb heavy metals, including Pb, Cd, Zn, Ni, Cr (III) and Cu, as well as Mo. Similar sorptive properties are also displayed by other mineral phases, including aluminium (hydr)oxides and amorphous aluminosilicates (Sabbas et al., 2003).

In the case of HFO, the general surface complexation reaction describing sorption of divalent cations can be simplified as:

$$\equiv Fe - OH^0 + Me^{2+} \Leftrightarrow \ \equiv Fe - OMe^{+} + H^{+}$$

where the symbol ≡ indicates bonds at the surface and $Fe\text{-}OH^0$ represents $[Fe(OH)_3]_n$ (Sabbas et al., 2003).

As well as established in literature, oxyanion surface adsorption complexation with Fe oxides is very important (Cornelis et al., 2008). HFO and amorphous Al oxides are ubiquitous in many alkaline wastes (Meima and Comans, 1997a; Freyssinet et al., 2002; Piantone et al., 2004). They usually are more important in the context of adsorption than crystalline oxides due to their much higher specific surface area.

During weathering, freshly precipitated HFO are, however, progressively transformed into crystalline oxides (Meima and Comans, 1997a), which reduces their adsorptive capability (Cornelis et al., 2008). Most oxyanions can form inner-sphere complexes with Fe oxides surfaces. Adsorption of oxyanions at alkaline pH modelled according to the diffusive layer approach is shown in Fig. 7. The strength of adsorption varies and hence also the pH at which oxyanions are desorbed from HFO surfaces (Cornelis et al., 2008).

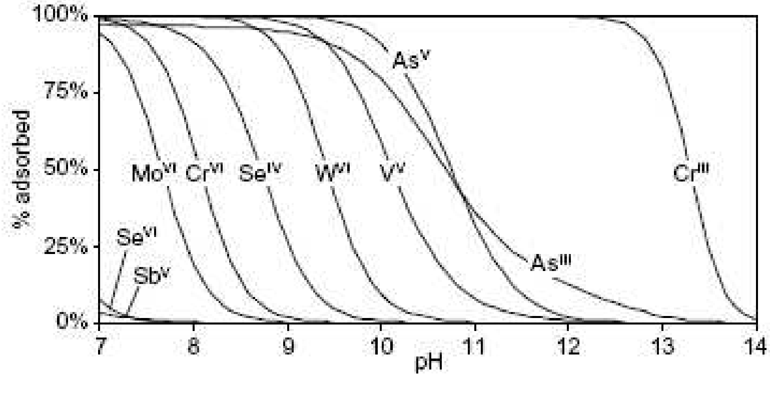


Fig.7: Modelling of adsorption of oxyanions on hydrous ferric oxides (Cornelis et al., 2008).

From Fig. 7 it is possible to observe that in alkaline wastes with pH>12, adsorption is probably only significant in the case of As^{III}, Cr^{III} and Sb^{III} and oxyanion leachability is reduced below pure-phase saturation by adsorption or solid solution formation with other abundant minerals in alkaline wastes. During weathering, however, the leachate pH can be lowered to as low as 8. At that pH, adsorption by Fe oxides is also relevant for Sb^{V} and Mo^{VI} and probably also for As^{V}, Cr^{VI}, Se^{IV}, V^{V} and W^{VI} oxyanions (Cornelis et al., 2008).

In spite of their abundance, adsorption to amorphous Al oxides is much less considered than to HFO. Amorphous Al oxides are, however, much less prone to mineral transformations and may therefore control oxyanion leaching in weathered residues (Meima and Comans, 1997a).

The presence of complexing agents can also significantly alter the extent of contaminant leaching from MSWI residues. Complexing agents can be either organic or inorganic in their nature; dissolved organic carbon (DOC) and chloride are the main complexing agents of concern for such materials. DOC has been extensively shown to be responsible for increasing copper release from predominantly inorganic waste forms. Model predictions for copper leaching were strongly determined by the complexation of this metal with dissolved humic and fulvic acids, the major reactive components of dissolved organic carbon in MSWI bottom ash leachates (Meima and Comans, 1999; Meima et al., 2002; Polettini and Pomi, 2004; Dijkstra et al., 2006; Arickx et al., 2009).

Oxidation/reduction reactions can also play a role in determining the release of contaminants from MSWI residues. Leaching of contaminants from waste incineration residues can be affected by the redox conditions according to two main mechanisms. One mechanism relies on the different solubility and toxicity of the contaminants under concern for MSWI residues depending on their oxidation state. These issues influence both the strength of the leachate and the related potential environmental impact (Sabbas et al., 2003). For example, it is well known that in an alkaline environment Cr(III) may be rapidly oxidized by atmospheric oxygen to Cr(VI), which is much more toxic and mobile than Cr(III). However, for Cr(III) to be oxidized to Cr(VI), high values of the redox potential are required (Sabbas et al., 2003; Cornelis et al., 2008).

The second mechanism through which the redox conditions affect leaching is related to the fact that the stability of the mineral phases capable of immobilizing metal ions through precipitation and/or sorption phenomena is dependent on the oxidation/reduction potential. Thus, Fe(III) and Mn(VI) (hydr)oxides can be transformed into more soluble forms of Fe(II) and Mn(II) under moderately reducing conditions. Under severely reducing conditions, S(VI) is reduced to elemental sulphur and sulphide, resulting in the precipitation of metal sulfides, which are among the less soluble metal forms (Sabbas et al., 2003).

The above mentioned mechanisms can lead to either synergistic or antagonistic interactions, so that the influence of redox processes on leaching may result in either mobilization or demobilization of contaminants (Sabbas et al., 2003).

For bottom ash monofills, the presence of unburned organic material and H_2 generally leads to reducing conditions; in such cases, the leaching behaviour of contaminants is the result of, on the one hand, complexation by DOC and, on the other hand, precipitation of less soluble species, including for example insoluble sulfides (Sabbas et al., 2003).

1.2.2 Gas production

MSWI residues in landfill sites can cause gas generation of a biotic or abiotic nature. The low biodegradable organic carbon content of MSWI residues generally leads to the production of biogas amounts significantly lower if compared to MSW landfill gas. Abiotic gas, instead, is produced by chemical oxidation, in the presence of water, of elemental metals, including Al, Fe and Cu (Sabbas et al., 2003).

The aspect of gas production has been considered in literature, above all because of swelling phenomena when ashes are used for cement-based products (Aubert et al., 2004; Pera et al., 1997).

Aluminium is a major constituent of bottom ash and, due to its high solubility at pH>9.5 and to its lower redox potential if compared to other elements, it is regarded as the main element responsible for abiotic gas production. Moreover, a significant fraction of Al in MSWI residues is in its elemental form, which can undergo the following redox reactions, leading to hydrogen gas generation:

$$2Al^0 + 3H_2O \rightarrow Al_2O_3 + H_2$$

$$Al^0 + 2H_2O \rightarrow AlOOH + 1.5H_2$$

$$Al^0 + 3H_2O \rightarrow Al(OH)_3 + 1.5H_2$$

However, the chemistry of aluminium corrosion is not completely understood at present, due to the variability of local conditions throughout the landfill mass (Sabbas et al., 2003).

Mizutani et al. (2000) evidenced that abiotic gas production is almost complete after several months, so hydrogen generation can be considered a short-term process. However, even though no specific studies have been carried out, some experimental data suggest that hydrogen gas production can also evolve over a longer term (Sabbas et al., 2003).

Delayed hydrogen production can be due to different reasons:

- isolated aluminium particles in MSWI residues are generally surrounded by a reaction rim of $Al(OH)_3$ and additionally by hydrocalumite ($Ca_2Al(OH)_6Cl\cdot 2H_2O$) and ettringite ($[Ca_3Al(OH)_6]_2(SO_4)_3\cdot 26H_2O$). These coatings or by products may result in the retardation of hydrogen production. However, such rims can dissolve, leading to a permanent release of hydrogen.
- a significant number of ash particles are enclosed in glassy phases formed during incineration, which act as a barrier against the reaction between water and aluminium.

However, due to their alkaline nature, such glassy phases can be altered, so aluminium particle will come into contact with the hydration water (Sabbas et al., 2003).

1.2.3 Temperature development

MSWI residues storage is affected by heat generation as a result of different exothermic reactions, such as hydration of alkaline and alkaline earth oxides, corrosion of metals and carbonation of portlandite. These reactions can cause a temperature increase up to 90°C in MSWI residue landfills (Sabbas et al., 2003). The main effects of this temperature enhancement are:

- acceleration of weathering/hydration reactions as long as the material in the landfill is wet or humid;

- over a long term, formation of salt rims as a consequence of drying;
- modification of precipitation/dissolution and complexation equilibria.

Moreover, temperature increase may lead to evaporation of some dissolved gaseous compounds (CO_2, O_2) from the leachate and as a consequence may exert an effect on the redox potential and the concentration of complexing agents (Sabbas et al., 2003).

1.3 MSWI bottom ash pre-treatment options

This chapter will focus on the various mitigating measures aimed at reducing the potential environmental impacts from incineration residues reuse or disposal. MSWI BA, in fact, does not always comply with regulatory criteria for utilization. This implies that treatment prior to utilization may be required. A commonly applied method to stabilize material properties is a minimum sample storage period of several weeks up to a few months to age the material. However, this treatment may not be sufficient and additional treatment to remove critical components, e.g. through washing of salts, Cu and Mo may prove necessary (van der Sloot et al., 2001).

Based on the treatment principles, the pre-treatment options can be further grouped into three broad categories including:

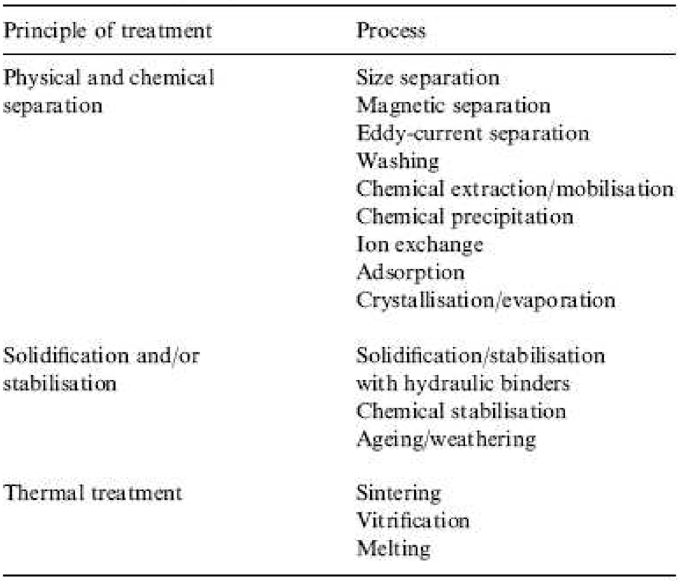
- physical or chemical separation processes;
- solidification and/or stabilization processes, and
- thermal treatments.

As asserted by Sabbas et al. (2003), in general it may be stated that the basic principles of the measures to mitigate the environmental impact of incineration residues are based on variations in either (a) the total content, (b) the availability for leaching or (c) the release rate of contaminants into the environment (Fig. 8); combinations of one or more of these three mechanisms are also possible.

For instance, washing pre-treatments aimed at removing e.g. readily soluble salts act according to mechanism (a), so that the availability for leaching is reduced as a consequence of the reduction in total content. Stabilization pretreatment modify the release rate of contaminants [mechanism (c)] and may also reduce the availability for leaching when chemical immobilization mechanisms are involved [mechanism (b)].

It is important to stress that when selecting the proper treatment method(s) for a given incineration residue, both its short- and long-term environmental behaviour under the expected conditions must be considered carefully. It should also be emphasized that most of the available treatments generate a number of waste streams and are also responsible for raw material and energy consumption. Thus, the technical, environmental and economic applicability of any treatment option should be judged on the basis of an appropriate evaluation of the overall mass and energy balances under a life-cycle assessment framework (Sabbas et al., 2003).

Table 3 reports the various treatment options applicable to waste incineration residues prior to their reuse or final disposal according to the classification discussed above. The most common treatment processes will be dealt with in the following paragraphs.



Principle of treatment	Process
Physical and chemical separation	Size separation
	Magnetic separation
	Eddy-current separation
	Washing
	Chemical extraction/mobilisation
	Chemical precipitation
	Ion exchange
	Adsorption
	Crystallisation/evaporation
Solidification and/or stabilisation	Solidification/stabilisation with hydraulic binders
	Chemical stabilisation
	Ageing/weathering
Thermal treatment	Sintering
	Vitrification
	Melting

Table 3: Main options for treatment of incineration residues prior to reuse or final disposal (Sabbas et al., 2003).

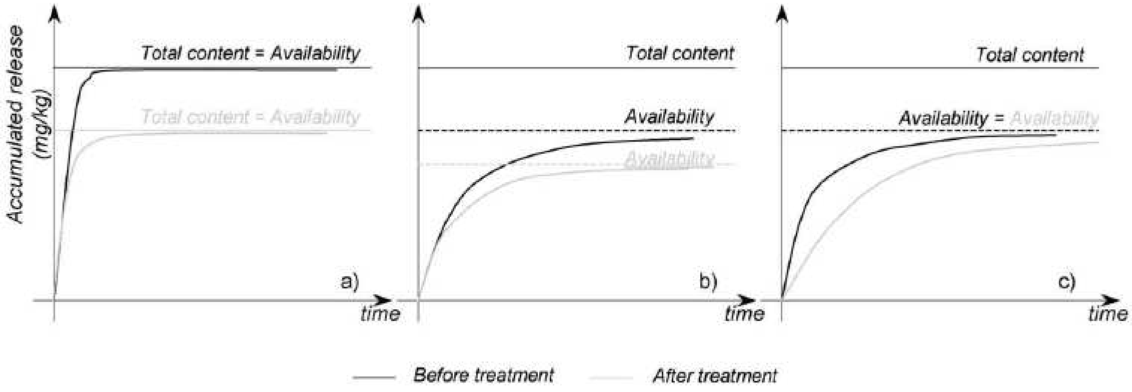


Fig. 8: Principles of mitigating measures in respect to total content, availability and release rate (Sabbas et al., 2003).

1.3.1 Physical and chemical separation

The aims of the mechanical processing are the recycling of metals and the production of a building material that complies with the structural engineering and environmental relevant requirements for the specific field of application. The mechanical processing methods are combined of several components, which are used principally for the production of defined particle size classes and the separation of ferrous and non ferrous metals as well as unburned residues.

The choice of the used components and the order in the method processing depends mainly on the quality of the original material and the requirements for the specific fields of application (e.g. depositing, using as building material). Mixing plants with less complex process technology separate only the ferrous metals, to make a storing on deposits possible. Mixing plants with a more complex process technology are able to produce a material, that can be used in building industry. In modern plants a washing process for MSWI bottom ash can be installed in addition to the mechanical processing.

There are three different methods of operating, which are differentiated by the place of the mixing plant an the available storage capacity for the MSWI bottom ash:

- Parallel operation for the MSW incinerator plant and the mixing plant for MSWI bottom ash with interim storage of the MSWI raw BA;
- Parallel operation for the MSW incinerator plant and the mixing plant for MSWI bottom ash without interim storage of the MSWI raw BA;
- Different times of operation for the MSW incinerator plant and the mixing plant for MSWI bottom ash with interim storage of the MSWI bottom ash.

The third method is the most applied because with different times of operation for the MSW incinerator plant and the mixing plant it is possible to work with only one shift and the costs for operation stuff can thus be reduced.

Another advantage is deduced from the natural drainage of the MSWI bottom ash during the interim storage because a minor moisture content has a positive effect on the following processes (screening, metal separation).

- ***Particle size separation***

Screening or separation of ashes into oversized and undersized fractions can be beneficial and in some cases necessary for utilization purposes (Wiles, 1996).

Particle size-based separation is generally carried out for two main purposes. One aim is accomplished through isolating the fraction(s) of the material (usually the finest fraction), which is more concentrated in contaminants (Stagemann et al., 1995; Chimenos et al., 1998; Chimenos et al., 2003), thus reducing the environmental impact of the residual stream. In this case, selecting the appropriate cut size for separation is of crucial importance in order to reduce effectively the leachability of the contaminants in question. One major drawback to this kind of separation is that for bottom ash the finer fraction usually constitutes a considerable portion of the total mass o f the material (the percentage passing at the 2mm sieve is in the order of 30% by weight) (Sabbas et al., 2003).

The second aim of particle size separation is to produce a material where the engineering properties, such as particle size gradation and hydraulic conductivity, are more suitable for subsequent utilization. Yet fine material can potentially create problems in bottom ash reuse, in that it is highly sorptive for water, asphaltic cement and Portland cement. For instance, when MSWI bottom ash is to be reused as a coarse aggregate in asphalt or concrete mixtures, a screening pre-treatment to remove the 1- or 2-mm undersize fraction and the 40-mm oversize fraction is commonly applied. This has the additional benefit of reducing Cd, Cr, Cu and possibly sulphates leachability from the material (Sabbas et al., 2003).

- ***Magnetic and eddy current separation***

According to Reijnders (2005), BA from municipal incinerators tends to contain significant amounts of iron and non-ferrous metals such as Ag, Cu, Pb, Sn and Zn and small pieces of metal. This can be separated from the rest of the ash by eddy current and magnetic techniques in a profitable way.

The quality of ferrous and non-ferrous metals in bottom ash is highly dependent on the effectiveness of the source separation programs in a given region, or on the presence of automated magnetic and eddy-current source separators used in the production of MSWI bottom ashes. MSWI bottom ashes from incinerator facilities can contain 7-10% ferrous scrap and approximately 1-2% nonferrous metals. In case of BA from RDF combustion facilities may be less due to more extensive processing of the MSW prior to combustion (Wiles, 1996).

The economics of recovery these scrap materials is in turn dependent on the fluctuating market for scrap steel, and ultimately the demand for finished steel. Normally, primary scrap must be de-tinned and decontaminated of organic material in order to concentrate the iron inventory prior to use. Ferrous metals processes through an incinerator are effectively de-tinned and relatively clean of organic contaminants, and thus are generally highly sought after as recyclable ferrous scrap.

In the case of BA utilization, the removal of ferrous and nonferrous metals must be completed prior to utilization. Metals like Al, Fe and Zn are susceptible to corrosion attack in an alkaline media, resulting in the generation of hydrogen gas and corrosion products, which may cause swelling (especially because of metallic Al).

- ***Washing and chemical extraction***

Among the chemical separation treatments, washing with water is one of the simpler processes for removing highly water-soluble constituents from waste incineration residues. The soluble constituents, typically removed as a consequence of washing, are mainly represented by chloride and alkali ions. Conversely, due to the highly alkaline nature of incineration residues, the effectiveness of washing on trace metals removal has proved to be relatively low, in that they mostly form sparingly soluble compounds under alkaline conditions (Sabbas et al., 2003).

Bottom ash is commonly quenched when exiting the combustion chamber; however, in most cases the relatively low L/S ratios and the residence time in the quenching tank prevent thermodynamic equilibrium of the dissolution process from being attained. Thus, bottom ash after quenching still is typically characterized by a residual content of soluble components, which can be further extracted through a washing treatment. Due to the above-mentioned reasons, washing of bottom ash is a simple measure that could easily be combined with the quenching stage at the combustion plant. However, washing alone may not be adequate for bottom ash to reach a suitable level of quality for subsequent utilization according to established regulatory limits (Sabbas et al., 2003).

Thus, the washing treatment may be carried out beneficially in combination with other processes, e.g. chemical mobilization or ageing, although a number of studies have indicated that mobilization of soluble salts mostly occurs during the initial washing stage (Sabbas et al., 2003).

Chemical extraction/chemical mobilization processes may be applied both to bottom ash and to APC residues. As far as bottom ash is concerned, treatments consisting of sodium carbonate or sodium bicarbonate addition are beneficial. This form of treatment has the effect of mobilizing sulphates through the formation of soluble Na_2SO_4 and precipitation of $CaCO_3$ (Sabbas et al., 2003).

As reported by Van Gerven et al (2007) extraction of heavy metals with organic complexants has been extensively used to clean contaminated soils.

Typical extracting agents include ethylenediaminetetra-acetic acid (EDTA), diethylenetriaminepenta-acetic acid (DTPA) and nitrilotriacetic acid (NTA), of which the first is the most studied. Kinoshita et al. (2005) used oxalic acid and citric acid to remove heavy metals from bottom and fly ash from automobile tire combustion. Citric acid gave the best results. Pedersen et al. (2005) removed heavy metals from MSWI fly ash by electrodialysis with ammonium citrate and sodium citrate as assisting agents.

Van Gerven et al. (2007) investigated a treatment method where bottom ash was extracted with organic solutions. Six different complexants (acetic acid, ammonium citrate, citric acid, oxalic acid, sodium EDTA and tartaric acid) were investigated in different concentrations (0.1-0.5 M) and with different contact times and washing steps. Ammonium citrate appeared to be the most promising agent.

From these studies it was demonstrated that the most difficult metals to remove were: Cu, Ni, Pb, Co and Zn, while better results in extraction were achieved for Cd, Fe, Mn and Mg.

As highlighted by Van Gerven et al. (2007), the amount of steps to be performed, the use of expensive reagents and the production of wastewater represent important drawbacks in view of practical installations.

1.3.2 Solidification and stabilization

The main purpose of solidification and stabilization is to produce a material whose physical (specific surface area, porosity, tortuosity, etc.) and chemical properties are more favourable with respect to reducing the leachability of contaminants out of the waste matrix (Sabbas et al., 2003).

In terminology, stabilization is a process of converting a toxic waste to a physically and chemically more stable form, that is, alters hazardous waste chemically to produce a less toxic or less mobile form. It involves chemical interactions between waste and the binding agent. By comparison, solidification converts liquid waste, semisolid sludge or a powder into a monolithic form or granular material that will allow relatively easy handling and transportation to landfill sites (Glasser, 1997). It does not necessarily imply that any form of chemical reaction has occurred. The objectives of solidification/stabilization are to achieve and maintain the desired physical properties and to chemically stabilize or permanently bind contaminants (Chen et al., 2009).

The best approach to solidification and stabilization is to chemically stabilize, then solidify the waste (Wiles et al., 1996). The most common binders used are inorganic systems based on cement and pozzolanic materials, although for some hazardous waste also thermoplastic binders, synthetic polymers and organophylic clays have been used (Wiles et al., 1996).

Treatments with hydraulic or chemical binders generally yield good leaching properties at relatively low costs. However, solidification/stabilization with hydraulic binders results in increased amounts to be landfilled and the physical encapsulation from the binders cannot be considered to last in the long term (Sabbas et al., 2003).

Aging and weathering processes are applied in order to promote mineralogical changes as a consequence of altering mineralogical phases in MSWI residues over time. As a result of hydration, carbonation or oxidation/reduction reactions significant reduction in trace elements (including heavy metals as Cd, Cu, Pb, Zn and Mo) and leaching can be achieved. This can also give rise to pH decrease, contaminant sorption processes as well as formation of more stable minerals (Meima and Comans, 1997a; Meima and Comans, 1999).

Aging and weathering can be beneficially applied particularly to reactive materials such as bottom ash, as this is composed of high-temperature solids, which are metastable under natural conditions and are therefore likely to undergo mineralogical changes (Sabbas et al., 2003). For this reason in EU countries, mainly in Germany, weathering of bottom ash for a period of 1-3 months before final disposal or utilization represents the most commonly employed method (Chimenos et al., 2000).

Chemical stabilization have also been proposed. It involves chemical precipitation of heavy metal-incorporating insoluble compounds and/or heavy metal substitution/adsorption into various mineral species (Sabbas et al., 2003). The principal forms of chemical agents used include sulfides, soluble phosphates, ferrous iron sulphates and carbonates (Sabbas et al., 2003).

Wiles (1996) reports the WES-PHix Ash Immobilization Process, which uses water-soluble phosphates and alkali to reduce metals solubility by the formation of insoluble (or less soluble) mineral phases. Treatment by phosphate may result in insoluble phosphate compounds of lead, copper and zinc. The reduction of Pb leachability was confirmed by test conducted by EPA. This evaluation did not confirm that Cd was chemically treated (Wiles, 1996).

- ***Solidification/stabilization with hydraulic binders***

The objectives of solidification/stabilization (s/s) are to achieve and maintain the desired physical properties and to chemically stabilize or permanently bind contaminants.

The high strength, low permeability and relatively high durability of hydraulic cement make it a good binder for this waste management technique (Chen et al., 2009).

The use of alkaline cements for waste treatment and conditioning of liquid, semi-solid and particulate wastes for disposal has an extensively documented history and a well established technology (Glasser, 1997).

The overall process of cement hydration includes a combination of solution processes, interfacial phenomena and solid-state reactions. It is extremely complex, especially in the presence of heavy metals. The selection of cements and operating parameters depends upon an understanding of the chemistry of the s/s process (Chen et al., 2009).

In addition to cement, also lime and/or pozzolanic materials can be used.

Cement-based s/s is a very complex process because of the variability of wastes, combined effects of the solution equilibrium and kinetic processes coupled with the surface and near surface of cement phases. The possible immobilization mechanisms of heavy metals could be: (1) sorption, (2) chemical incorporation (surface complexation, precipitation, co-precipitation), and (3) micro- or macro- encapsulation (Chen et al., 2009).

Sorption of heavy metals on cement hydration products includes physical adsorption and chemical adsorption. Physical adsorption phenomena occur when contaminants in the solution (pore water) are attracted to the surfaces of particles because of the unsatisfied charges of the particles. Chemical adsorption refers to high affinity and specific adsorption, which generally occurs through covalent bonding. The surface charges, chemical reactions involving surface functional groups and specifically adsorbed ions greatly modify the binding capacity of hydration products of cement for toxic metals (Chen et al., 2009). In the precipitation of cement hydration products, heavy metals ions may be adsorbed on their surfaces and then enter the lattice to form a solid solution, altering their structures (crystallinity, particle size) and solubility (Chen et al., 2009).

In most cases of cement-based s/s systems, the dominant fixation mechanism for heavy metals is through the chemical precipitation of low solubility species. According to the knowledge of cement chemistry, in cement-based s/s systems, heavy metals can be precipitated as hydroxides, carbonates, sulphates and silicates (Chen et al., 2009). Hydroxide precipitation occurs when the pH of a solution of dissolved metal ions is raised to some optimum level for a specific metal. The optimum pH is different for each metal and for different valence states of a single metal. Carbonate precipitation sometimes have has an advantage over hydroxide precipitation when metal carbonates are less soluble than corresponding hydroxides (Asavapisit et al., 1997).

Heavy metal compounds could be occluded (physically encapsulated) by C-S-H. It is suggested that nickel and cadmium hydroxides are incorporated into hydrated cement matrices (Chen et al., 2009).

Weak stabilization efficiency typically have been recorded for soluble salts. Furthermore, due to their strong amphoteric behaviour treatment of zinc and lead with cement- and lime-based processes may be problematic, unless incorporation in the crystal lattice of the hydration products occurs or appropriate additives are used (Sabbas et al., 2003).

- ***Ageing and weathering***

Weathering is a process which naturally occurs in incineration residues as a consequence of several factors such as pH, redox potential, temperature and humidity conditions as well as the concentration of certain components (e.g. CO_2) in the application site. Weathering results in the occurrence of slow mineralogical changes over time, which may alter the leaching of heavy metals from the material either in the medium or in the long term. Due to the weathering and the related neoformation of minerals, key factors such as pH are subjected to changes over time (Sabbas et al., 2003).

Weathering of bottom ash is a process which deserves particular concern. Incinerator bottom ash is unstable under atmospheric conditions because it is formed at high temperatures and thereafter cooled fairly rapidly. Weathering, therefore, will change the mineralogical characteristics of the material. Typically, such solids will thereby undergo a number of chemical reactions while in the landfill, leading to more stable mineral phases or phase assemblages (Meima and Comans, 1997a).

Weathering is the result of a complex series of several interrelated processes. Major alteration processes that have been reported are hydrolysis of oxides of Ca, Al, Na and K, dissolution/precipitation of hydroxides and salts of these main cations, carbonation, complexation with organic and inorganic ligands, surface complexation, surface (co)precipitation, sorption and formation of solid solutions as well as oxidation/reduction, neoformation of clay-like minerals from glasses (Belevi et al., 1992; Meima and Comans, 1997a; Meima and Comans, 1999). All of the mineralogical and chemical changes caused by such processes are also accompanied by physical changes such as pore cementation, changes in grain size and pore size distribution, which in turn alter the hydrological characteristics of the material (Sabbas et al., 2003).

Hydrolysis starts immediately after bottom ash quenching and can be prolonged over the time span of temporary storage or landfilling of the material (Belevi et al., 1992;

Johnson et al., 1995), as long as it is in contact with water. Hydrolysis involves the transformation of oxides of Ca, Na and K and non-noble metals like Al and Fe into the corresponding hydroxide species (e.g. $CaO \rightarrow Ca(OH)_2$, $Al_2O_3 \rightarrow Al(OH)_3$) (Belevi et al., 1992).

As a consequence of quenching, calcium- and aluminum-containing phases can also dissolve and other minerals can be formed as a result of dissolution/precipitation phenomena (Belevi et al., 1992; Meima and Comans, 1997a) for instance, ettringite can be formed according to the reaction (Meima and Comans, 1997a):

$$6Ca^{2+} + 2Al^{3+} + 3SO_4^{2-} + 38H_2O \leftrightarrow 12H^+ + Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O_{(S)}$$

The formation of C-S-H phases was also detected, as well as the neo-formation of clay-like minerals from the corrosion of glasses (Zevenbergen et al., 1998). Zevenberger et al. (1998) reported that transmission electron microscopic (TEM) examination and comparison of fresh bottom ash and bottom ash from different weathering stages have revealed widespread decomposition of the glass phase and formation of secondary aluminosilicates with weathering proceeding. Examination of 4-years old ash showed that an amorphous hydrous aluminosilicate (allophane) was the first reaction product of glass weathering. These secondary aluminosilicates were found as discrete flakes and as weathered rims on the surface of glass particles. In 12 years old ash they found direct evidence of neoformation of well-ordered primitive clay (illite) from glasses.

Carbonation is caused by the uptake of atmospheric CO_2 by the initially alkaline material, which leads to a decrease in pH and to the precipitation of calcite (Meima and Comans, 1997b; Meima and Comans, 1999). CO_2 absorption results in final pH values in the range of 8 to 8.5 (Meima and Comans, 1999). In this state the equilibrium between calcite and CO_2 (forming HCO_3^- with water) under the influence of gypsum dominates the system as a buffer.

The effect of weathering on trace elements leaching is likely to be significant because pH is a dominant parameter in metal solubility and complexation and pH has also been recognized experimentally to be a very significant parameter in trace element leaching from waste material and contaminated soils. At $pH \cong 8$ the solubility minimums are reached for most of the solid phases controlling the leaching of such heavy metals as Cd, Pb, Zn, Cu and Mo (Meima and Comans, 1999) (Fig. 9).

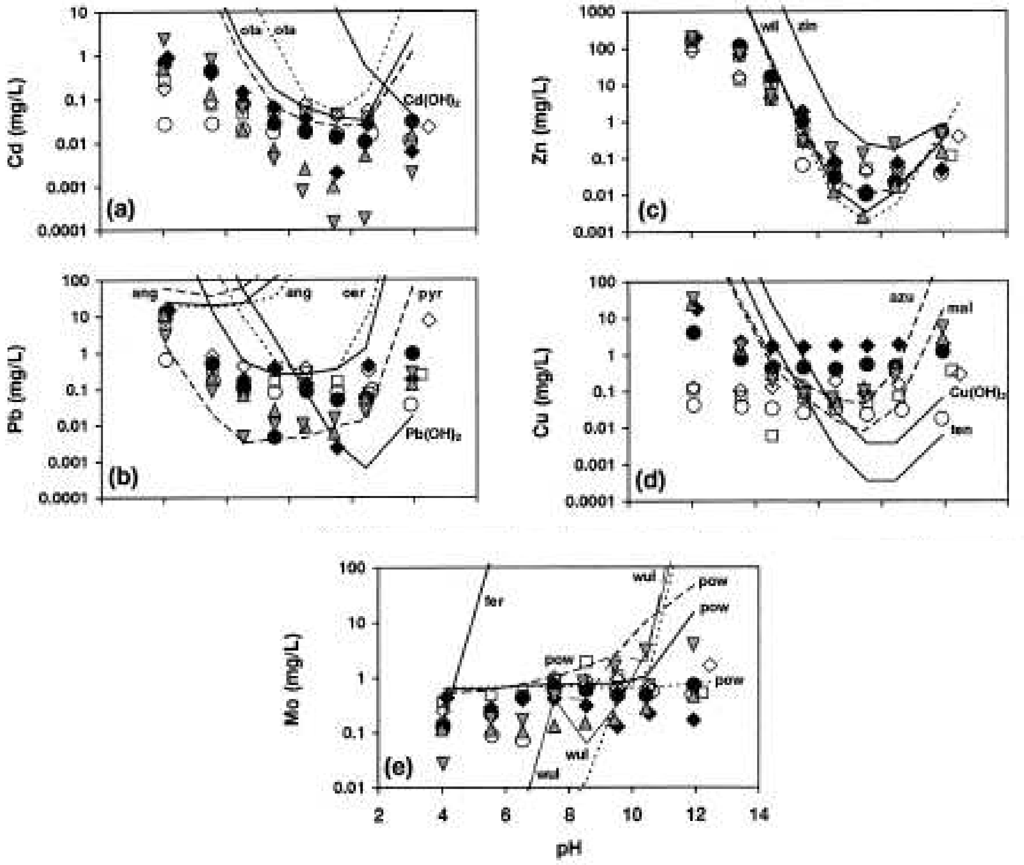


Fig. 9: Total dissolved Cd (a), Pb (b), Zn (c), Cu (d) and Mo (e) in bottom ash leachates as a function of pH. Lines indicate MINTEQA2 predictions assuming equilibrium with different mineral phases (Meima and Comans, 1999).

Sorption onto neoformed minerals, including both adsorption and co-precipitation processes, also seems to play a role in reducing contaminant leaching from weathered bottom ash. Sorption, in particular, is potentially an important mechanism in controlling the leaching of Cd, Zn, Cu, Pb and Mo (Meima and Comans, 1999). Reactive sorbent minerals such as Fe/Al-(hydr)oxides are present in large amount, particularly in weathered MSWI bottom ash. Each of the elements Cd, Zn, Cu, Pb and Mo has a high affinity for Fe/Al-hydroxides (Meima and Comans, 1999).

Moreover, fresh calcite that precipitate as a result of carbonation may also provide a number of sorption sites for certain elements, e.g. Cd and Zn, that have been shown to display a high affinity for this phase (Meima and Comans, 1999). Results from Meima and Comans (1999) indicated that the affinity of heavy metals for these minerals increases with increasing pH, whereas Me-hydrolisis and Me-complexation with carbonate may lead to higher total dissolved concentrations at strongly alkaline pH.

Behaviour of heavy metals in a weathered bottom ash heap was also studied by Piantone et al. (2004). They found that similar to the highly variable distribution of newly formed mineral phases, the distribution of heavy metals in weathered bottom ash heaps is random and dependent on the crystal-chemical characteristic of the secondary phases in which they are trapped. Nevertheless, some noticeable trend were identifiable: subtle but systematic uptake of Pb and Zn by carbonates, of Pb by ettringite, and of As by Fe oxides. Also the uptake of heavy metals from calcite was clearly demonstrated. Moreover, Fe oxides, both well and poorly crystallized, are known for their ability to trap numerous anions and cations (Piantone et al., 2004).

However, leaching of sulphates from weathered bottom ash has been found to increase if compared to fresh bottom ash (Bodénan et al., 2000), probably as a result of ettringite carbonation, which leads to the precipitation of gypsum.

Similar results were found by Freyssinet et al. (2002), whose study involved identifying and quantifying the physico-chemical maturation mechanism during 18 months in a large heap of MSW bottom ash. At the beginning of maturation a high Ca/SO_4 molar ratio with respect to gypsum and ettringite was observed (Fig. 10). The Ca excess decreased considerably with maturation, reaching a plateau after about 90 days with a molar ratio close to 3. The system reached a second plateau at around day 200 with a molar ratio of about 1.5, showing that Ca concentration at the heap outlet was successively controlled by different inorganic species. A number of principal phases can release calcium in the ash, i.e. portlandite, Ca-alumino-silicates and sulphates. At the onset of monitoring, most calcium seemed to be provided primarily by non-sulphated species. The ratio close to 3 at the fist plateau indicated a preferential release of sulphates and calcium by ettringite, the rest of the Ca excess being furnished by portlandite or Ca silicates. The second plateau, instead, would indicate leachate control by sulphates, in particular gypsum (Freyssinet et al., 2002).

According to Piantone et al., 2004, calcite, Fe oxides, ettringite and anhydrite appeared to be the most common secondary phases in the ash. This was consistent with the observations of other researchers (Kirby and Rimstidt, 1993; Eighmy et al., 1994).

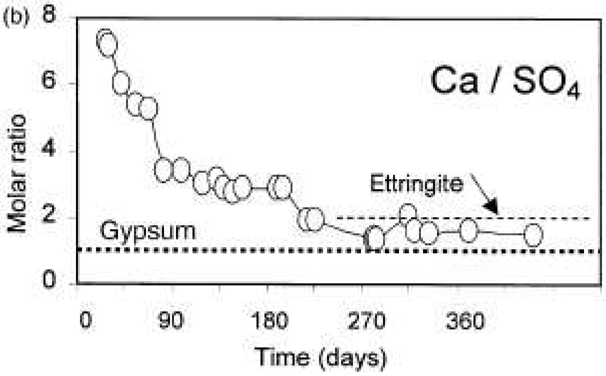


Fig. 10: Kinetics of change of the Ca/SO_4 molar ratio with maturation (Freyssinet et al., 2002).

Furthermore, quartz was unambiguously detected and widely distributed as a newly formed hydrated mineral paragenesis (Piantone et al., 2004). Although the presence of very fine quartz being inherited from the original MSWI bottom ash cannot be dismissed (Eusden et al., 1999), several considerations point towards this mineral being authigenic. It would seem that in bottom ash heaps, silica weathered during alkaline leaching is stabilized in interstitial pathways with carbonation of hydrated lime and an associate decrease in pH. Silica then precipitates and transform into quartz during ageing (Piantone et al., 2004). These hypothesis are consistent with a high solubility of primary quartz in alkaline media, as demonstrated by thermodynamic modeling from Freyssinet et al. (2002).

Anhydrite, another phase that is widespread throughout the ash, can come from: (i) residual anhydrite, (ii) high temperatures due to oxidation of the SO_2, (iii) hydrothermal processes, (iv) the oxidation of S (Piantone et al, 2004). The alkaline environment created by portlandite and the presence of SO_4^{2-} ions is likely to foster the formation of ettringite, as long as there is Al available in the environment. Aluminum is generally present in MSWI bottom ash in residual form (Piantone et al., 2004).

As reported by Piantone et al. (2004), aluminum hydroxides can come from: (i) alumino-gels derived from metal Al that dissolves in the alkaline environment and then precipitates in the form of hydroxide as the environment becomes increasingly acid, (ii) destabilized ettringite that produces carbonates, calcium sulphates and hydroxides.

Ageing and weathering can also be artificially enhanced to accelerate the chemical reactions responsible for the fixation of contaminants within the waste matrix. With a view to this, accelerated carbonation has been proposed as an efficient treatment for reducing leaching of soluble salts, Pb and Zn, although it has been shown to have the potential of mobilizing sulphates (Sabbas et al., 2003).

1.3.3 Thermal treatment

The thermal treatment of incineration residues is used extensively in some countries to obtain reduced leaching from the residues and reduced volume, as well as treated material that is suitable for reuse. Thermal treatment, in fact, offers the advantage of complete inertization of bottom ash ad fly ash and is expected to be an attractive alternative for a sustainable long-term use of bottom ash (Ferraris et al., 2009). According to Sabbas et al. (2003), thermal treatments can be grouped into three categories: vitrification, melting and sintering.

- Vitrification is a process whereby residues are mixed with glass precursor materials and then combined at high temperatures into a single-phase amorphous, glassy products. Typical vitrification temperatures are at 1000-1500°C. The retention mechanisms are chemical bonding of inorganic species in the residues with glass-forming materials, such as silica, and encapsulation of residue constituents by a layer of glassy material.
- Melting is similar to vitrifying, but this process does not include the addition of glass material and results in a multiple-phased product. Often several molten metal phases are produced. It is possible to separate specific metal phases from the melted product and recycle these metals, perhaps after refinement. Temperatures are similar to those used in vitrifying.
- Sintering involves heating the residues to a level at which bonding of particles occurs and chemical phases in the residues reconfigure. This leads to a denser product with less porosity and a higher strength. Typical temperatures are around 900°C. When MSW is incinerated, some level of sintering will typically take place in the incineration furnace. This is especially the case if a rotary kiln is used as a part of the incineration process.

There are several academic works on the characterization and re-use of vitrified bottom ash for several potential applications, e.g., glass ceramics, glass- and glass-ceramic matrix composites, glass fibers, and porous glasses obtained with vitrified bottom ashes (Appendino et al., 2004; Cheeseman et al., 2005; Monteiro et al., 2006). Few of these potential applications are currently fully exploited in industry, mostly because of the lack of economic incentive (Ferraris et al., 2009).

Properties of sintered bottom ash have been studied by Bergfeldt et al. (1997), Selinger et al. (1997), Bethanis et al. (2002) and Cheeseman et al. (2005). All these researches indicated a reduced leaching from sintered products compared to the original waste. Results from XRD on sintered residues revealed that diopside ($CaMgSi_2O_6$) was the principal crystalline phase, with significant amounts of clinoenstatite ($MgSiO_3$) and wollastonite ($CaSiO_3$), and minor amounts of albite ($NaAlSi_3O_8$) and hematite (Bethanis et al., 2002; Cheesman et al., 2005). Bergfeldt et al. (1997) found an increase in gehlenite ($Ca_2Al[(SiAl)_2O_7]$) and akermannite $Ca_2Mg[Si_2O_7]$ in the sintered products. Quartz and calcite peaks decreased on sintering and had completely disappeared by 1080°C, due to the formation of crystals of the pyroxenoids group, such as diopside and wollastonite (Bethanis et al., 2002).

As regards the effect of sintering process on acid neutralization capacity, Cheeseman et al. (2005) found similar ANC behaviour for not sintered and 1050°C sintered bottom ash, except for the pH range between 5 and 6, where the untreated BA sample showed a higher buffering capacity. This different behaviour was explained by the decomposition of $CaCO_3$ during thermal treatment with formation of CaO and CO_2 and the subsequent encapsulation of CaO into both amorphous and crystalline phases present of the sintered material. Bergfeldt et al. (1997) found a slight increase in ANC for BA sintered at lower temperatures (1000°C) and a decrease for BA sintered at higher temperatures (1065°C). The raise of ANC was explained by the artificial atmosphere used for the sintering process, which had an excess of oxygen and carbon dioxide. Higher partial pressure of CO_2, in fact, raises the decomposition temperature of carbonates. Moreover, the oxidizing atmosphere favours the formation of metal oxides. Hence, the raise of ANC was observed at a pH range of 5-3, where neutralization by metal hydroxides ($Al(OH)_3$, $Fe(OH)_3$) was effective.

Leaching in distilled water for 48h showed a significant reduction in leaching of most metals, and particularly Na, K, Al and Cu. However, data also indicated increased leaching of Cr, Cd and Zn (Cheeseman et al., 2005). Bergfeld et al. (1997) found an insignificant influence of sintering on the availability of Ca and heavy metals and a general decreased release during column test.

Melting of MSWI ashes has been studied by: Ecke et al. (2001), who considered the melting of BA though electric arc; Jung et al. (2005), who studied the metal behaviour of melted ash from eight ash-melting and three gasification-melting facilities; Lin and Chang (2006), who investigated the melting at 1400°C of a mixture of different type of MSWI ashes.

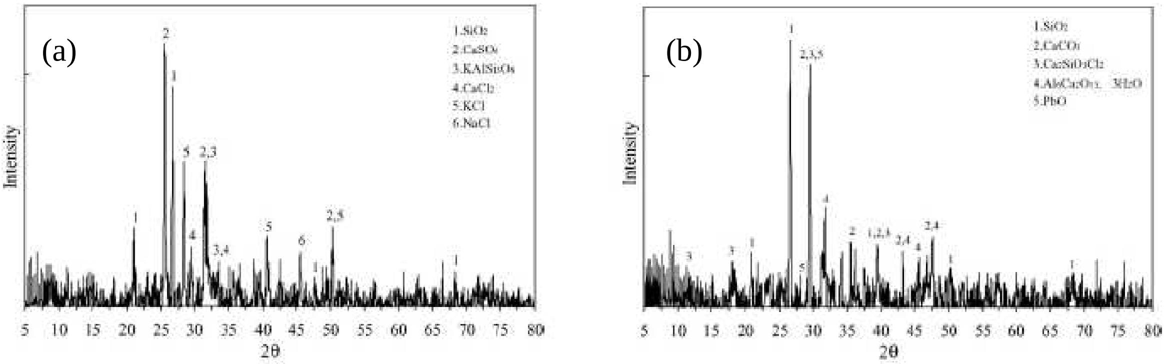


Fig. 11: XRD patterns of cyclone ash (a) and bottom ash (b) (Lin and Chang, 2006).

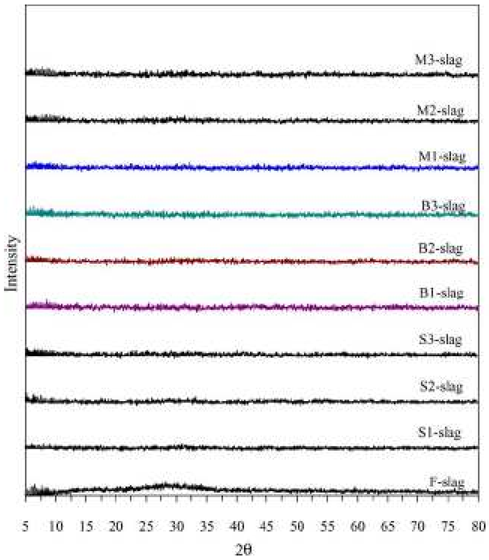


Fig. 5. XRD patterns of slags produced from MSWI ash.

Fig. 12: XRD patterns of slags produced from MSWI ash (Lin and Chang, 2006).

XRD analysis from Lin and Chang (2006) indicated a significant difference in the MSWI ash sample and the slag structures (Fig. 11 and 12); the former had a much more crystalline structure, while the latter showed an amorphous glassy matrix.

Ecke et al. (2001) observed that electric arc melting significantly increased the potential for physical binding. Compared with bottom ash, slag was found to have 1 order of magnitude lower mass specific area. Although 80 wt% of the slag consisted of particles smaller than BA, slag had a specific surface area about ten times smaller than bottom ash, indicating a much smoother surface.

As regards metals mobility, melted BA had a chemically restructured matrix, having the potential to stabilize metals (Ecke et al., 2001). In particular it was found that melting of bottom ah reduced the availability of elements such as Cr, Cu, Zn, Pb and Ca, whereas the mobility of Cd, Al, Fe and Ni resulted to be barely affected (Ecke et al., 2001). Similar results have been found by Lin and Chang (2006).

Chapter 2: Size separation of gasification residues

This section investigates the characteristics of bottom ash (BA) from two municipal refuse derived fuel (RDF) gasification plants as a function of particle size. For instance, both technical and environmental parameters were determined, including: grain size distribution, specific gravity, compaction behaviour, hydraulic conductivity, water content and chemical composition. Besides, leaching characteristics were also investigated by means of the EN 12457-2 batch leaching test, the TS 14429 Acid Neutralization Capacity (ANC) test and the Availability Test (NEN 7371).

Results from the EN 12457-2 batch leaching test were compared with the Italian law limits for either landfilling (as inert or not hazardous waste) or reuse. One of the two analyzed BA samples (named A) showed levels of heavy metals always below the Italian regulatory limits for reuse (except for Cu in the fraction >1mm), the other BA sample (named B) displayed concentrations of Pb (only for the grain size in the range 1-2 mm), Cu, Cr and Ni above the limits for reuse and of Pb (still for the above mentioned fraction), Cu and Cr above the limits for inert waste landfilling. The different behaviour of these residues was attributed to the characteristics of the RDFs delivered to the gasification plants, but also the wear of the furnace refractories might have exerted some influences (Ecke et al., 2001; Kwak et al., 2006).

The vitrified structure of the tested residues, as a consequence of the high operating temperature of the gasification plants, reduced availability of metals for leaching. The formation of a glassy structure decreases the surface area and reduces the mobility of metals, which are entrapped within the amorphous matrix (Ferraris et al., 2009).

Results from ANC test confirmed the glassy structure of the residues: a sharped decrease of pH with the addition of acid indicates that the tested BA were made up of a larger proportion of glassy materials with hydrophobic characteristics (Johnson et al., 1995).

Tests results demonstrated that some kind of pre-treatment could be necessary for the residues to fulfill heavy metals law limits. The utilization of size separation as a pre-treatment was also discussed.

2.1 Introduction

At present in Italy over 32 million tons or approximately 550 kg/cap. of municipal solid waste are produced yearly: 36.3% is recycled or reused, 11.9% makes up the waste to energy stream and 51.8% is landfilled (ISPRA, 2009).

According with ISWA State of the Art Report (2006), Italian waste to energy plants produce about 680000 tons of BA yearly, which represent about 15% of the total amount of treated waste and 85% of the overall residues of thermal processes.

BA is a granular and heterogeneous material which is mainly composed of high-temperature solids (glass, ceramic, minerals and unburned organic matter), rapidly cooled down when the residue is quenched after exiting the combustion chamber.

In Italy BA is generally disposed in landfill, although several European Countries have recently developed regulation aimed at encouraging its utilization in construction applications rather than its final disposal (Rocca et al., 2009). Furthermore, in Italy there is no specific legislation for waste incineration BA reuse and valorisation; the only reuse option that is currently adopted is its use a secondary raw material in cement production (M.D. 186/06).

The long-term potential leachability of heavy metals from BA is one of the most important factors in the assessment of the potential hazards associated with landfilling or reuse in construction applications. The evaluation of the environmental compatibility of BA is necessary before the utilization, treatment or disposal of these residues. In addition to the environmental aspects, the new material will have to meet technical specifications similar to those of natural materials traditionally used for the same purposes (van der Sloot et al., 2001).

The use of vitrified bottom ash is expected to eliminate the above mentioned environmental drawbacks: recent works demonstrated that heavy metals are immobilized within the vitrified matrix (Kwak et al., 2006; Ferraris et al., 2009). For instance, melting of MSW at high temperature reduce the availability of Cr, Cu, Zn and Pb for leaching as the formation of glassy material decreases the surface area and entraps the metals within the amorphous glassy matrix (Ecke et al., 2009). However, vitrification of BA is a very energy consuming process due to the high temperatures required; therefore, related costs can be significant and impair its advantages.

The vitrification treatment can be avoided by adopting modern incineration plants, which operate at temperatures above 1600°C and use waste as a fuel (Ferraris et al., 2009).

Different studies demonstrated that BA arising from standard MSW combustion plants exhibit chemical and morphological characteristics depending upon their particle size distribution (Chimenos et al., 1998; Chimenos et al., 2003). Furthermore, bulk composition of samples collected from many facilities indicated that the finest particle fraction has a relative high content of heavy metals (Chimenos et al., 1998; Stagemann et al., 1995; Chimenos et al., 2003).

In this chapter the results of an experimental study carried out to investigate the characteristics of BA from two RDF gasification plants are presented. Much concern was devoted to evaluate the behaviour of the different particle size fractions, with the aim of assessing suitability to be reused.

2.2 Materials and methods

Characterization was carried out on two representative samples of BA (referred to as sample A and sample B, respectively) collected after quenching from two fixed-bed gasification facilities. Plant A was fed with RDF and coal powder and used enriched air as oxidant factor, plant B was fed with RDF and employed pure oxygen as oxidant factor; both operated at atmospheric pressure, with a maximum temperature of about 1600°C.

Sampling was performed through quartering and additional quartering steps in order to derive homogeneous and representative samples to undergo the laboratory analysis. Portions of the samples were dried at 105°C for 24 h to evaluate water content (according to the UNI EN 1097-5:2000) and sieved (according to Raccomandazioni AGI, 1994) to assess grain size distributions and to identify the most significant grain size classes and subclasses (sample A: 0-0.105, 0.105-0.25, 0.25-0.5, 0.5-1, >1 mm; sample B: 0-0.105, 0.105-0.25, 0.25-0.5, 0.5-1, 1-2, >2mm). The size distribution curves were built from the weight fractions of the samples passing through ASTM stainless steel sieves of decreasing size.

Chemical characterization of BA involved determination of chemical composition and leaching behaviour, while the physical and technical characterization involved determination of water content, grain size distribution, specific gravity, compaction behaviour and hydraulic conductivity.

To detect chemical composition, each ground sample was digested using a HNO_3/HCl/HF mixture in a Teflon bomb heated in a microwave oven. The samples were then analysed to determine the concentrations of the following metals: Pb, Cu, Zn, Cd, Cr, Ni, Mn, Fe and As.

According to the Italian law in force, the UNI EN 12457-2 batch leaching test was carried out to evaluate the different heavy metals leaching behaviour of each grain size class (Fig.1). After equilibration, the final pH was recorded, the suspension was 0.45 μm filtered and the clear filtrate was divided in two samples: one sample was acidified with concentrated HNO_3 and used for the analysis of metals (Pb, Cu, Zn, Cd, Cr, Ni, Mn, Fe); the other sample was left untreated and used to determine anions' concentrations (fluorides, chlorides, phosphates nitrates and sulphates).

Fig.1: EN 12457-2 batch leaching test.

Anions and metals concentrations detected in the eluates were compared with law environmental criteria to assess the feasibility of landfilling as inert waste (M.D. 201/05) or reuse (M.D. 186/06).

The Acid Neutralization Capacity (ANC) test is a leaching procedure which is able to provide informations on the buffering capacity of a given material, its phase composition, as well as its leaching behaviour under different environmental conditions; in particular it allows the resistance to acidification of a material to be investigated, the presence of solid phases that are stable to be determined and pH ranges to be identified. The test was carried out following the UNI CEN/TS 14429.

15 g of material was dried at 40°C and then reduced dimensionally by ball mill to less than 1mm. It was then put into contact with 150 ml of acid nitric solutions, at increasing acid concentrations, and shacked for 48h. The acid addition schedule was based on the buffering capacity of the material, which was estimated through a 48 h preliminary test. For every sample, 15 sub-samples with different acid concentration solutions were considered. After 48 h, the pH values were measured in the leachates and then plotted against the relative amount of acid added. The suspensions were 0.45 μm filtered and the clear filtrates were used for the analysis of metals (Pb, Cu, Zn, Cd, Cr, Ni, Mn, Fe, As) and anions (Cl, SO_4).

The risks associated with the presence of potentially hazardous constituents in waste materials, with respect to their mobility and ecotoxicological significance, are determined by their leaching potential rather than their total content (van der Sloot et al., 1997). Hence, the Availability test was also carried out, according to the NEN 7371:2004 procedure, in order to estimate the fraction of the total content which can be long-term leached under natural conditions.

The test consists of a pH-controlled extraction procedure which works at subsequent pH of 7 and 4: each one of these pH values was kept constant for 3 hours by addition of a 0.1 M HNO_3 solution; the two eluates were 0.45 μm filtered and combined into one sample for analysis. The availability test was performed on 40°C dried and <0.105mm ball-milled samples.

Metals concentrations in eluates were detected with Atomic Absorption Spectrophotometry (AAS) through Perkin Elmer AAnalyst 200 and with Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS) through Perkin Elmer HGA 700 with AAS Perkin Elmer 1100 B. Anions concentrations were determined with Ion Cromatography through Dionex ICS 1000.

All measurements were conducted at least in double, with the exception of the ANC test, which was run on a single replicate.

The evaluation of the specific gravity was carried out following the CNR UNI 10010: an appropriate amount of a representative sample of BA was 40°C dried, ball milled and then introduced inside a glassy pycnometer, which was then filled with deionized and de-aerated water; BA was left under water for about 4 h to allow solid structure's imbibition; specific gravity was obtained through the comparison between the space occupied by BA and water, respectively. The trial was made up by two independent specimens, so the final value represents the average of the two outcomes.

Fig.2: Proctor test for evaluation of compaction behaviour.

In order to investigate the feasibility to reuse BA in road construction, the compaction behaviour of this residue was investigated through the Proctor test (Fig.2): this trial, typically performed on soils, determines the relationship between dry bulk density (γ_d) and moisture content (w) under specific compaction energy (Standard Proctor test: E=592 kJ/m^3, Modified Proctor test: E=2700 kJ/m^3). Samples of BA, characterized by different moisture contents, were compacted in a cylindrical mould following the CNR n°69 Standard. At last, dry bulk density values obtained for each specimens were plotted against the relative moisture contents to gain the Proctor curve of the material: usually a soil’s Proctor curve is characterized by the most high dry bulk density value (maximum) which corresponds to a specific moisture content value (optimum).

Hydraulic conductivity of BA was indirectly determined through Hazen formula, which relates this parameter to the effective diameter D_{10}.

2.3 Results and discussion

2.3.1 Physical and mechanical properties

Sample A and sample B were characterized by water content values of 0.05% and 4.02% respectively. This difference might be due to different storage and transportation conditions of residues.

Fig. 3 shows that both samples dimensions fell within the range between sand and gravel. The two size distribution curves begin in the field of fine gravel, appear more articulated in the field of sand and are almost vertical, so the two samples could be considered poorly graded (sample A: CU=2.83, sample B: CU=5.65). The grain size distribution curves allowed to classify the samples through classification systems: both samples were qualified as SP (clean and poorly graded sand) according to USCS and as A-1-a (rock, gravel and sand fragments, excellent to good road sub-base) according to HRB.

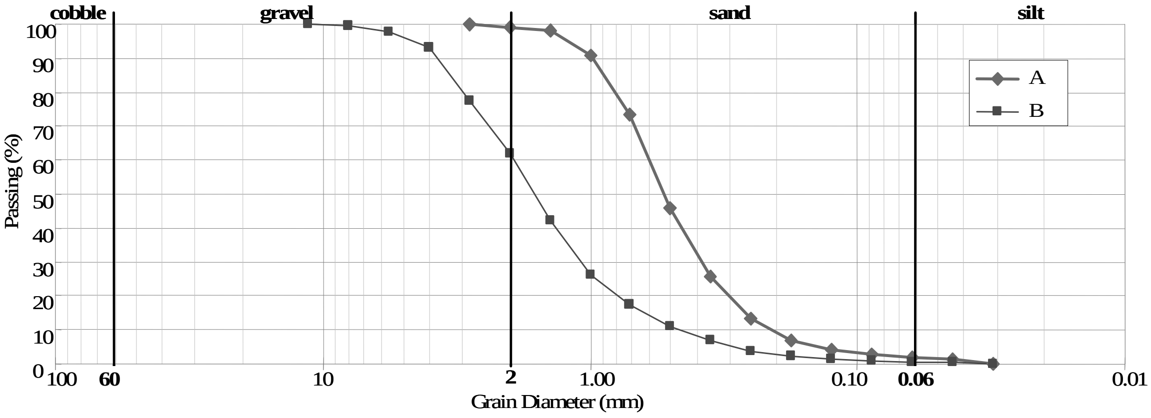


Fig. 3: Grain size distribution of samples A and B.

Specific gravity was evaluated only for sample B. The result was 2.913 g/cm^3, which is just a little bit higher than characteristic soil values (2.6÷2.75 g/cm^3).

Before performing compaction test, a dry standard Proctor trial was carried out on sample B. A 105°C dried and representative sub-sample was submitted to energy application to evaluate crushing and pulverization particles trend: this single specimen provided a dry unit weight value (γ_d=16.971 kN/m^3). From the knowledge of specific gravity and dry unit weight values it was possible to estimate void index (e=0.684) and porosity (41%) values. A comparison between the two grain size distribution curves respectively obtained from raw and compacted subsample (which was taken from the lower part of cylindrical mould) highlighted that crushing did not seem to be a remarkable trend for sample B.

Standard and Modified Proctor tests (Fig. 4) provided these results: in both cases γ_d trend was always increasing and not much susceptible to moisture content changes; sample B seemed to be susceptible to higher compaction energy application, as higher γ_d values met equal *w* values in Modified test.

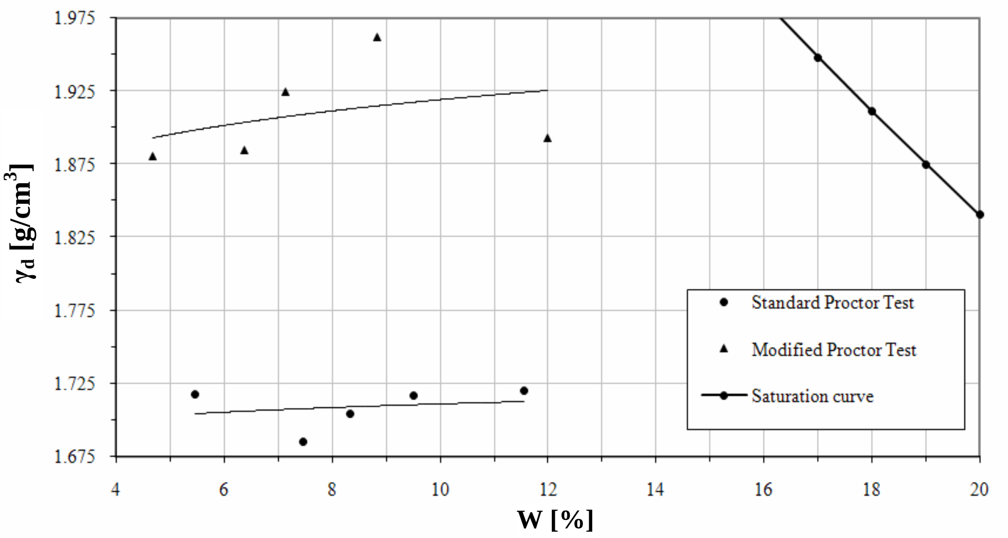


Fig. 4: Standard and Modified Proctor test on sample B.

Hazen formula provided an hydraulic conductivity of 0.2025 cm/s ($2*10^{-3}$ m/s) for sample B; comparing this value with those ones typical of soils, it was possible to assess that it was characterized by a good permeability standard; as a result it could allow a good water drainage.

2.3.2 Chemical characterization and leaching behaviour

The chemical composition of the examined materials, reported in Table 1, indicates that the major metals were Fe, Mn, Cu and Cr. Ni, despite its lithophilic behaviour, was not present in significant amounts. Zn, which is a volatile element, could still be found in sample A in appreciable concentrations. Pb and Cd, according to their volatile behaviour, were not present in significant amounts.

For both the considered samples, heavy metals resulted to be enriched in the finest fraction. This result was in accordance with results from other authors (Stageman et al., 1995; Chimenos et al., 1998; Chimenos et al., 2003).

	A			B		
(mg/kg)	<0.5mm	0.5-1 mm	>1mm	<1mm	1-2 mm	>2mm
Pb	0.9	0.7	0.6	36	54	36
Cu	370	290	230	2000	750	460
Zn	280	320	240	31	22	23
Cd	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	128	126	123	990	730	475
Ni	25	19	17	37	26	25
Mn	645	615	570	570	450	320
Fe	7070	5050	4860	6500	4900	4170

Table 1: Bulk composition of BA samples (n.d.= not detectable).

Fig. 5 shows pH values and metals and anions concentrations determined in the leachates from EN 12457-2 batch leaching test; the value obtained for each parameter was compared with the limit posed by the Italian law in force for landfilling as inert or not dangerous waste and reuse.

In order to achieve a deeper analysis of materials leaching behaviour, the finest fractions were further subdivided. Hence, the test was performed on the following sieved fractions: 0-0.105, 0.105-0.25, 0.25-0.5, 0.5-1, 1-2 and >2mm (>1mm for sample A).

Analysis of the eluates indicated that all the considered samples were alkaline in nature, with a pH between 8.6 and 9.9 that didn’t differ appreciably with grain size; for sample B only, a one-point pH reduction with grain size decreasing was observed.

For sample A, Pb was always found below the instrumental detection limit of 5 µg/L. Contrasting with results from bulk composition, for sample B the 50 µg/L limit for disposal in inert waste landfill or reuse was not accomplished only for the 1-2 mm fraction; for the other portions, Pb concentrations were always below 10 µg/L.

Cu was found to exhibit a very different behaviour in the two considered samples. In sample A, Cu concentration showed a decreasing trend from the coarse to the finest fraction: this would allow BA to be disposed in a sanitary landfill for inert waste. Fraction above 1mm exceeded the reuse limit.

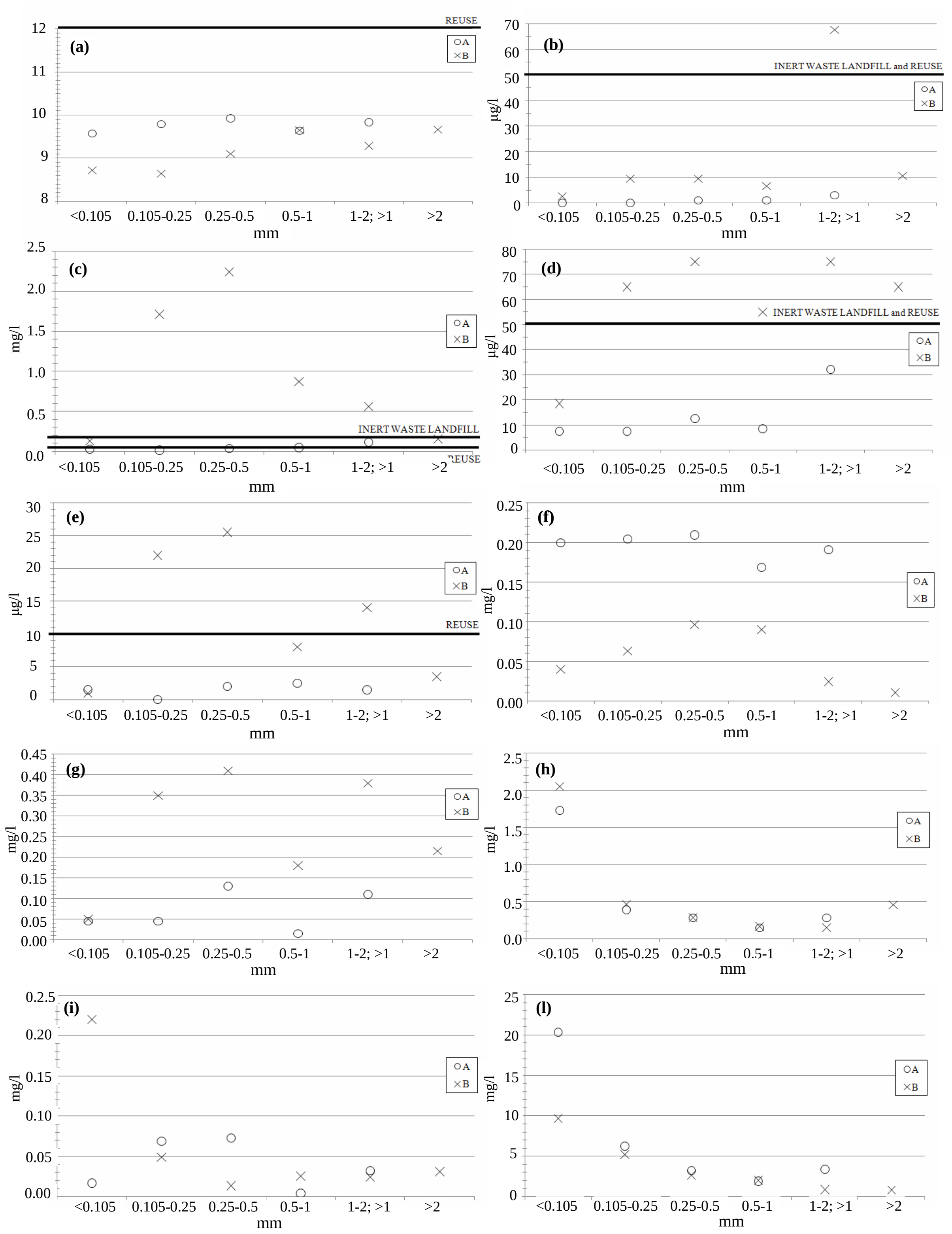


Fig. 5: Results of EN 12457-2 leaching test for pH (a), Pb (b), Cu (c), Cr (d), Ni (e), Mn (f), Fe (g), Chlorides (h), Nitrates (i), Sulphates (l) and Italian law limits for not hazardous and inert landfilling (Ministerial Order 03/08/05) and reuse (Ministerial Order 05/02/98).

For sample B, Cu concentration in the leachate was always higher and exceeded the limit for disposal in inert waste sanitary landfill. The main contribution to leaching was attributed to the fraction between 1 and 0.105mm, which represented about 26% of total BA.

Sample A exhibited Cr contents always below the limit for reuse and inert waste landfilling, with a slight increase in the size fraction above 1mm. Sample B showed concentrations always above the same limit, except for the finest fraction.

Concentration of Ni in leachates from sample A was always below 5 μg/l, with quite a constant trend among the different grain size classes. Sample B showed higher concentrations, particularly in the fractions between 0.5 and 0.105mm.

For Fe and Mn, the higher concentrations were associated to fractions between 1 and 0.105mm. However, the Italian law in force does not pose any limit for these metals.

Chlorides, nitrates and sulphates concentrations increased with particle size decreasing; however, for all these elements, the detected values were very far below law limits.

For both samples and all grain size classes subjected to analysis Zn, As and Cd were always below the detection limits of 0.1 mg/l, 25 μg/l and 1 μg/l, respectively.

Availability test NEN 7371 was carried out on <0.5, 0.5-1 and >1mm classes for sample A and on < 1, 1÷2 and > 2 mm classes for sample B in order to assess their leaching potential. Figure 6 and 7 show a comparison between results of Chemical Composition and Availability test; for each element, the percentage available for leaching is reported in Table 2. For all the grain size classes subjected to analysis, the amounts of heavy metals available for leaching were small fractions of the overall contents. This result is representative of a glass fraction rich material, where the vitrified matrix, which is a consequence of high operating temperatures, leads to a reduction of surface area and to the trapping of heavy metals (Ecke et al., 2009).

Availability of Pb from sample B resulted to be a function of particle size, with a significant decrease of availability for the coarse fraction. For sample A, Pb concentration in the eluates from NEN 7371 was always under the 5 μg/l instrumental detection limit.

In sample A Cu seemed to be less leachable in the coarse fraction. This tendency, however, was not confirmed from sample B.

Partially in contrast with results from EN 12457-2 leaching test, differences in availability between grain size classes were not noticeable for none of the other considered elements.

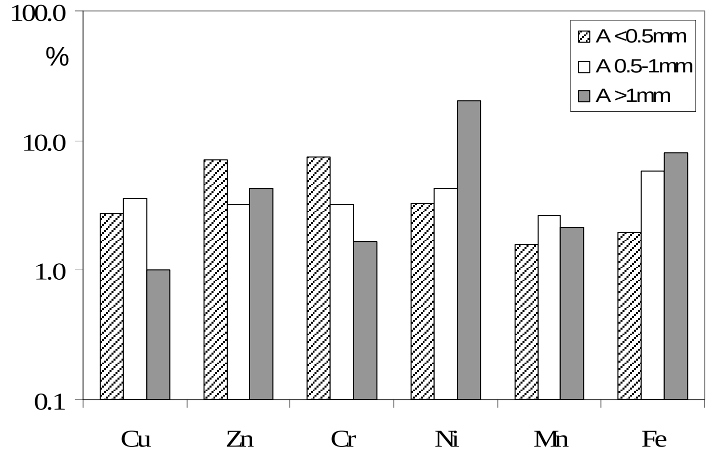


Fig. 6: Availability of heavy metals for sample A, normalized to total concentration.

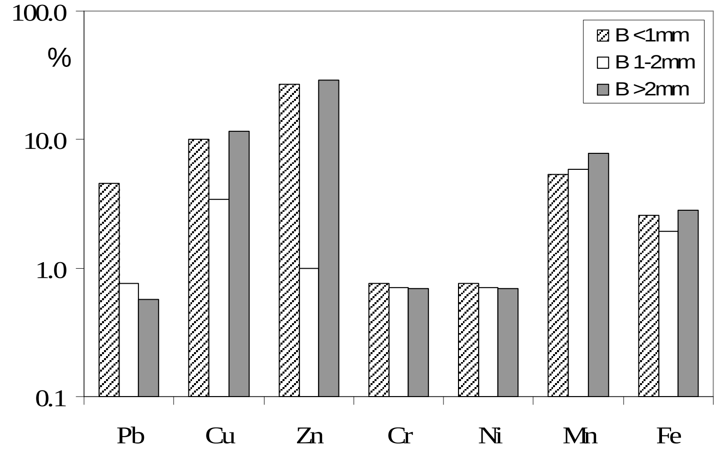


Fig. 7: Availability of heavy metals for sample B, normalized to total concentration.

%	Pb	Cu	Zn	Cr	Ni	Mn	Fe
A <0.5mm	n.d.	2.75	7.12	7.50	3.28	1.57	1.94
A 0.5-1 mm	n.d.	3.57	3.20	3.22	4.26	2.65	5.80
A >1mm	n.d.	0.00	4.28	1.65	20.18	2.14	8.03
B <1mm	4.57	10.02	27.04	0.76	0.76	5.35	2.57
B 1-2 mm	0.76	3.41	n.d.	0.71	0.71	5.84	1.93
B >2mm	0.57	11.63	29.08	0.70	0.70	7.78	2.80

Table 2: Fraction of metals available for leaching with respect to total concentration.

ANC test was conducted on both total samples, on >1, 0.5-1 and <0.5mm classes for sample A and on < 1, 1÷2 and > 2 mm classes for sample B. The shape of titration curves, shown in Fig. 8 and 9, confirmed the vitrified framework of these residues, which was announced by the results of Availability test: fast decrease of pH values with increasing acid addition indicates that the material is made up of a larger proportion of glassy materials with hydrophobic characteristics (Johnson et al., 1995). The shape of the curves could be explained by the degradation of calcite to carbon dioxide and incorporation of CaO into the glassy silicate structures (Selinger et al., 1997; Bethanis et al., 2001; Cheeseman et al., 2003; Cheeseman et al., 2005).

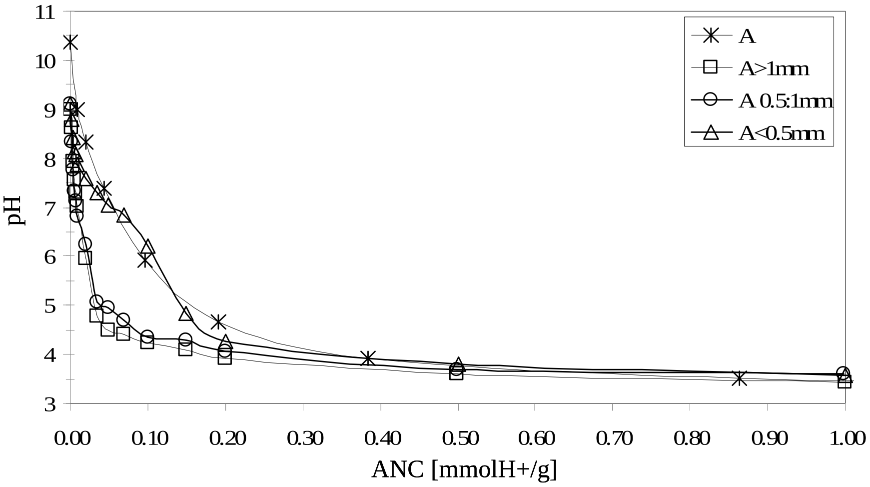


Figure 8: Titration curves for sample A and different grain size fractions.

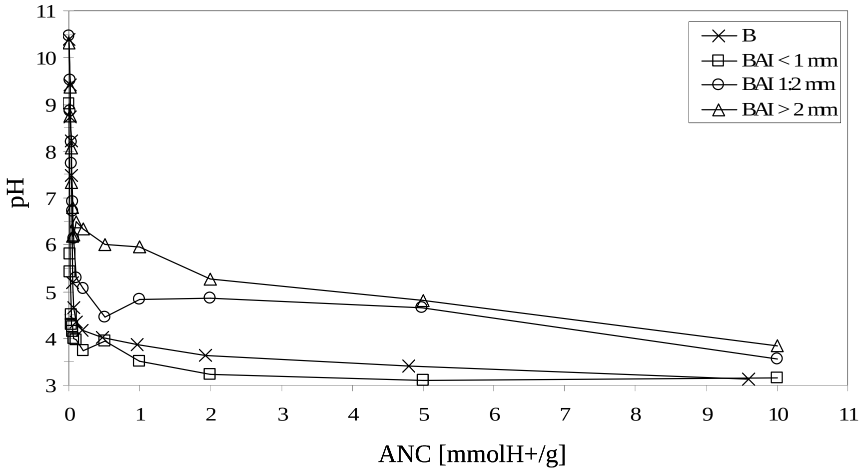


Figure 9: Titration curves for sample B and different grain size fractions.

Fig. 10 reports the behaviour of heavy metals at different pH values for samples A and B. For all the fractions subjected to analysis, the observed trend was characterized by the increase of heavy metals concentrations with pH decreasing and by a limited release in the alkaline pH range.

In the pH range of reduced release from 7 to about 9, the coarse fraction was the one with the lowest leaching, for almost all the considered metals. This was in accordance with the previous results.

Amphoteric metals such as Pb and Zn should be characterized by a V-shape solubility curve, with increasing solubility under both strongly acidic and strongly alkaline conditions (Sabbas et al., 2003).

With reference to Fig. 10, for pH values above 6, Pb solubility resulted to be very low for all the considered samples. Above pH 8 the concentration of lead for sample A was under the 5 µg/l detection limit of the instrument. Concerning sample B, in alkaline conditions no differences could be found between the different grain size classes leaching. In acidic condition, instead, according to results from EN 12457-2 leaching test, the 1-2mm fraction resulted to give the highest contribution to Pb leaching.

In sample B, Cu showed a minimum in leachability at pH 8 to 9, with a marked increase in acidic conditions. No significant differences in behaviour were observed between the different size fractions. Above pH 7 leaching of copper from sample A was comparable to that from sample B. In acidic conditions, however this sample showed a considerably lower leachability increase, with about one order of magnitude difference for pH values below 5.

According to Stumm and Morgan (1996) and van der Sloot et al. (2001) typical solubility curve of Zn have a minimum between 10 and 11. As regards the results reported in Fig.10, all the considered samples had a comparable behaviour. Above pH 8 all the eluates had Zn concentrations very close to the instrumental detection limit of 0.1 mg/l.

According to Sabbas et al. (2003) and Cornelis et al. (2008), solubility curves of oxyanion-forming elements such as As, Mo and Cr usually show a solubility decrease in alkaline ranges (>10). Here, solubility of Cr appeared to be reduced above pH 7, with similar detected concentrations for all the considered samples. With reference to sample B, in acidic conditions (below pH 6) the main contribution to leaching was given by the fractions >1mm.

Leaching of Ni resulted maximum in acidic conditions and lower in alkaline range. This counted especially for sample B, while sample A showed a flatter solubility curve. Contrasting with results from EN 12457-2 leaching test, in alkaline conditions solubility of Ni resulted to be higher for sample A than for sample B.

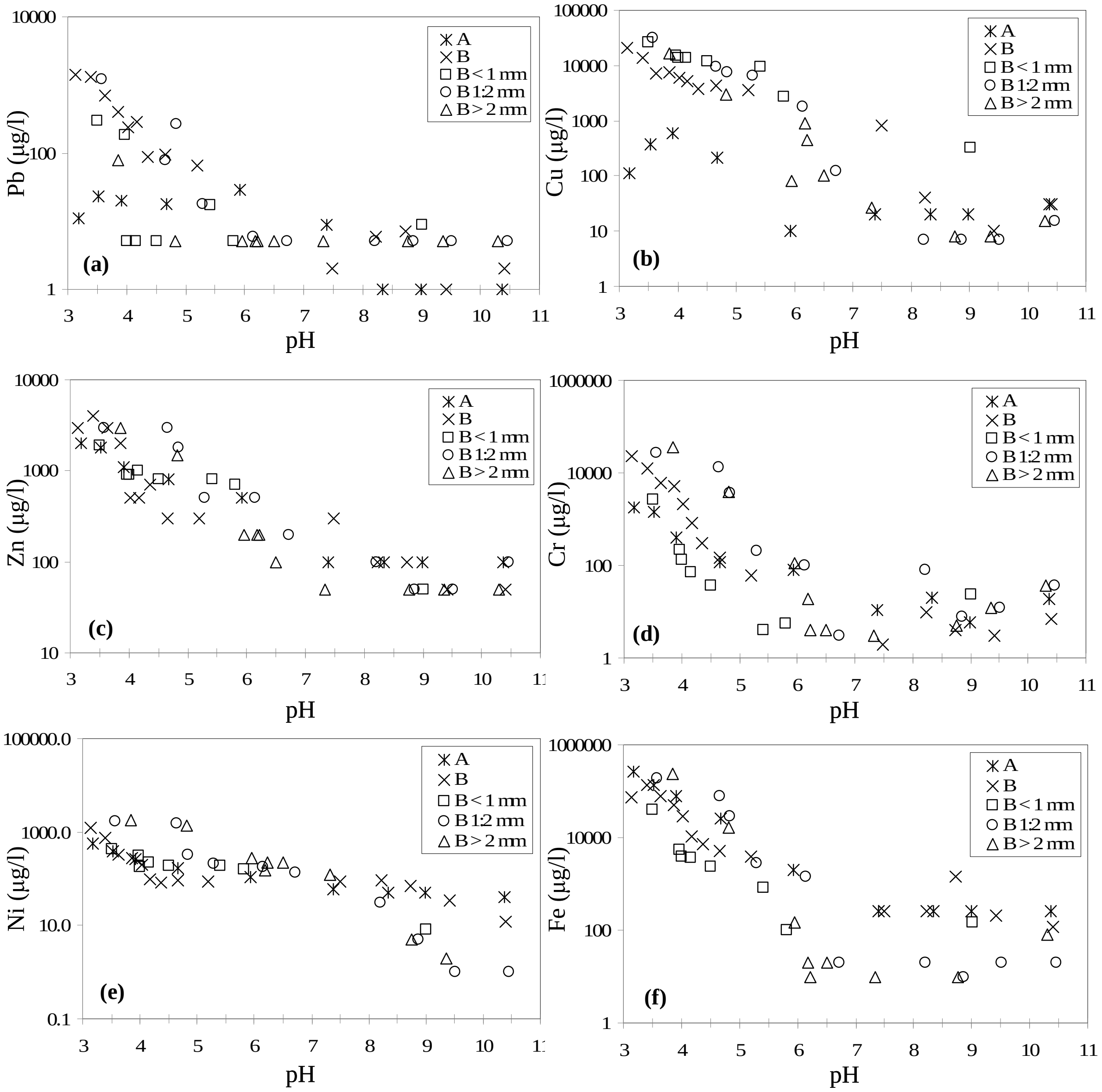


Figure 10: Heavy metals mobility for the whole samples A and B and for sample B size classes.

According to Stumm and Morgan (1996) and Dijkstra et al. (2006) Fe leaching curves generally approach a V-shape, with a minimum for pH values between 7-8. With reference to results depicted in Fig. 10, solubility of Fe was higher below pH 7 and almost constant above that pH value. In alkaline conditions, differently from results of EN 12457-2 leaching test, Fe concentrations detected in the eluates from sample A were higher respect to that from sample B. Concerning sample B, as observed for Cr, in acidic conditions the main contribution to leaching was given by the fractions >1mm.

For sample A, the increase in heavy metals leaching in alkaline conditions, compared to results from EN 12457-2 leaching test, could be explained by a tendency to a slow contaminants release. For sample B, in fact, concentrations detected in eluates from EN 12457-2 leaching test and from TS 14429 were comparable in alkaline conditions, confirming that the contaminants release was almost complete after 24 hours of contact.

2.4 Conclusions

The present chapter concerned the evaluation of the characteristics of BA from two municipal RDF high-temperature gasification plants, as a function of particle size.

Results from physical and mechanical investigations indicated that both samples could be classified as SP (clean and poorly graded sand) according to USCS and as A-1-a (rock, gravel and sand fragments, excellent to good road sub-base) according to HRB. Specific gravity was evaluated for sample B and found a little bit higher than characteristic soil values. Standard and modified compaction tests indicated that the dry weight of the materials was not much susceptible to moisture content changes, but it was, instead, sensible to higher compaction energy application.

Hazen formula provided an hydraulic conductivity of about $2*10^{-3}$ m/s. Comparing this result with that typical of soils, it was possible to assert the good water drainage of the material.

Chemical characterization showed a marked difference in behaviour and quality for the two considered residues. Since the two gasification plants were very similar, these differences could be attributed to the characteristics of the RDFs delivered, but also the wear of the furnace could have exerted some influences in terms of heavy metals content (Ecke et al., 2001; Kwak et al., 2006).

Metals and anions concentrations in leachates from sample A were always below the limits for reuse and inert waste landfilling.

For sample B the release of heavy metals appeared to be a limitation for reuse, but also, for some grain size fractions, for landfilling as inert waste. Italian law limits for not hazardous waste landfilling were always widely fulfilled.

Results from Availability test were representative of a glass fraction rich material, where the vitrified matrix, which is a consequence of high operating temperatures, leads to a reduction of surface area and to the trapping of heavy metals. Significant differences in availability between grain size classes were not noticeable for none of the considered elements.

ANC test showed titration curves characterized by a fast decrease of pH with increasing acid addition. For all the fractions subjected to analysis, the observed trend was characterized by the increase of heavy metals concentrations with pH decreasing and by a limited release in the alkaline pH range.

In the pH range of reduced release from 7 to about 9, the coarse fraction was the one with the lowest leaching, for almost all the considered metals.

The possibility of performing a size separation pre-treatment could be considered for sample B, which resulted to be the most contaminated. For this residue, even if a correlation between metals content and grain size, and above all between metals leaching and grain size is almost lacking, a size separation pre-treatment could be considered. This was true especially for Cu and Ni, by which the fraction between 0.5 and 0.105 mm resulted to be more contaminated. For Cr, this kind of treatment would have no effect on the leaching characteristics, which appear to be almost the same for each grain size, even if chemical composition indicated the finest fraction as the richest in this element.

Chapter 3: Natural ageing of MSW and wood waste incineration residues

This section investigates the effects of natural weathering on the characteristics of bottom ash (BA) from Municipal Solid Waste (MSW) and wood waste incineration in terms of mineralogy, heavy metals leaching and volume stability of the residues.

The materials were analyzed at different steps of treatment (fresh, 4 weeks and 12 weeks aged) and then all samples were characterized for their chemical and mineralogical composition, volume stability and both short as well as long term leaching behaviour of main elements and heavy metals.

The results from the experimental campaign indicated that MSWI bottom ash is more sensible to the weathering treatment than wood waste bottom ash: in the first case carbonation reaction caused almost the total dissolution of portlandite $Ca(OH)_2$ to form calcite ($CaCO_3$), while, for the second, portlandite was present in significant amounts and the pH of the eluates were above 12 even at the end of the 12 weeks of ageing treatment. Beneficial effects on leaching were observed for zinc and lead.

Furthermore, the 12 weeks ageing treatment resulted to be effective to guarantee the volume stability required by German law for reuse in road construction.

3.1 Introduction

In many European countries incineration plays an important role in waste management. High standard of emission control can be reached by modern flue gas cleaning technologies, consequently, the major part of the pollution potential is generally associated with the solid residues such as air-pollution-control (APC) residues and bottom ash (van der Sloot et al., 2001; Hyks and Astrup, 2009).

Many European countries (especially Germany, The Netherlands, France and Denmark) reuse a great part of MSWI bottom ash as secondary building material, in road sub-bases and in the construction of embankments. The opportunity of reuse this kind of residues necessitates a judgment of their short and long-term behaviour, concerning both environmental and technical aspects (Hyks and Astrup, 2009). In particular, the leaching of contaminants from bottom ash has received a growing attention over the years, and many leaching tests have been designed by regulatory agencies in order to comprehend the mechanisms of trace elements mobility and to simulate field leaching scenario (Chimenos et al., 2000; van der Sloot et al., 2001).

In order to comply with legal leaching limits there are several available options for treating MSW combustion residues: solidification, stabilization, vitrification, classification by granulometric size particles and ageing or weathering. The choice of the treatment depends on site specific conditions, utilization or disposal objectives and law requirements (Chimenos et al., 2000).

When an ash treatment method must be chosen, much attention must be payed to investments and operating costs. For this reason in EU countries, mainly in Germany, weathering of bottom ash for a period of 1-3 months before final disposal or utilization represents the most commonly employed method (Chimenos et al., 2000).

Bottom ash show a complex mineralogical composition consisting, mainly, of silicates, oxides and carbonates, as well as secondary phases like amorphous glass phases, iron metals and feldspars and trace substances as metals, alloys, sulphates and salts (Pfrang-Stotz and Reichelt, 2002). These amounts of trace metals and soluble salts vary daily, depending on the input of the household refuse; the sampling of freshly quenched stockpiled bottom ash is needed to assess the behaviour of these residues. Most of the high-temperature solids contained in incinerator bottom ash are metastable under atmospheric conditions because they are formed at high temperatures in the combustion chamber and then cooled rapidly via a quench tank. Therefore, under ambient conditions, and especially during the first three months of weathering, they undergo further mineralogical processes (Meima and Comans, 1997a; Chimenos et al., 2000; Pfrang-Stotz and Reichelt, 2002; Polettini and Pomi, 2004).

Weathering consists of several interrelated processes. Meima and Comans (1997) suggest that the main alteration processes consist of the hydrolysis of oxides of Ca, Al, Na, and K, dissolution/precipitation of hydroxides and salts of these cations, carbonation, and formation of clay-like minerals from glasses. During the carbonation process, atmospheric CO_2 is absorbed by the initially alkaline bottom ash; calcite ($CaCO_3$) thus formed precipitates until the material is in equilibrium with atmospheric $CO_{2.}$ pH decreasing causes also $Al(OH)_3$ and amorphous aluminosilicates to precipitate, because Al solubility is strongly reduced with the pH decrease from 10 to 8-8.5 (Meima et al., 2002).

Chemical and mineralogical changes caused by such processes greatly affect metal solubility as well as speciation.

Different studies have been performed towards MSWI bottom ash weathering processes (Zevenbergen et al., 1994; Meima and Comans, 1997a; Meima and Comans, 1997b; Meima and Comans, 1999; Chimenos et al., 2000; Freyssinet et al., 2002; Chimenos et al., 2003; Polettini and Pomi, 2004; Piantone et al., 2004; Rosende et al., 2008), however few data are currently available on the effect of this treatment on wood waste bottom ash.

In this chapter the results of the application of short term natural ageing to MSW and wood waste incinerator BA are presented. The relationship between pH values obtained and the leaching behaviour of the main trace elements are investigated, paying attention to the mechanisms of weathering and chemical reaction involved.

An evaluation of residues volume stability is also proposed.

3.2 Materials and methods

Four fresh bottom ash samples were collected from different plants situated in the south part of Germany. Two plants treated MSW (samples W1 and W2), while the other two were used for wood waste. The first biomass plant treated AI and AII categories wood waste (sample B1), while the other plant treated AI, AIII and AIV wood waste (sample B2). In all the considered plants the hot bottom ash is quenched in a water tank, immediately after incineration. Follow-up treatments include the removal of large pieces of unburned materials, the separation of magnetic particles, and size reduction by crushing. All these treatments require about three weeks.

Subsequently, bottom ashes are posed in storage piles for at least three months before reuse, in order to allow weathering reactions (Fig.1). Representative samples were taken from the new-created pile and then after 4 and 12 weeks (Fig.2). For sample W1 it was possible to have also a raw sample (taken before pre-treatments), while for W2 a 1.5 years weathered sample was taken too. Because of technical problems, the weathering process of sample W2 and B2 was conducted only for the first 4 weeks in the open air, while for the other 8 weeks it proceeded in a chamber at room temperature. During the laboratory-scale weathering, humidity was weekly checked and maintained about constant through addition of demineralised water.

All samples needed a pretreatment prior to analysis, such as subdividing and size reduction.

The metal scrap in BA were manually separated and then ash samples were subdivided using a riddle. A first size reduction down to <4mm or <1mm was carried out by means of a crusher before grinding. A subsample of about 200g of each BA sample was ground in a ball mill and sieved using a sieve with a mesh size of 0.125mm. Further subdivision was carried out in a rotating sample divider.

Fig.1: Bottom ash storage pile.

Fig.2: Sampling of bottom ash (a) and detail of the sampled material (b).

Bottom ash moisture was first determined by drying subsamples at 105°C for 24h. To detect elemental composition, each ground sample was digested using a HNO_3/HCl/HF mixture in a Teflon bomb heated in a microwave oven.

For each sample the 0.063-0.09mm fraction was then examined by X-ray diffractometry to identify the mineralogical composition.

Concerning the leaching characteristics, as regulatory tests, the EN 12457-4 and the EN 12457-2 procedures (in Germany and in Italy respectively adopted) were used. In order to study the long term leaching behaviour of the considered materials, the Availability Test (according to NEN 7371), a column test (according to EN 14405) and CEN/TS 14429 pH-dependence leaching test for evaluation of the Acid Neutralization Capacity (ANC) were carried out.

The Availability test is a pH controlled extraction test, which allows estimating the fraction of the total concentration present, which can be leached under natural conditions in the long term. The test consists of two successive extractions (of three hours each) of a finely ground (<0.125mm) sample, with a total liquid-to-solid ratio of 100. The suspension (ground sample and deionized water) is kept in agitation by means of a magnetic stirrer, and the pH value is kept constant to 7 (first extraction step) and 4 (second extraction step) by addition of 1M HNO_3 with an automatic titration apparatus.

Column test, instead, is a dynamic leaching test and simulates the time resolution of the leaching process. The leachant is pumped through a column filled with the residues (flow-through test). By collection of different amounts of the leachate, the liquid-to-solid ratio (L/S) is varied between 0.1 and 5 (for a cumulative value of 10) and the effect of rain or groundwater on the residues under the long-term scenario is simulated: analysis of the eluates at defined quotients between the volume of the water used for the column test and the quantity of the testing material, in fact, results in a temporal splitting of the elution process (Bergfeldt et al., 1997).

The ANC test is a leaching procedure that is able to provide information on the buffering capacity of a given material, its phase composition, as well as its leaching behaviour under different environmental conditions. In particular, the ANC test allows the resistance to acidification of the material to be investigated and the presence of solid phases that are stable to be determined and pH ranges to be identified

(Giampaolo et al., 2002). If the curve showing the pH of the final eluate is plotted as a function of the amount of acid added, then it can be regarded as a titration curve. If the slope of the curve decreases at some point (i.e., a plateau occurs) this can be ascribed to the presence of particular solid phases able to resist a decrease in pH (Giampaolo et al., 2002).

The resulting solutions were filtered and temperature, pH and Eh were measured. Clear filtrates were divided into two samples. One sample was acidified with concentrated HNO_3 and was used for the analysis of heavy metals in the leachate: Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Ba, Pb and As by Total Reflecting X-Ray Fluorescence Analysis (TXFA) and Cd, CrVI, Hg, Mo, Sb and Se by ICP-OES. The second sample was left untreated and subjected to ion chromatography in order to analyze chloride and sulphates. On the untreated samples from EN 12457-4 and EN 12457-2 also DOC, AOX, COD, phenol index and cyanide were measured.

In order to evaluate the volume stability of the considered materials at different steps of ageing, the M HMVA-StB 05 Mineralogical Test Method was applied.

3.3 Results and discussion

3.3.1 Characterization of the material and evolution of leaching behaviour during weathering

The chemical composition of the examined materials, reported in Table 1, indicates that the main trace elements were Ti, Cr, Co, Cu, Zn, Ba, Pb, Ni. According to their lithophilic behaviour Cu, Ni and Cr are among the trace elements present in waste combustion bottom ash (Polettini and Pomi, 2004). Ba and Cr are usually present in the same concentration level in all the residues (Hjelmar, 1996). Zn and Pb, which are more volatile elements, are usually enriched in the fly ash and acid gas scrubbing residues (Hjelmar, 1996). Also Ti and Co are present in significant amounts.

The course of natural weathering for each sample was monitored through the results of the leaching tests. The pH and the concentration of calcium and heavy metals in the leachate were measured and the results are shown in the corresponding figures (Fig. 3a and 3h).

The results of the EN 12457-2 and EN 12457-4 compliance test indicated that all the considered samples were alkaline in nature, with a pH between 11.2 and 11.8 for waste bottom ash and 12.5 and 13.1 for biomass bottom ash.

	W1				W2				B1			B2		
(mg/kg)	raw	fresh	4w	12w	fresh	4w	12w	1.5y	fresh	4w	12w	fresh	4w	12w
K	13900	12000	22700	13100	13000	36900	12000	10800	20100	19400	13800	21300	13800	14800
Ca	45400	73300	99500	144000	66600	150000	144000	152000	34200	61300	133000	70300	136000	128000
Ti	9100	3820	6920	6240	5370	14100	6360	7130	16800	12400	13100	6280	5940	6480
V	141	93	<70	n.d.	112	288	n.d.	n.d.	221	180	n.d.	323	n.d.	n.d.
Cr	429	415	1060	821	486	1650	547	684	159	269	616	1800	1160	958
Mn	1930	1240	2580	1010	1680	5480	929	1240	1790	1390	929	4670	1390	1860
Fe	31400	33300	63600	53600	52200	136000	54800	59000	10500	13700	16600	147000	70100	76400
Co	209	206	619	n.d.	504	1310	n.d.	n.d.	115	149	n.d.	1200	n.d.	n.d.
Ni	286	287	583	314	314	1200	157	236	149	176	236	1060	314	314
Cu	2210	968	2730	2720	1890	6540	1600	2880	931	697	719	724	1200	1360
Zn	4190	2300	5610	5300	3990	11200	4740	4980	3710	2090	2650	1760	2250	2010
As	45	<40	n.d.	n.d.	<40	n.d.	n.d.	n.d.	<40	n.d.	n.d.	<40	n.d.	n.d.
Rb	59	60	51	n.d.	<15	64	n.d.	n.d.	44	35	n.d.	61	n.d.	n.d.
Sr	232	709	357	338	528	623	423	338	371	303	423	290	338	338
Ba	2250	1790	2090	1790	2820	5910	2240	2330	4930	4390	3580	2090	3400	2960
Pb	1990	941	2520	1670	1200	3060	1300	2320	1900	1130	928	3890	2510	2140
C	18600	9300	8000	13400	17000	22900	19200	25200	11100	9500	11300	24000	21600	14700
S	6900	4900	5800	6000	5500	6100	4100	5500	2100	2900	3300	1500	1700	900
F	500	406	n.d.	n.d.	702	n.d.	n.d.	n.d.	399	n.d.	n.d.	141	n.d.	n.d.
Cl	4200	4770	n.d.	n.d.	3290	n.d.	n.d.	n.d.	1240	n.d.	n.d.	521	n.d.	n.d.

Table 1: Chemical composition of Bottom Ash samples used for this study (n.d. = not detectable).

The initial alkaline pH of bottom ash is related to the content of alkaline and alkaline earth elements and metal oxides, which form hydroxides during hydrolysis. The presence of $Ca(OH)_2$ is due to calcinations reactions at combustion temperatures in the furnace, involving calcite ($CaCO_3$), gypsum ($CaSO_4 \cdot 2H_2O$) or anhydrite ($CaSO_4$) to generate CaO, CO_2 or SO_2 in the reaction. During the quench treatment, most of the CaO is hydrolyzed and forms the corresponding hydroxide $Ca(OH)_2$ (Meima and Comans, 1997; Steenari et al., 1999; Chimenos et al., 2000; Polettini and Pomi, 2004; Piantone et al., 2004). XRD analysis from different authors (Meima and Comans, 1997; Kirby et al., 1993) as well as in this research (Table 2), showed the presence of calcite, gypsum and anhydrite in fresh quenched bottom ash, corroborating that they were not completely calcinated. Nevertheless, these minerals have very low solubility at a pH greater than 12 (Chimenos et al., 2000).

Concerning the fresh samples W1 and W2, if the solution pH were controlled by $Ca(OH)_2$, the pH would be approximately 12.3. Since the solution pH is lower (between 11.2 and 11.8), the solution is undersaturated with respect to the aforementioned phase (Johnson et al., 1995). The W1 raw sample, instead, has a pH of

12.4-12.8 and the eluates could be lightly oversaturated with respect to $Ca(OH)_2$. These pH values, however, could also be due to the presence of NaOH and KOH.

After 12 weeks, the W1 sample has still a pH between 11.4 and 11.7 and the leachates were undersaturated in portlandite. This results, coupled with data from XRD analysis, suggest that no significant amounts of $Ca(OH)_2$ were present in bottom ash.

		W1				W2				B1			B2		
Phase	Formula	raw	fresh	4w	12w	fresh	4w	12w	1.5y	fresh	4w	12w	fresh	4w	12w
Quartz	SiO_2	xx	xxx	xxx	xxx	xxxx	xxx	xxx	xxxx	xxx	xxx	xxx	xxxx	xxxx	xxxx
Haematite	α-Fe_2O_3	xx	xx	xx	xx	xx	xx	x	x	xx	xx	xx	x	x	x
Magnetite	Fe_3O_4	x	xx	xx	xx	xx	xx	xx	x	x	xx	xx	xx	x	x
Gehlenite	$Ca_2Al_2SiO_7$	xxx	xx	xx	xx	xx	xx	xx	xx	xxx	xx	xx	xx	x	x
Akermanite	$Ca_2MgSi_2O_7$	xx	xx	xx	xx	xx	x	xx	x	x	x	x	x	x	x
Kalifelspar	$KAlSi_3O_8$	xx	xx	xxx	xxx	x	x	x	x	xx	xx	xx	xx	x	x
Plagioclase	$(Na,Ca)[(Si,Al)AlSi_2O_8]$	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Diopside	$CaMgSi_2O_6$	x	x	xx	x	x	x	x	x	x	x	x	x	x	x
Halite	NaCl	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Apatite	$Ca_5(PO_4)_3(OH)$	xx	xx	xx	xx	xx	xx	x	x	x	x	x	x	x	x
Portlandite	$Ca(OH)_2$	x	x	n.d.	n.d.	x	x	x	n.d.	xx	x	x	xx	xx	x
Calcite	$CaCO_3$	xxxx	xxxx	xxxx	xxxx	xxx	xxxx	xxxx	xxxx	xxx	xxxx	xxxx	xxx	xxx	xxxx
Anhydrite	$CaSO_4$	xxx	x	xx	xx	x	x	x	x	xxx	xx	x	x	x	x
Gypsum	$CaSO_4 \cdot 2H_2O$	n.d.	x	n.d.	x	n.d.	n.d.	x	x	x	n.d.	x	n.d.	n.d.	n.d.
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$	x	x	x	xx	x	x	x	x	x	x	x	x	x	x

Table 2: Mineral phases detected with xrd analysis. xxxx = main constituent (>20%), xxx = minor constituent (10-20%), xx = accessories (5-10%), x = traces (<5%).

Sample W2 shows a pH after 12 weeks between 10.64 and 10.73. According to geochemical modeling from Polettini and Pomi (2004), a pure system containing the minerals gibbsite ($Al(OH)_3$), gypsum ($CaSO_4 \cdot 2H_2O$) and ettringite, have an equilibrium pH of about 10.33, which is close to the measured value. The pH of the 1.5 years old sample (between 8.7 and 9) can be reasonably well explained by the presence of calcite ($CaCO_3$). The completeness of the weathering process is typically characterized by pH 8.5, when the precipitation of calcite occurs and the material is in equilibrium with CO_2 (Meima and Comans, 1997; Polettini and Pomi, 2004; Rendek et al., 2007).

Wood waste samples have very high initial pH (between 12.9 and 13.1 for sample B1 and between 12.5 and 12.7 for sample B2). For both samples the elevated initial pH and the high concentration of leached calcium supports the assumption that pH is controlled by the solubility of $Ca(OH)_2$. Furthermore, according to the calcium concentration and the solubility of calcium hydroxide at this pH range, the solutions appear oversaturated, even if the possible presence of alkaline species as NaOH and KOH could explain the high pH values detected. The pH for samples B1 and B2 resulted to be still very high at the end of the ageing period.

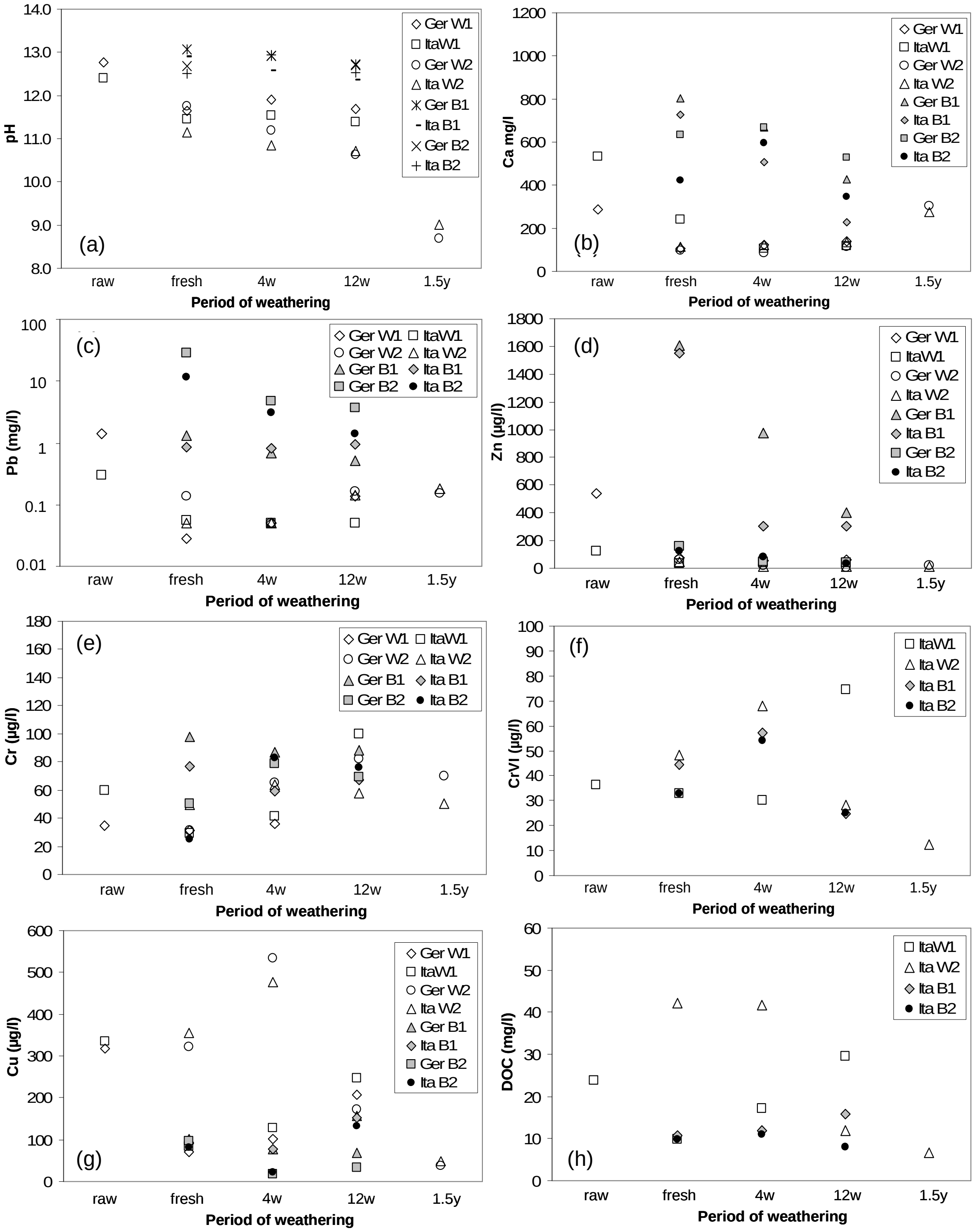


Fig. 3: pH (a) and leaching concentrations of Ca (b), Pb (c), Zn (d), Cr (e), CrVI (f), Cu (g) and DOC (h) from natural weathered bottom ash samples with time. Abbreviations are: Ger, German leaching test EN 12457-4; and ITA, Italian leaching test the EN 12457-2.

The solubility of lead is quite constant for the two waste bottom ash samples, despite the pH decrease. By contrast, the two wood waste bottom ash samples show a sensitive lead concentration decrease, especially for sample B2, which has an almost stable pH for the whole weathering period. The dissolved lead concentration obtained in all the samples studied shows an undersaturation with respect to lead hydroxide, anglesite ($PbSO_4$) and cerrusite ($PbCO_3$). Similar findings have been found by other authors (Chimenos et al., 2000).

The lower lead solubility may be a result of sorption processes and/or formation of more stable mineral phases (Kersten et al., 1997; Meima and Comans, 1997a; Chimenos et al., 2000). Meima and Comans (1998) and Polettini and Pomi (2004) supposed that low Pb leaching for naturally aged bottom ash could be related to the strong affinity of Pb towards surface complexation onto Fe and Al (hydr)oxides.

Chromium concentration in the leachates remains quite constant during all the weathering time and sometimes it tends to slightly increase. A predominant fraction of it is present as CrVI. Similar results have been found by Kersten et al. (1997).

Zn concentration shows a decreasing trend for all the considered samples. A good description of Zn concentration is provided by the solubility curve of willemite (Zn_2SiO_4), while zincite (ZnO) appears to be too soluble to explain Zn leaching at high pH (Dijkstra et al., 2006). Either surface precipitation or surface complexation mechanism of Zn onto bottom ash phases including Fe and Al (hydr)oxides may possibly explain the observed leaching behaviour (Polettini and Pomi, 2004).

As asserted by other authors (Chimenos et al., 2000; Meima and Comans, 1997a; Meima and Comans, 1999; Chimenos et al., 2003, Meima and Comans, 1998) the leaching of Cu from fresh MSWI does not seem to occur via a concentration-limiting mechanism. Furthermore, the dissolved Cu in leachates is strongly determined by the complexation with dissolved humic and fulvic acids, the major reactive components of dissolved organic C (DOC) in MSWI bottom ash leachates. The high degree of complexation of Cu with DOC is caused by the higher affinity of this metal for specific binding to humic substances, relative to Ni, Zn and Cd (Johnson et al., 1996; Dijkstra et al., 2006).

Cu concentrations are oversaturated with respect to $Cu(OH)_2$ for waste samples and undersaturated with respect to $CuCO_3$. Wood waste bottom ash, instead, have Cu concentrations undersaturated or comparable with $Cu(OH)_2$ solubility, but always quite constant with the evolution of the weathering process. It is interesting to note how the behaviour of Cu concentrations, for all samples, is always comparable to that of DOC concentration. Therefore, Cu solubility can be well explained by the complexation processes with dissolved organic C described above. The decrease in leachability of Cu and DOC observed for samples W2 and B2 can be explained by the adsorption of natural humic substances and copper complexes onto neo-formed aluminium (hydro)oxides (Rosende et al., 2008).

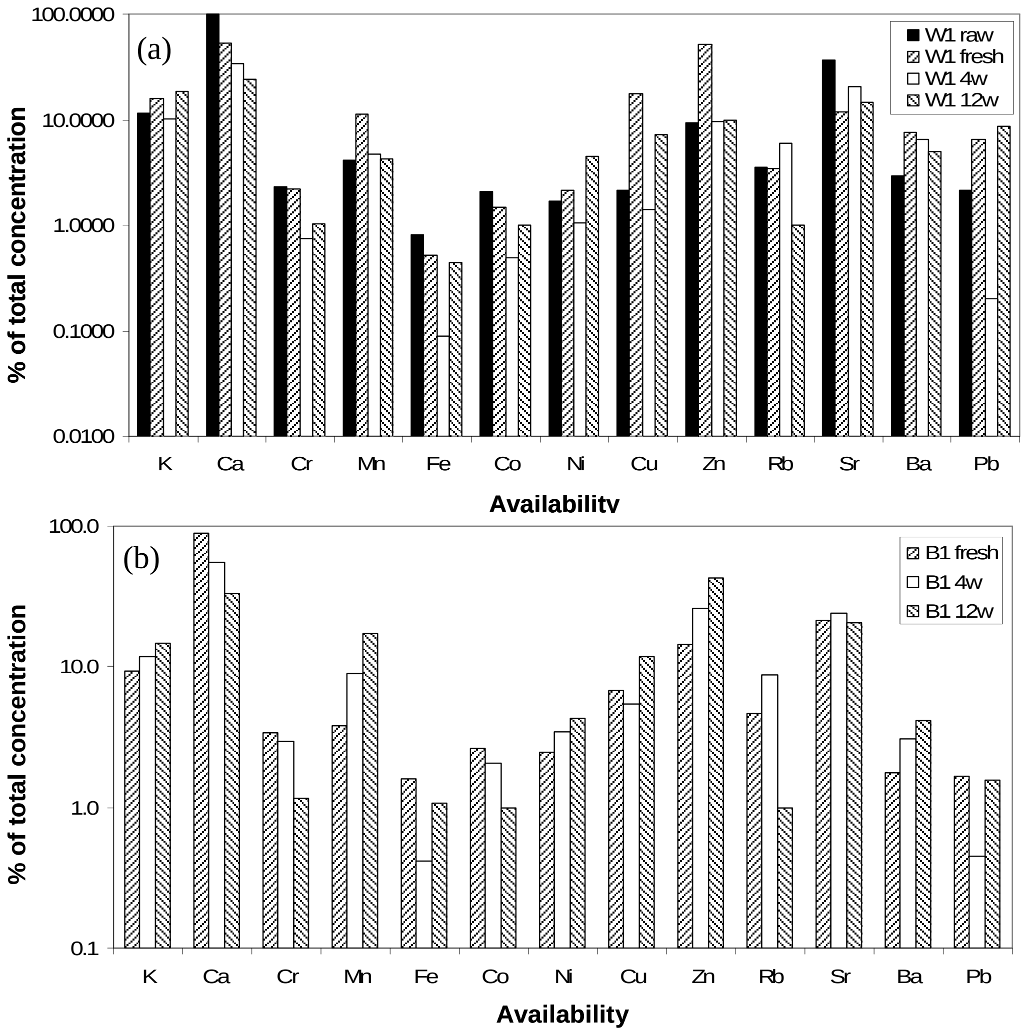


Fig. 4: Availability of main elements and metals normalized to total concentration for sample W1 (a) and B1 (b).

The leachate concentration of heavy metals is rather independent from its total content. More important is the availability of the metal, which is influenced by the particle surface area, the mineralogical environment of the metal and the mechanical stability of the particles. Figure 4 compiles the availability concentration of major elements for W1 and B1 samples at the different stages of weathering. Results show that only the availability of Ca, Cr, Co and Rb decreased with the advancing of the weathering treatment. For sample W1 the availability of Ni and Cu resulted to be increased, while for sample B1 the mobility of Ni, Cu, Mn, Zn and Ba was enhanced. The other considered elements did not undergo significant changes in availability.

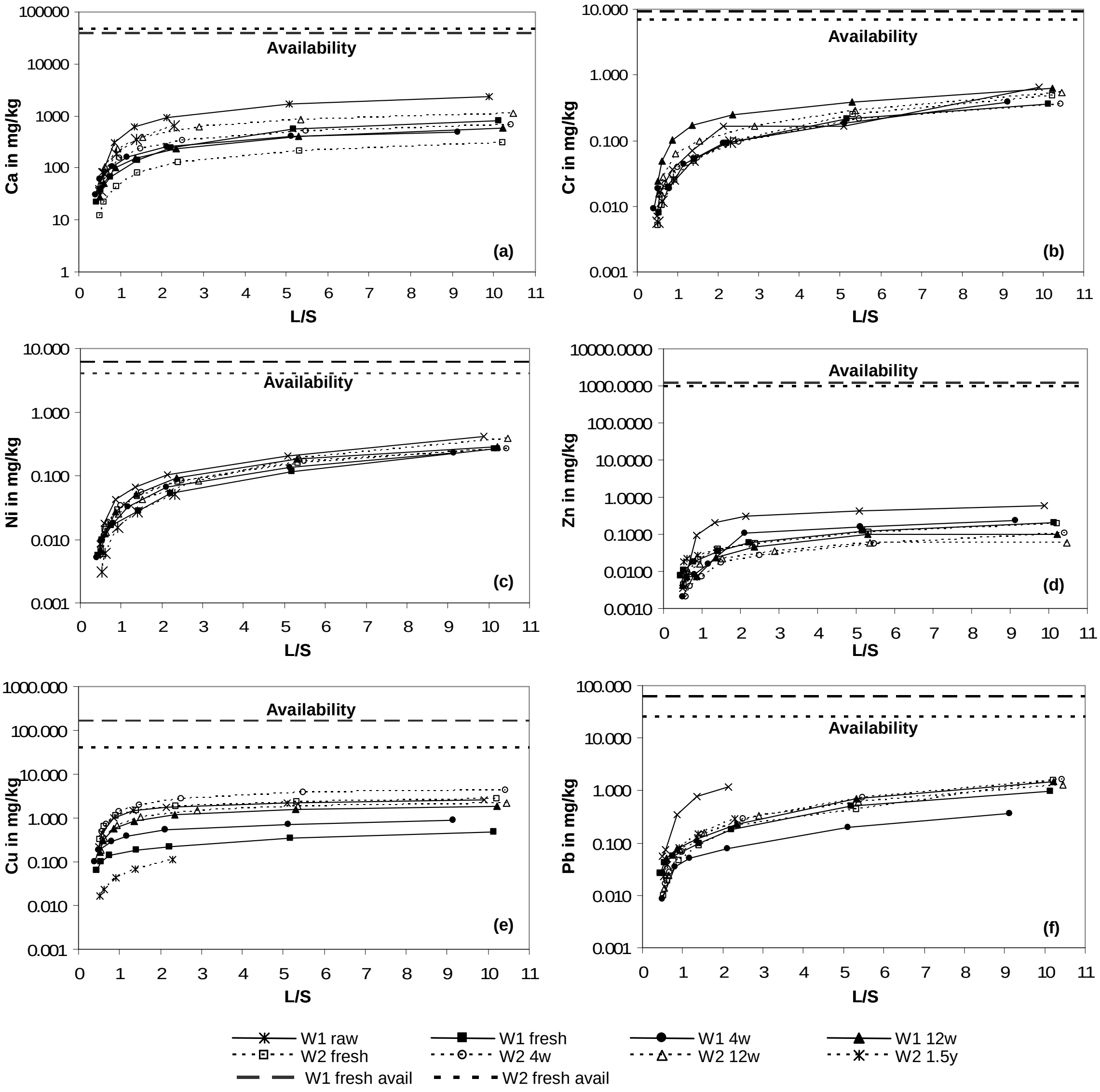


Fig.5: Availability and elution of Ca (a), Cr (b), Ni (c), Zn (d), Cu (e) and Pb (f) for samples W1 and W2.

Figures 5 and 6 report the results of column and availability test for Ca, Cr, Ni, Zn, Cu and Pb for all the considered samples; concerning the availability test only the results of the fresh materials are reported.

Results from column tests show that the leaching of calcium remains almost stable for all the considered samples. For sample W1 there is a little decrease, but the slope of the curves have only a very little reduction with the evolution of the weathering process, confirming that, even for the aged samples, leaching of Ca is not complete at a L/S of 10. Almost the same behaviour can be observed for the other samples.

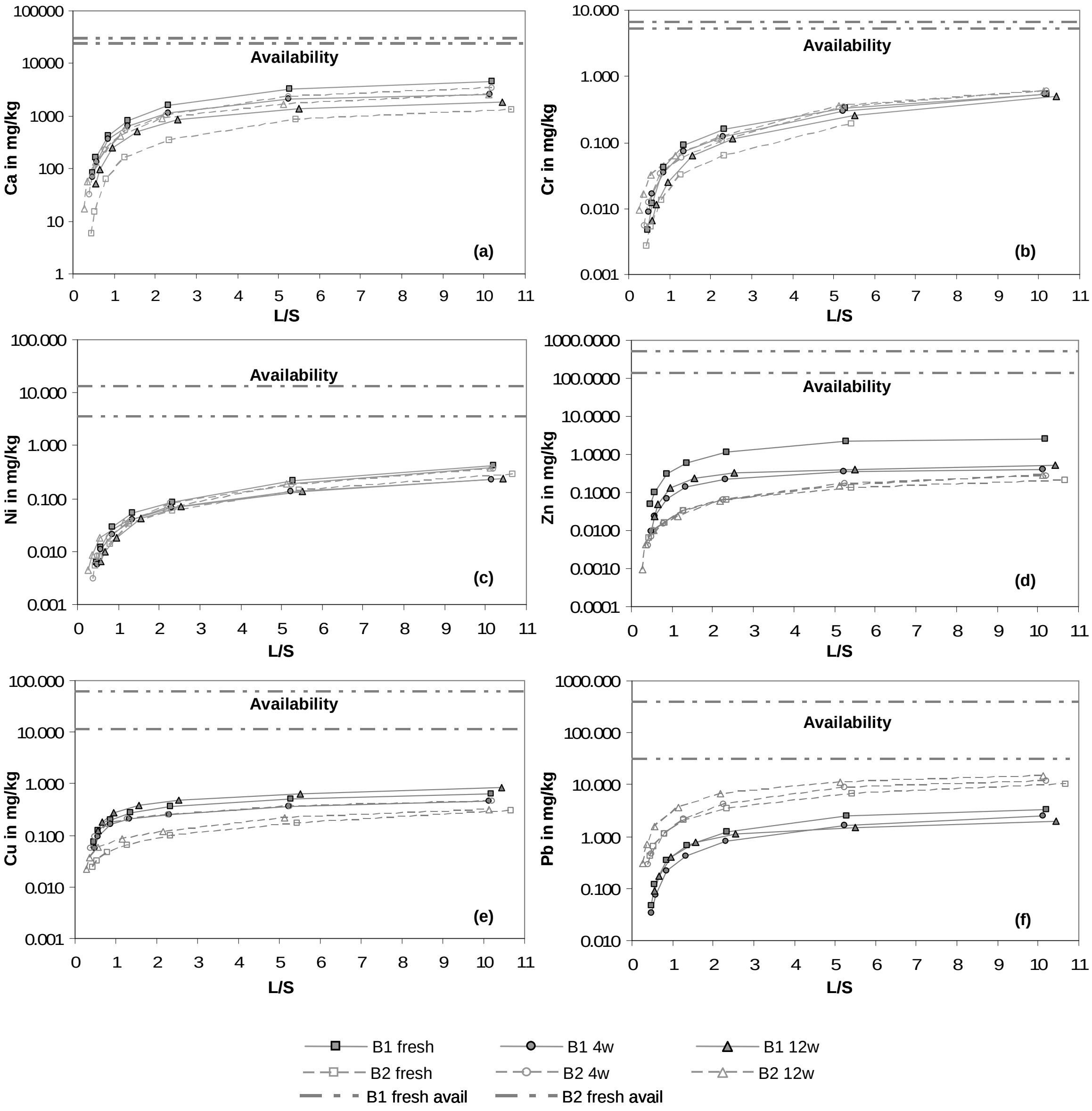


Fig.6: Availability and elution of Ca (a), Cr (b), Ni (c), Zn (d), Cu (e) and Pb (f) for samples B1 and B2.

Still with reference to results from column test (Fig. 7), a marked behaviour difference can be instead seen considering the Ca/SO_4 leaching ratio. For all samples, except W2, at the beginning of maturation there was a high Ca/SO_4 molar ratio with respect to gypsum and ettringite, so most calcium seemed to be provided primarily by non-sulphated species (Freyssinet et al., 2002). Sample W1 after 4 weeks reaches a molar ratio of about 2, showing a preferential release of calcium and sulphates by ettringite. The molar ratio of about 1 at 12 weeks, instead, would indicate leachate control by sulphates, in particular anhydrite and gypsum. Sample W2 has a stable Ca/SO_4 ratio of about 1 for the whole ageing period, probably due to significant presence of anhydrite. Wood BA samples, instead, show high Ca/SO_4 ratios for all the ageing period, probably due to the high presence of portlandite, even after 12 week of weathering treatment.

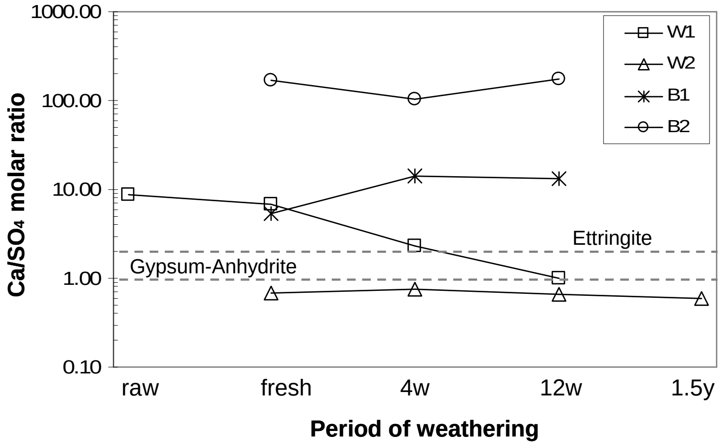


Fig.7: Kinetics of change of the Ca/SO_4 molar ratio.

For the other considered elements, column test confirmed the German and Italian leaching tests results: even if not all the analyzed elements are reported here, only Zn seems to be affected in a sensible way by the weathering treatment. For Zn it is possible to observe a general light decrease in leached concentration and the tendency of aged material to first complete the leaching.

3.3.2 Effect of weathering treatment on the Acid Neutralization Capacity (ANC) of the materials

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, haematite, etc.) and chlorides (Kirby and Rimstidt, 1993; IAWG, 1995; Eusden et al., 1999; Speiser et al., 2000).

As observed in the previous part of this chapter, the presence of $Ca(OH)_2$ in the bottom ash is due to the calcinations reactions of natural or synthetic calcite ($CaCO_3$), gypsum ($CaSO_4 \cdot 2H_2O$) or anhydrite ($CaSO_4$), generating CaO and CO_2 or SO_2. During the quench treatment, most of the CaO is hydrolysed, and forms the corresponding hydroxide $Ca(OH)_2$.

As asserted by Sabbas et al. (2003), as a consequence of quenching, calcium- and aluminium- containing phases can also dissolve and other minerals can be formed as a result of dissolution/precipitation phenomena; for instance, ettringite can be formed, according to the reaction:

$$\mathbf{6Ca^{2+} + 2Al^{3+} + 3SO_4^{2-} + 38H_2O \leftrightarrow 12H^+ + Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O_{(S)}} \quad (1)$$

Anhydrite, another phase that is widespread throughout the ash, can come from: (i) residual anhydrite, (ii) oxidation of the SO_2 due to high temperatures, (iii) hydrothermal processes, (iv) the oxidation of S (Clozel-Leloup et al., 1999). As asserted by Piantone et al. (2004), the presence of anhydrite instead of gypsum, which is thermodynamically expected in such an environment, is hard to explain: gypsum might be present in a poorly cristallized phase that cannot be detected with XRD. The alkaline environment created by portlandite and the presence of SO_4^{2-} ions is likely to foster the formation of ettringite, as long as there is Al available in the environment (Piantone et al., 2004).

In all the considered materials, XRD analysis (Table 2) showed portlandite to be present in the fresh samples. Samples B1 and B2 have high initial pH, which can be related to the presence of this mineral. In some cases, pH values higher than 12.3, which is the equilibrium pH for portlandite, could be due to the presence of alkaline species as NaOH or KOH. However, alkalis are not able to exert a buffering capacity, therefore a resistance to acidification is not related to their presence (Giampaolo et al., 2002).

Sample B1 show a first plateau corresponding to equilibrium pH of $Ca(OH)_2$ (Fig.8), which is visible for the fresh and the 4 weeks weathered samples, while it disappears for the 12 weeks sample. This plateau is also present for the fresh and 4 weeks aged sample B2, while, with the proceeding of the weathering treatment, according to XRD results, the $Ca(OH)_2$ content decreases, and the plateau is not visible any more.

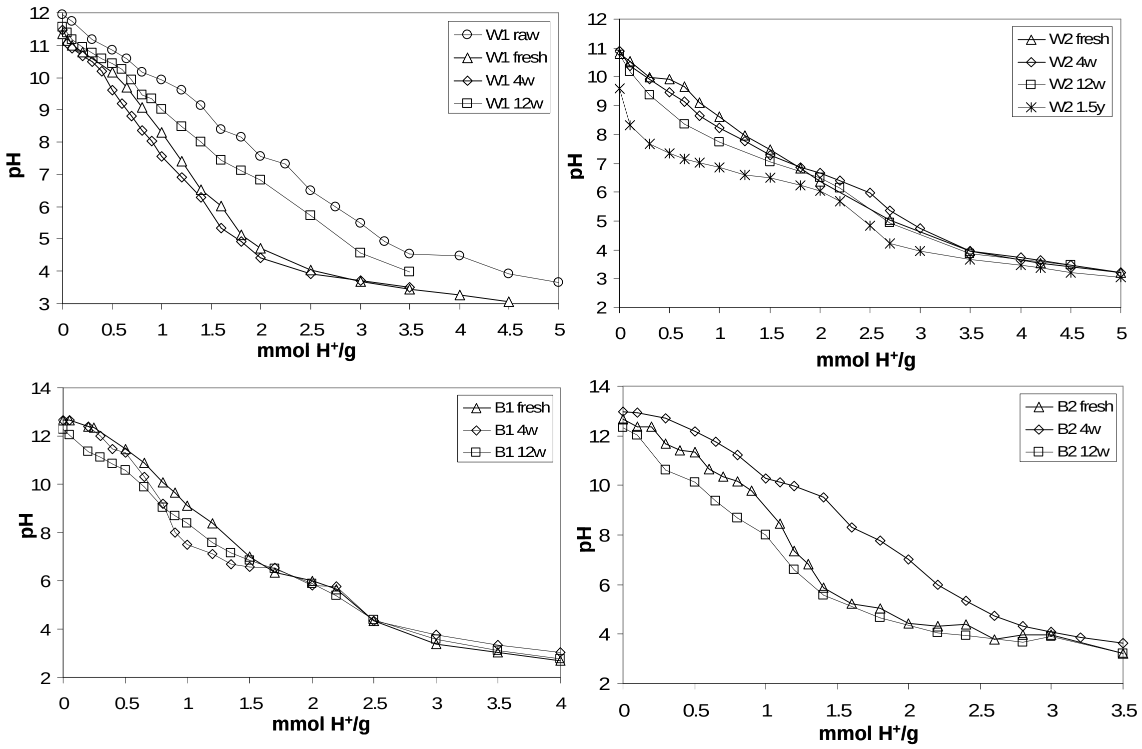


Fig. 8: ANC curves for all the considered samples.

The MSW samples have lower initial pH respect to biomass samples. Moreover, for both the considered materials, even if XRD results show that $Ca(OH)_2$ is present in the not aged samples, it is not possible to identify plateaus corresponding to the presence of the above mentioned mineral. In these cases, the absence of a clear plateau could indicate that the quantity is not enough to sensitively control the pH.

XRD analyses of carbonated MSWI BA (Meima et al., 2002; Polettini and Pomi, 2004) showed an increase in the amount of calcite and quartz, a decrease in corundum and the disappearance of ettringite upon both natural and artificial ageing.

Reasonably, calcite formed as a result of CO_2 uptake by the initially alkaline bottom ash. In addition, precipitation of calcite can be related to depletion in ettringite and anhydrite from fresh material, in that, according to mass-action law, precipitation of calcite requires the dissolution of other less stable Ca-containing minerals (Polettini and Pomi, 2004).

The presence of calcite have been revealed by XRD analysis in all the considered samples, with increasing amounts with the proceeding of the treatment, even if plateaus between pH 6 and 7 are noticeable only for samples W2 and B1.

In the 12 weeks weathering treatment sulphates reactions are also expected to occur. Bottom ash pH, in fact, is controlled largely by Ca minerals and pCO_2, but soluble Al and sulphates also play a role (Comans and Meima, 1994; Meima and Comans, 1997a). The dissolution of ettringite upon carbonation, which leads to the precipitation of gypsum, have been observed by several authors (Meima and Comans, 1997; Meima et al., 2002; Polettini and Pomi, 2004) and may result in increased sulphates leaching (Bodènan et al., 2000; Polettini and Pomi, 2004).

In the present study, it is possible to observe the depletion of ettringite and an increasing presence of gypsum only for sample W2. For this sample, with reference to figure 9, it is possible to see also a progressive enhanced leaching of sulphates with time. For the other samples ettringite slightly increased with time and sulphates leaching decreased or resulted almost stable, as if according to reaction (1). Gypsum was not detectable, or, at most, present in traces.

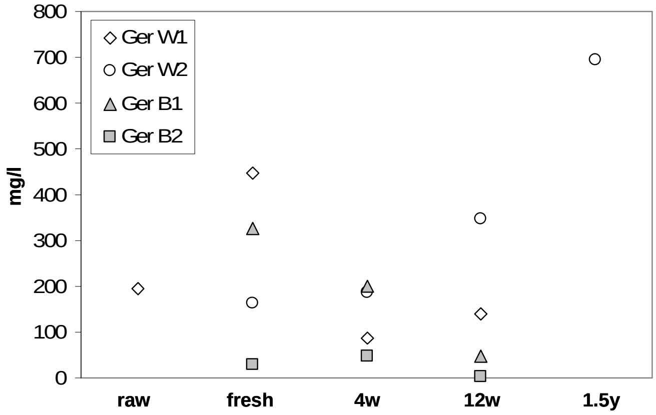


Fig. 9: Leaching of sulphates from natural weathered BA samples with time (EN 12457-4 test).

The presence of ettringite could explain the plateau corresponding about to pH 11 present in the titration curve of the 12 weeks weathered sample B1. With reference to such issue, Giampaolo et al. suggested that the stability values for ettringite are not as easily determined as it is for the other hydrated phases. Nevertheless, some investigators revealed the presence of crystalline ettringite at pH values from 11.5 to 11.8 and a noncrystalline phase similar in composition to ettringite for pH values from 12.5 to 12.8. Although the additional stability range of 9.8 to 11.2 has been proposed, recent findings seem to suggest that ettringite may not be stable at pH lower than 11.

Also the presence of a plateau at pH corresponding to pH 10-11, detected for the 12 weeks aged sample W1, could be explained by the effect of sulphates minerals. Chimenos et al. (2000) and Polettini and Pomi (2004), in fact, suggest that for a pure system containing the mineral gibbsite ($Al(OH)_3$), gypsum and ettringite, thought geochemical modeling it is possible to predict an equilibrium pH of about 10-10.5.

However, the fate of sulphates during carbonation process has not been fully explained. Fernandéz-Bertos et al. (2004) reported an increase in gypsum detected during XRD analysis; 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.

In all the considered samples, quartz was found to slightly decrease with the weathering treatment. This is in contrast with the findings by different authors (Freyssinet et al., 2002; Meima et al., 2002 ; Polettini and Pomi, 2004 ; Baciocchi et al., 2009), who detected the formation of quartz as a result of carbonation. Meima et al. (2002) explained its occurrence with the dissolution of calcium silicate and consequent precipitation of calcite, thus increasing the availability of silicate ions, which form quartz or amorphous aluminosilicates.

3.3.3 Effect of weathering and pH on element leaching

The results of the pH-dependence tests are reported below for Ca, Cr, Zn, Pb, Cu and Fe. As can be noted by comparing the results obtained separately on the four different samples, the leaching curves of the different elements were quite similar. Furthermore, the shapes of the leaching curves of most of the investigated elements were not appreciably modified by the weathering treatment.

For Ca a reduction in mobility was observed for samples W2, B1 and B2 (Fig.10). This effect was detected above pH 9 for the 12 weeks above mentioned aged samples and above pH 6.5 for the 1.5 years weathered sample W2. For this last sample, mobility reduction can be related to the formation of Ca carbonate phases, which present a lower solubility than Ca-hydroxide or -silicate phases, as indicated also by previous studies (Meima and Comans, 1997a; Polettini and Pomi, 2004; Dijkstra et al., 2006). For the other weathered samples the formation of ettringite is likely to be responsible for the lower Ca leaching because leachates are close to saturation with respect to this mineral at alkaline pH and ettringite was detected by XRD analysis in these samples (Meima and Comans, 1997a). In the acidic pH range Ca solubility appeared to be controlled by gypsum, irrespective of the age and the materials (Dijkstra et al., 2006; Polettini and Pomi, 2004).

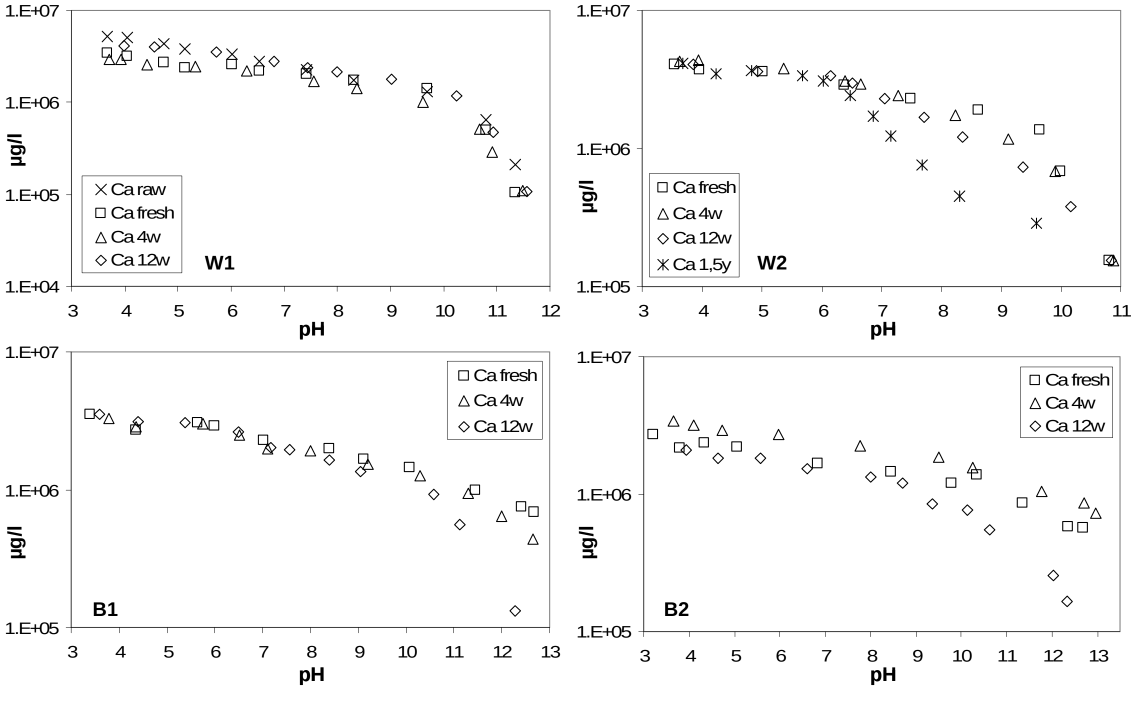


Fig.10: Measured concentrations of Ca as a function of pH

Due to the decrease in the natural pH of the slag caused by the weathering treatment, a slight enhancement of Cr release (Fig.11), in accordance with the results of the EN 12457 tests, was observed.

The decreasing solubility of Cr in alkaline ranges have been indicated by several studies (Paoletti, 2002; Chrysochoou and Dermatas, 2006; Van Gerven et al., 2005) to be due to the incorporation of oxyanion forming elements in ettringite or ettringite-like crystals by substitution of sulphates. For these pH values, solubility of Cr is also controlled by $BaCrO_4$ (Van Gerven et al., 2005). Ettringite has been shown to act as a host for various trace elements and oxyanions in particular (Gougar et al., 1996; Paoletti, 2002), but it can only persist at alkaline pH. When pH decreases, ettringite dissolves and sulphates and Cr come in the solution. Sulphates then precipitate with Ba, dissolving even more Cr. Furthermore, in acid conditions, oxyanions undergo sorption to amorphous Fe/Al-(hydro)xides (Meima and Comans, 1998; Paoletti, 2002; Van Gerven, 2005). This effect may lead to a decrease of their solubility in the leachate.

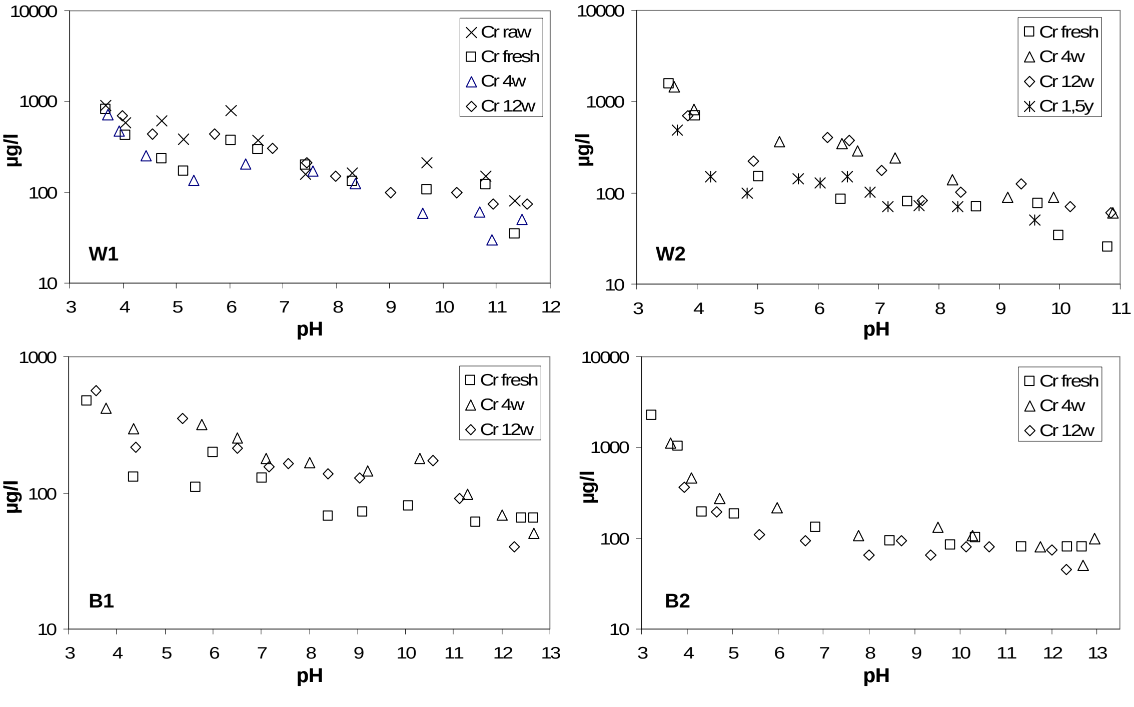


Fig.11: Measured concentrations of Cr as a function of pH

The leaching of Zn (Fig.12) is strongly dependent on the pH and the lowest concentrations are generally observed at pH 9.5. The increase in leachability at pH>10 is caused by the formation of soluble anionic zinc hydroxyl complexes. Zn solubility control, for which zincite (ZnO) has been suggested as a likely mineral controlling Zn leaching, causes a minimum leachability of Zn at pH 9-10 (van der Sloot et al., 1996). In all the considered materials, however, zinc was found to be undersaturated with respect to both zincite and Zn hydroxide. The same undersaturation was also found by other authors (Meima and Comans, 1999; Polettini and Pomi, 2004; Dijkstra et al., 2006). Polettini and Pomi (2004) supposed that either surface precipitation or surface complexation mechanisms onto bottom ash phases including Fe and Al (hydr)oxides may possibly explain this leaching behaviour. Dijkstra et al. (2006) asserted that, as well as by surface precipitation, another adequate description of Zn concentration is provided by the solubility curve of willemite (Zn_2SiO_4).

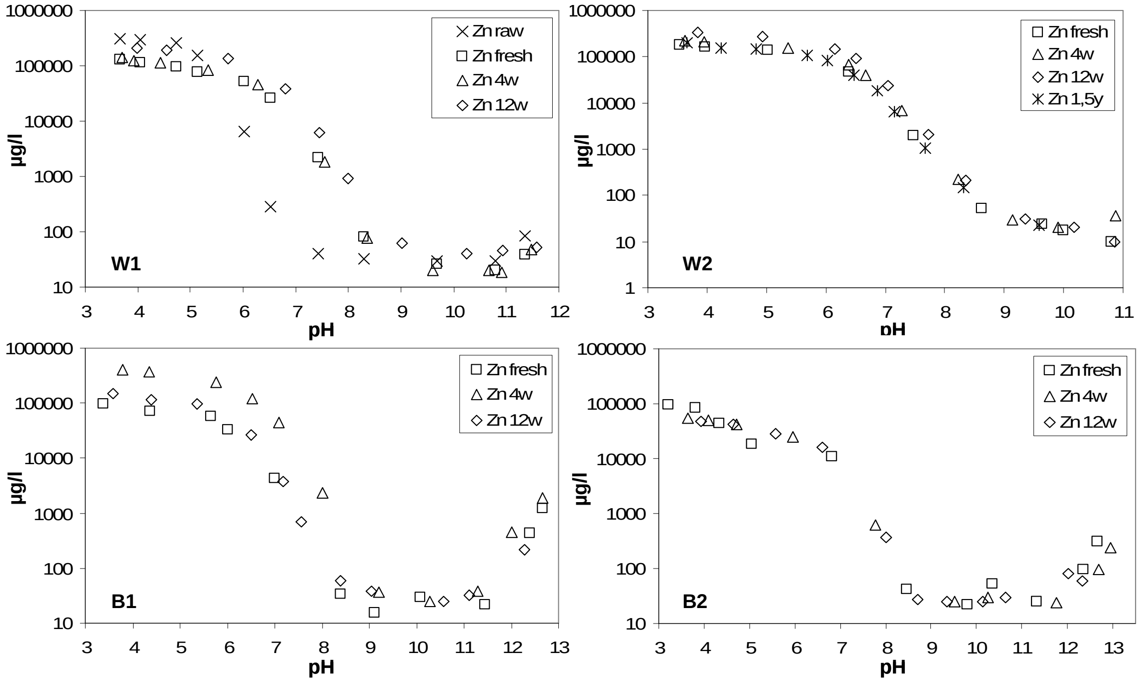


Fig.12: Measured concentrations of Zn as a function of pH.

The leaching of Pb (Fig.13) resulted to be relatively pH-independent in a wide range of pH. This leads to exclude solubility control by a pure mineral phase, rather indicating the occurrence of sorption mechanisms (Kersten et al., 1997; Meima and Comans, 1999). Dijkstra et al. (2006) also found model curves for Pb based on surface complexation to follow adequately the experimental data, while both hydrocerrusite ($Pb_3(CO_3)_2(OH)_2$) and cerrusite ($PbCO_3$) were found to be too soluble to explain the observed Pb concentrations. Similar to Cu, complexation of Pb with DOC is important (Dijkstra et al., 2006).

In the case of Cu (Fig.14), all the bottom ash leachates resulted to be oversaturated at high pH and undersaturated at low pH with respect to tenorite (CuO) and Cu hydroxide ($Cu(OH)_2$). Similar results have been found by Meima et al. (2002) and Polettini and Pomi (2004).

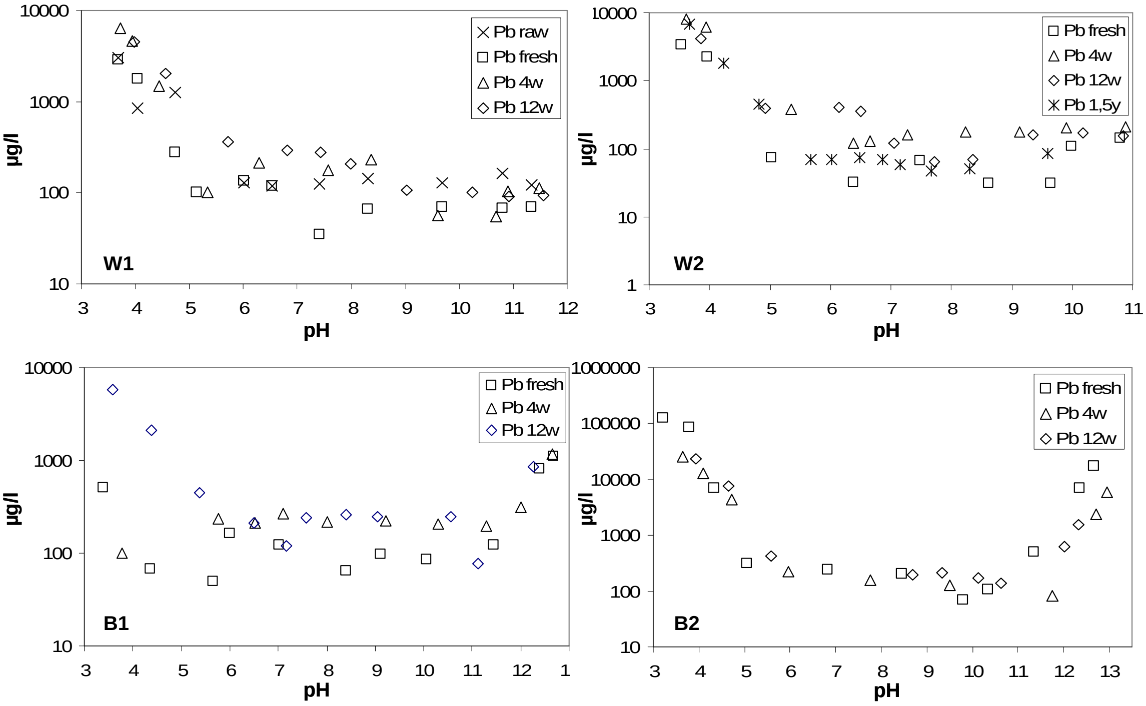


Fig.13: Measured concentrations of Pb as a function of pH

Speciation modeling 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 complexation with fulvic acids (FA) 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 (Meima et al., 2002; Dijkstra et al., 2006). Arickx et al. (2009) investigated the amounts of reactive Fe/Al (hydr)oxides in bottom ash samples during three months of natural weathering treatment. For amorphous Fe they concluded that no increase occurs, while Al (hydr)oxides increased considerably.

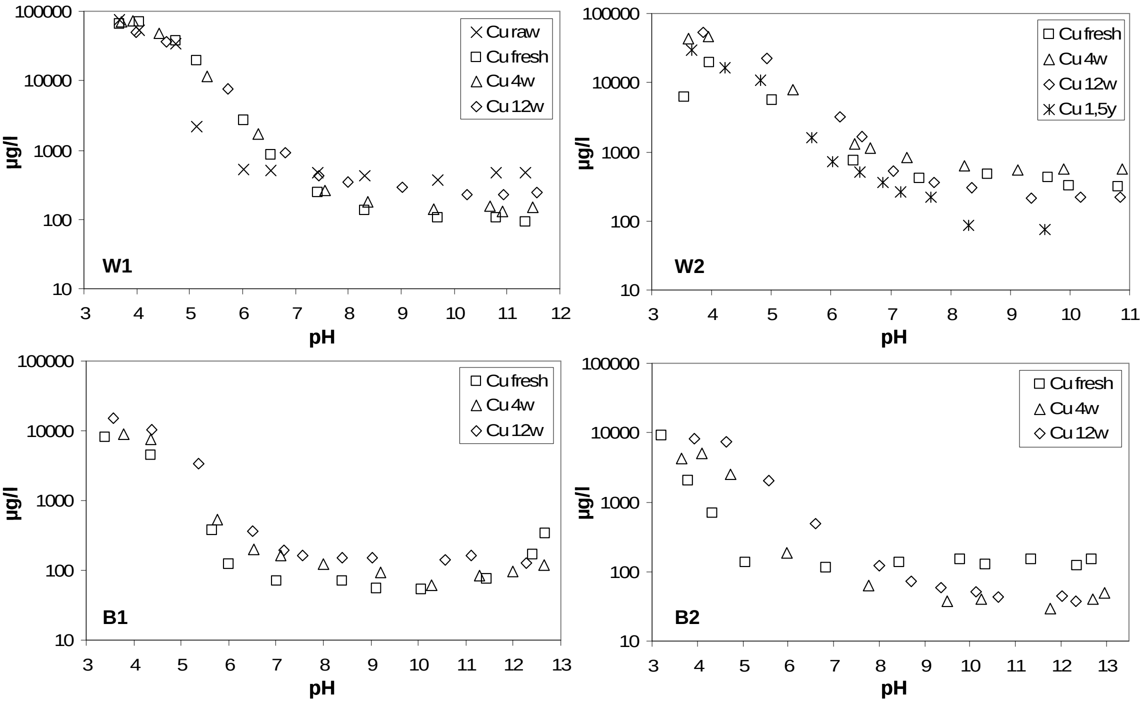


Fig.14: Measured concentrations of Cu as a function of pH.

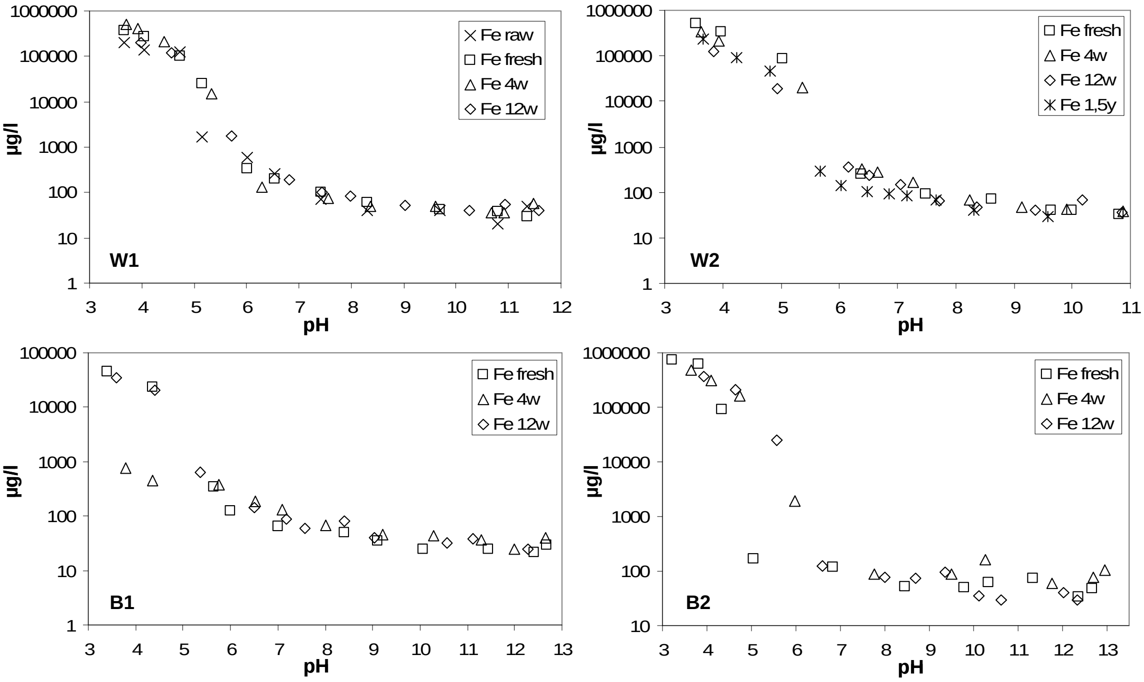


Fig.15: Measured concentrations of Fe as a function of pH.

Provided that fulvic acids (FA) is the Cu controlling factor for enhanced Cu leaching, due to the formation of Cu-FA complexes, stronger adsorption of FA to Fe/Al (hydr)oxide in the solid phase, due to a decrease in pH and neoformation of Al (hydr)oxide, causes a decrease in Cu leaching. Meima et al. (2002), in addition, observed that the leaching of Cu from naturally weathered and carbonated MSWI bottom ash is considerably lower than that of artificially carbonated. In the long term, the oxidation of Fe particles and the transformation of glasses via allophane-like mineral into clay minerals, for example, will result in the formation of additional sorption sites (Zevenberger et al., 1994; Meima and Comans, 1999).

Fe leaching curves generally approach a V-shape an is characteristic for the solubility of Fe(hydr)oxides such as ferrihdrite ($Fe(OH)_3$) (Meima and Comans, 1997a; Dijkstra et al., 2006).

3.3.4 *Effect of weathering on volume stability*

Among the various applications proposed for weathered bottom ash, e.g., sound barrier, fills, or embankment, in view of the composition of this material and its physical properties, two main uses have predominated: as unbound road construction materials and as an aggregate in concrete (Chimenos et al., 2005).

However, the neoformed phases, as well as other chemical reactions that take place during the natural weathering of bottom ash, induce expansions and pavement cracking and must be taken into consideration prior to bottom ash utilization. Four main causes of bottom ash swelling can be listed:

- <u>formation of gel from oxidation of metallic aluminium</u>

At high pH (>10), the metal is dissolved with emission of hydrogen. This reaction can occur when there is contact between metal and water or OH^- ions:

$$\mathbf{4Al + 4(OH)^- + 4H_2O \rightarrow 6H_2 + 4AlO_2^-}$$

However iron reduction could end up the same results. In fact, many studies showed expansion near iron particles (Alkemade et al., 1994). When the pH goes down to 9-10, aluminium hydroxide forms a $Al(OH)_3$ gel:

$$\mathbf{AlO_2^- + 2H_2O \rightarrow Al(OH)_3 + OH^-}$$

- <u>ettringite formation</u>

This reaction takes place when the material is saturated with water

$$\mathbf{Al_2O_3 + 3CaSO_4 + 3Ca(OH)_2 + 28H_2O \rightarrow (CaO)_2(Al_2O_3)(CaSO_4)_3(H_2O)_{31}}$$

- lime and magnesium oxide hydration

The free calcium oxide and magnesium oxide cause instability by their transformation into hydroxide.

$$\mathbf{CaO + H_2O \rightarrow Ca(OH)_2}$$

$$\mathbf{MgO + H_2O \rightarrow Mg(OH)_2}$$

The resulting expansion appears less important than the two other mechanisms (Pecqueur et al., 2001).

- anhydrite hydration to form gypsum

On of the most important volume increasing reaction is the hydration of anhydrite to form gypsum:

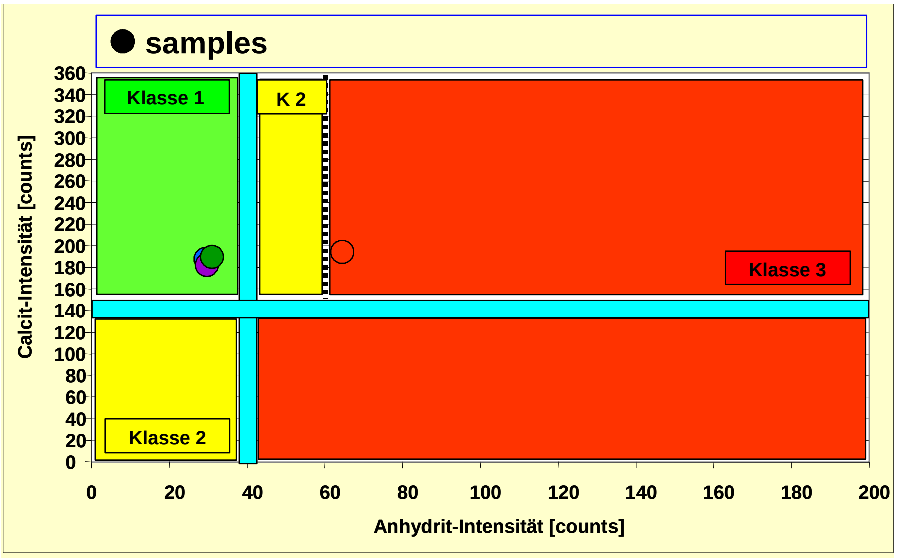
$$\mathbf{CaSO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O}$$

This reaction has an associated volume increase up to 63%.

In this work, in order to evaluate the volume stability of the considered materials, the mineralogical test method was used (M HMVA-StB 05). This method is part of the German quality control system for using aggregates in road construction since 2005.

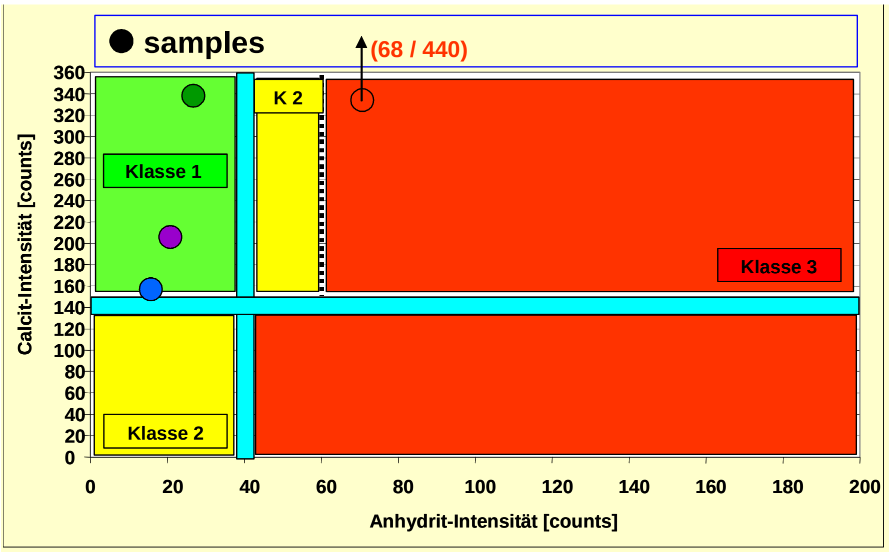
The mineralogical method is based on the determination of characteristic x-ray reflexions of mineral phases which characterizes the alteration stadium. Anhydrite and calcite are assumed as index minerals, while portlandite, ettringite and gypsum as additional index minerals. The determined intensities of calcite and anhydrite are reported in the classification diagram, which allows an evaluation of the volume stability with reference to technical using of bottom ash.

Figures 16-19 report the diagrams for all the considered materials. In the following diagrams class 1 indicates the possible utilization of bottom ash without restrictions; class 2 indicates the possibility of reuse bottom ash but with restrictions; class three indicates that the utilization of bottom ash is not possible.



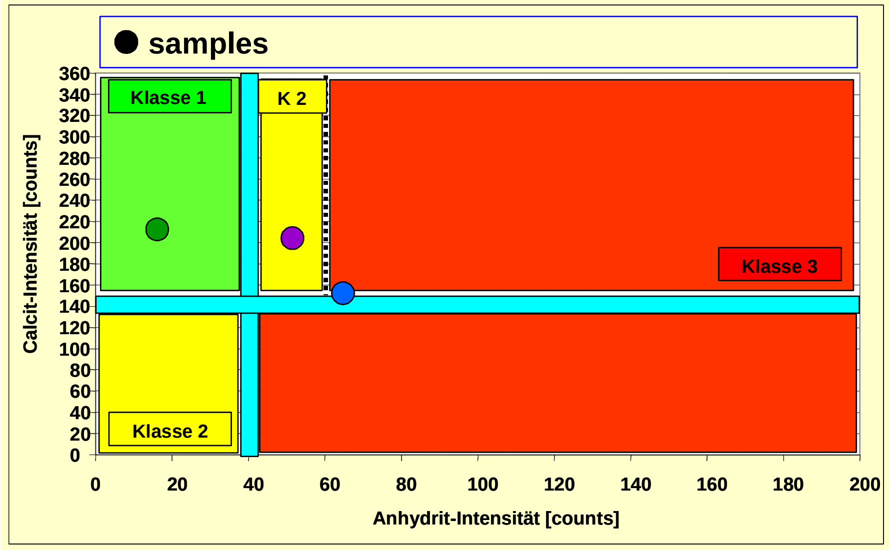
🔴	W1	raw bottom ash 10.02.2009:			anhydrite/calcite = 62 ct / 195 ct
🔵	W1	bottom ash	10.02.2009	fresh:	anhydrite/calcite = 24 ct / 187 ct
🟣	W1	bottom ash	10.03.2009	4 weeks:	anhydrite/calcite = 25 ct / 182 ct
🟢	W1	bottom ash	05.05.2009	12 weeks:	anhydrite/calcite = 33 ct / 198 ct

Fig.16: Volume stability diagram for sample W1



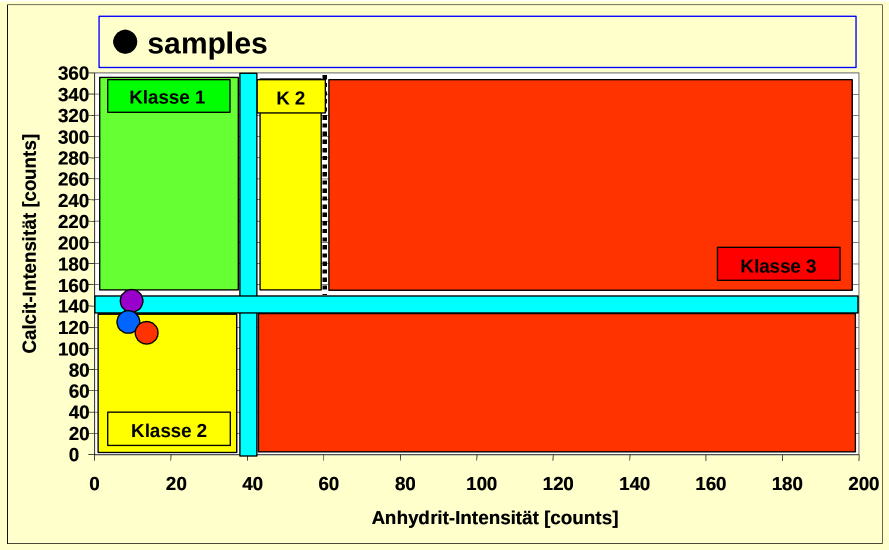
🔵	W2	bottom ash 18.02.2009	fresh:	anhydrite/calcite = 17 ct / 158 ct
🟣	W2	bottom ash 17.03.2009	4 weeks:	anhydrite/calcite = 20 ct / 208 ct
🟢	W2	bottom ash 17.06.2009	12 weeks:	anhydrite/calcite = 23 ct / 340 ct
🔴	W2	bottom ash (different material)	1 year:	anhydrite/calcite = 68 ct / 440 ct

Fig. 17: Volume stability diagram for sample W2



● B1 biomass ash 18.02.2009 fresh: anhydrite/calcite = 62 ct / 152 ct
● B1 biomass ash 17.03.2009 4 weeks: anhydrite/calcite = 52 ct / 203 ct
● B1 biomass ash 14.05.2009 12 weeks: anhydrite/calcite = 18 ct / 212 ct

Fig. 18: Volume stability diagram for sample B1



● biomass ash 18.03.2009: B2 fresh anhydrite/calcite = 16 ct / 118 ct
● biomass ash 23.04.2009: B2 4 weeks anhydrite/calcite = 13 ct / 141 ct
● biomass ash 22.06.2009: B2 12 weeks anhydrite/calcite = 22 ct / 275 ct

Fig. 19: Volume stability diagram for sample B2

At the end of the 12 weeks of weathering treatment, almost all the considered samples resulted be in class 1, so with possible utilization without restrictions. 1.5 years old W2 sample did not accomplish the mineralogical characteristics, while sample B2 resulted in improved volume stability characteristics, even if the characteristics of class 1 material were not completely fulfilled.

3.4 Conclusions

The present study showed the effect of short-term natural weathering treatment on the mineralogical, chemical and physical properties of MSW and biomass bottom ash, in terms of type of mineral phases, pH, leaching behaviour and volume stability.

Lead, zinc and copper were the main heavy metals to be released from the considered samples. After 12 weeks of weathering treatment, the concentration of leached zinc fell dramatically, while for lead, it was possible to observe a concentration decrease only for the biomass samples. Lead concentrations seemed to be independent of the pH of the bottom ash and undersaturated if compared to lead hydroxide, anglesite and cerrusite. Solubility of lead seemed to be a result of sorption processes and/or formation of more stable minerals. Cu leaching was well described by complexation processes with dissolved organic C. For the others contaminants studied no beneficial effect for leaching was observed. Availability and column leaching tests confirmed the above mentioned results.

ANC test permitted to carry on a deeper analysis of the weathering process, with particular reference to mineralogical transformation and behaviour of heavy metals.

The results from the experimental campaign indicated that allowing weathering reaction to proceed result in improved stability of the material, even if, contrasting with previous works from other authors (Chimenos et al., 2000; Chimenos et al., 2003; Pfrang-Stotz and Reichelt, 1997), the considered 12 weeks period appeared to be insufficient to comply with leaching law limits, especially for biomass samples.

On the contrary, the treatment resulted to be effective in order to comply with law limits concerning volume stability.

Chapter 4: Natural ageing of gasification residues

On the basis of the main results of previous studies, which were overviewed in Chapter 3, natural weathering treatment was applied to RDF high-temperature gasification residues in order to investigate the potential changes of the leaching characteristics of this material.

The study was conducted on a single bottom ash (BA) sample and, with reference to the results reported in Chapter 2, on different grain size fractions, in order to investigate the effect of weathering treatment for each grain size class.

The materials were analysed at different steps of treatment (fresh, 4 weeks, 8 weeks and 12 weeks).

At the end of the weathering treatment it was possible to observe a one point pH decrease and a beneficial effect on amphoteric elements leaching, such as Pb and Zn.

As regards oxyanion forming elements, such as Cr, weathering confirmed to have not a beneficial effect, with an increasing in Cr leaching for all the considered size classes.

After the treatment, Cr and Cu still resulted to be the most critical elements in view of recycling or landfilling as inert waste, especially with regard to the finest fraction.

4.1 Introduction

Although landfill remains the dominant disposal method for municipal solid waste (MSW), many industrialized countries are increasingly considering waste incineration to be a viable alternative. This is because in many parts of the world readily available landfill void space is becoming exhausted and there are often significant problems associated with locating new landfill sites (Bethanis et al., 2002). Although incineration in modern energy from waste plants reduces the volume of municipal solid waste (MSW) by up to 90%, it still produces significant quantities of residues (Cheeseman et al., 2005; Ferraris et al., 2009).

Solid waste management in industrialized countries increasingly aims to reduce the amount of waste requiring landfill, by developing viable reuse applications, so that wastes are beneficially used as resources (Chang et al., 1999; Woolley et al., 2001). Given the possible increasing reliance on waste incineration, developing new, higher value reuse applications for this material is an important research area. Beneficial reuse of wastes in construction replaces materials that would otherwise need to be extracted from the environment and this has associated sustainability benefits. In addition, key drivers such as the increasing costs of waste disposal and extraction of natural aggregates are making processing wastes such as BA into new construction products potentially viable (Cheeseman et al., 2005).

In order to reuse this kind of residues, a judgment of their short and long term behaviour, concerning both environmental and technical aspects must be given (Kirby and Astrup, 2009). To this purpose, in order to comply with leaching law limits, several option for treating MSW combustion residues have been developed, among which solidification, stabilization, vitrification, classification by granulometric size particles and ageing or weathering.

Melting of BA at high temperature reduces the availability of Cr, Cu, Zn and Pb for leaching as the formation of glassy material decreases the surface area and entraps the metals within the amorphous glassy matrix (Ecke et al., 2009; Ferraris et al., 2009). Hence, the utilization of vitrified BA is expected to decrease the environmental drawbacks.

Moreover, Zevenbergen et al. (1997) highlighted how microanalytical observations revealed that the BA matrix, which consists primarily of glasses that cover a large compositional range, is not chemically inert but ‘thermally activated’. Glass weathering may have important implications for the geochemistry of contaminants in a MSWI bottom ash disposal environment and must therefore be taken into account in assessing the environmental impact of these residues.

In this chapter the results of the application of short term natural weathering to RDF gasification BA are presented. The relationship between pH values ad the leaching behaviour of the main trace elements was investigated, with reference to different grain size classes.

4.2 Materials and methods

The considered BA sample was collected from a high temperature fixed-bed gasification facility. This plant was fed with RDF and employed pure oxygen as oxidant factor. It operated at atmospheric pressure, with a maximum temperature of about 1600°C.

Sampling was carried out immediately after quenching and performed through quartering and additional quartering steps in order to derive homogeneous and representative samples to undergo the laboratory analysis. Natural weathering was carried out with a sample of about 150 kg in a chamber at room temperature for three months (Fig. 1). During this period humidity was weekly checked and maintained about constant through addition of demineralised water. Representative samples were taken of the fresh material and after 4, 8 and 12 weeks.

Fig.1: Bottom ash laboratory-scale weathering.

Chemical characterization of BA involved determination of chemical composition and leaching behaviour.

All samples needed a pre-treatment prior to analysis, such as subdiving and size reduction. Subdivision into three grain size classes (>2mm; 1-2mm; <1mm) was performed through sieving with stainless steel sieves. Size reduction for leaching tests and chemical characterization was carried out by a ball mill.

To detect chemical composition, each ground sample was digested using a

HNO_3/HCl/HF mixture in a Teflon bomb, heated in a microwave oven. The samples were then analysed to determine the concentrations of the following metals: Pb, Cu, Zn, Cd, Cr, Ni, Mn, Fe and As.

As regards leaching characteristics, the UNI EN 12457-2 batch leaching test was carried out and the results were compared with the Italian law limits for reuse (M.D. 186/06) and inert waste landfilling (M.D. 201/05).

In order to provide informations about the long term leaching behaviour, the Availability Test (according to NEN 7371) and CEN/TS 14429 pH-dependence leaching test for evaluation of the Acid Neutralization Capacity (ANC) were carried out.

The Availability test is a pH controlled extraction test, which allows estimating the fraction of the total concentration present, which can be leached under natural conditions in the long term.

The ANC test is a leaching procedure that can provide informations on the buffering capacity of the material, its phase composition, as well as its leaching behaviour under different environmental conditions.

Metals concentration in the eluates was detected with Atomic Absorption Spectrophotometry (AAS) through Perkin Elmer Analyst 200 and with Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS) through Perkin Elmer HGA 700 with AAS Perkin Elmer 1100 B. Anions concentrations were detected with Ion Cromatography through Dionex ICS 1000.

All measurements were conducted at least in double, with the exception of the ANC test, which was run on a single replicate.

4.3 Results and discussion

The chemical composition of the examined material, reported in Table 1, indicates that the main trace elements were Fe, Mn, Cr and Cu. Ni is not present in significant amounts. Pb, Zn and Cd are volatile elements: the first two were present in low concentrations, while the third was not detectable in any analyzed sample.

The concentration of heavy metals was generally slightly higher in the fraction <2mm. Cu resulted to be enriched in the finest fraction, while Cr appeared to be approximately evenly distributed among the different size classes.

	fresh				4w			
(mg/kg)	B	B < 1 mm	B 1:2 mm	B > 2 mm	B	B < 1 mm	B 1:2 mm	B > 2 mm
Pb	33	35	23	18	18	20	20	17
Cu	2798	3004	2749	2439	2758	3151	2580	2441
Zn	63	88	73	63	80	75	70	75
Cd	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	2838	2808	2735	2450	2493	2491	2330	2434
Ni	190	193	180	158	148	161	155	138
Mn	797	840	806	715	703	691	690	643
Fe	30450	28900	28150	22250	26625	26498	26375	24065

	8w				12w			
(mg/kg)	B	B < 1 mm	B 1:2 mm	B > 2 mm	B	B < 1 mm	B 1:2 mm	B > 2 mm
Pb	25	33	28	32	23	23	30	15
Cu	2485	2810	2753	2584	2150	2813	2433	2218
Zn	65	68	60	52	38	48	45	40
Cd	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	2608	2670	2707	2430	2235	2553	2790	2508
Ni	168	190	192	185	116	140	119	137
Mn	660	723	721	648	495	543	588	525
Fe	26813	27813	28492	23567	14350	18850	20850	17800

Table 1: Bulk composition of BA samples at different steps of treatment (n.d.= not detectable).

The results of the EN 12457-2 compliance test (Fig. 2) indicated that all size fraction were alkaline in nature, with a pH of the fresh material between 10.2 for the coarse fraction and 9.8 for the finest one. For all the considered classes, a one-point pH decreasing with the proceeding of the weathering treatment could be observed.

On amphoteric elements weathering appeared to generally exert a stronger effect: Zn was never detectable in the examined materials, while Pb, always present in low concentrations, appeared to slightly decrease, except for the finest fraction, which gives the higher contribution for Pb leaching.

Cu concentrations were found to generally increase with ageing. Providing that at pH>7 the leaching of Cu is mainly controlled by complexation with fulvic acids (Meima et al., 2002; Dijkstra et al., 2006; Arickx et al., 2009), its behaviour could be correlated to the general slight increase in COD that was found in the eluates. Cu remained one of the most critical element in view of recycling or landfilling as inert waste, especially with respect to the finest fraction.

Consistently with results from previous studies (Van Gerven et al., 2005; Baciocchi et al., 2009) Cr leaching was enhanced by weathering for all the considered grain size classes. At the end of the weathering treatment Cr concentration exceeded the law limits for both inert waste landfill and reuse for all the considered fractions.

Ni and Fe leaching did not undergo significant variations. After 12 weeks treatment

Ni concentrations accomplished law limits for both reuse and inert waste disposal. For Fe Italian regulations do not pose any concentration limit.

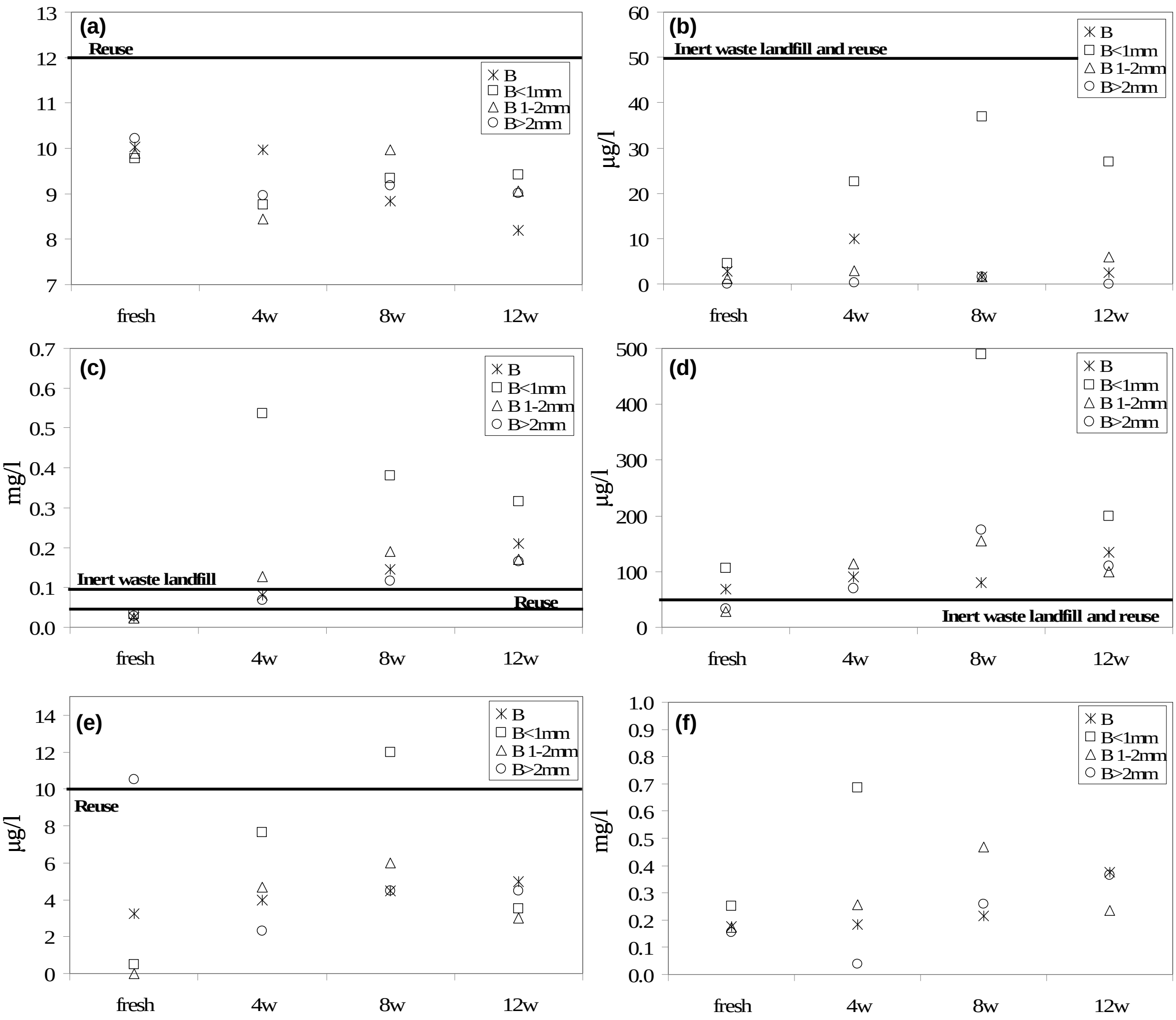


Fig. 2: Results of EN 12457-2 leaching test for pH (a), Pb (b), Cu (c), Cr (d), Ni (e) and Fe (f) and Italian law limits for not hazardous and inert landfilling (Ministerial Order 03/08/05) and reuse (Ministerial Order 05/02/98).

Figure 3 compiles the availability of main heavy metals, normalized to total concentration; for each element, the percentage available for leaching is reported in Table 2. The leachate concentration of heavy metals is rather independent from its total content. More important is the availability of a metal, which is influenced by the particle surface area, the mineralogical environment and the mechanical stability of the particles. Results of the availability test are very typical of a vitrified matrix, in which heavy metals are trapped in the amorphous matrix: for all the three grain size classes subjected to analysis, the amounts of heavy metals available for leaching are small fractions of the overall contents. Partially in contrast with results from EN 12457-2 test, differences in the availability are not noticeable for none of the considered elements.

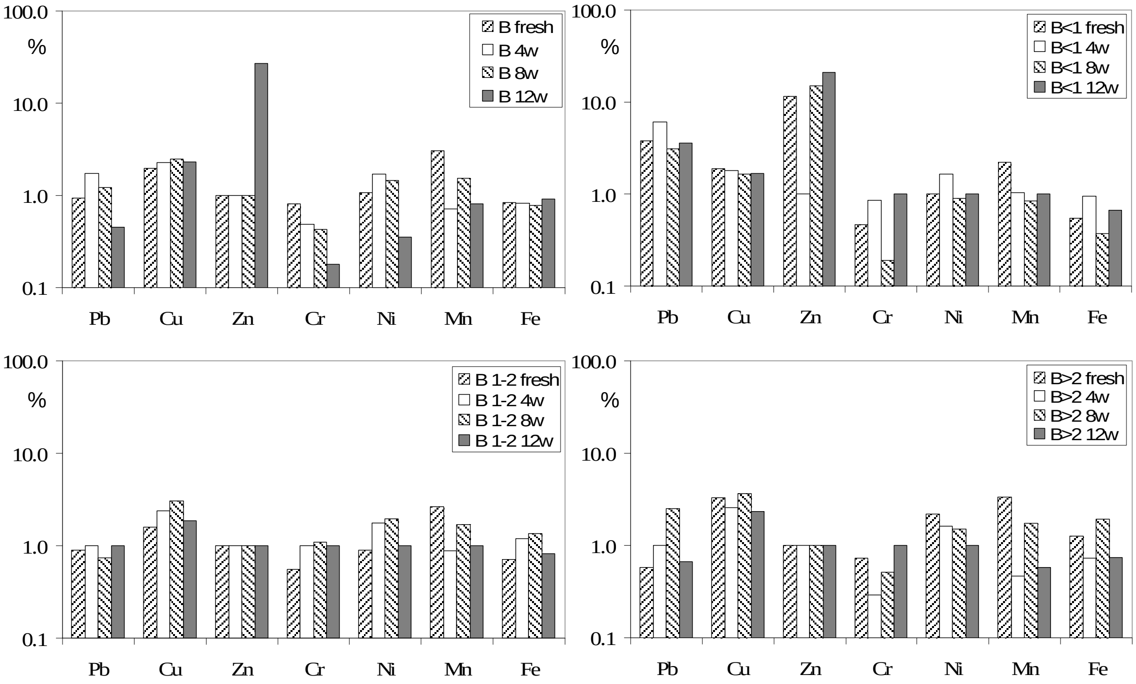


Fig. 3: Availability of main heavy metals normalized to total concentration.

%	Pb	Cu	Zn	Cr	Ni	Mn	Fe
B fresh	0.94	1.97	n.d.	0.81	1.07	3.07	0.83
B 4w	1.74	2.24	n.d.	0.49	1.72	0.72	0.83
B 8w	1.21	2.48	n.d.	0.43	1.45	1.53	0.78
B 12w	0.45	2.30	26.89	0.18	0.35	0.81	0.92
B <1mm fresh	3.75	1.89	11.54	0.47	1.00	2.24	0.55
B<1mm 4w	6.10	1.80	n.d.	0.85	1.64	1.03	0.96
B<1mm 8w	3.10	1.65	14.91	0.19	0.90	0.84	0.37
B<1mm 12w	3.58	1.68	21.17	-	-	-	0.66
B 1-2 mm fresh	0.90	1.59	n.d.	0.56	0.90	2.64	0.71
B 1-2 mm 4w	n.d.	2.36	n.d.	1.00	1.77	0.88	1.20
B 1-2 mm 8w	0.73	3.03	n.d.	1.09	1.97	1.69	1.35
B 1-2 mm 12w	1.01	1.86	n.d.	-	-	-	0.83
B>2mm fresh	0.58	3.29	n.d.	0.73	2.20	3.36	1.27
B>2mm 4w	n.d.	2.56	n.d.	0.29	1.61	0.47	0.73
B>2mm 8w	2.53	3.61	n.d.	0.51	1.50	1.74	1.92
B>2mm 12w	0.67	2.36	n.d.	-	-	0.58	0.74

Table 2: Fraction of metals available for leaching with respect to total concentration.

ANC test was conducted on the whole sample and on the finest fraction (<1mm). The shape of titration curves, shown in Fig. 4 and 5, confirmed the vitrified matrix of the material: fast decrease of pH values with increasing acid addition indicates that the material is made up of a larger proportion of glassy materials with hydrophobic characteristics (Johnson et al., 1995).

As confirmed by other authors (Selinger et al., 1997; Bethanis et al., 2001; Cheeseman et al., 2003; Cheeseman et al., 2005) the shape of the curves could be explained by the degradation of calcite to carbon dioxide and incorporation of CaO into the glassy silicate structures.

At the end of the weathering treatment the titration curves did not show significant changes.

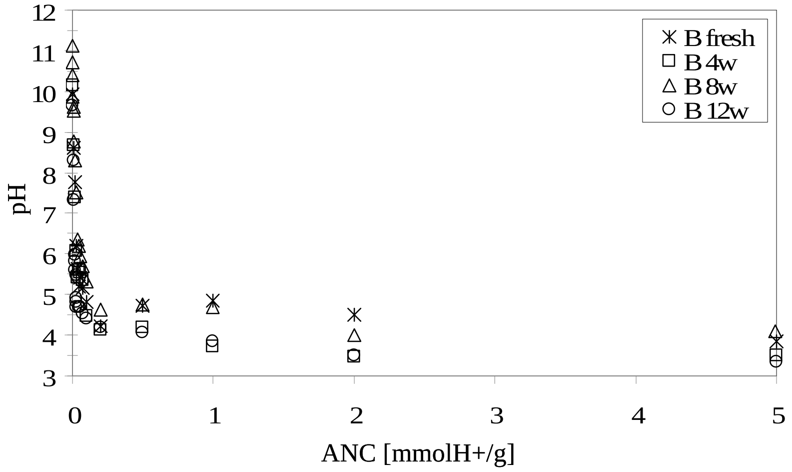


Fig. 4: Titration curves for sample B and different grain size fractions.

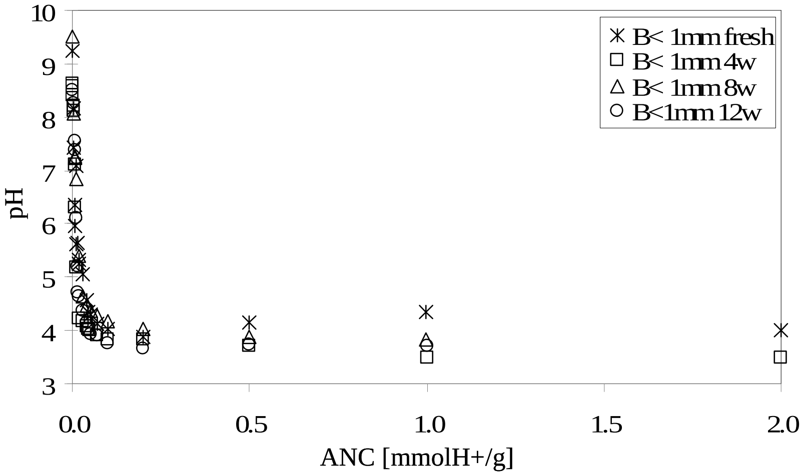


Fig. 5: Titration curves for sample B and different grain size fractions.

Fig. 6 and 7 report the behaviour of heavy metals at different pH values for both the considered samples at different ageing steps.

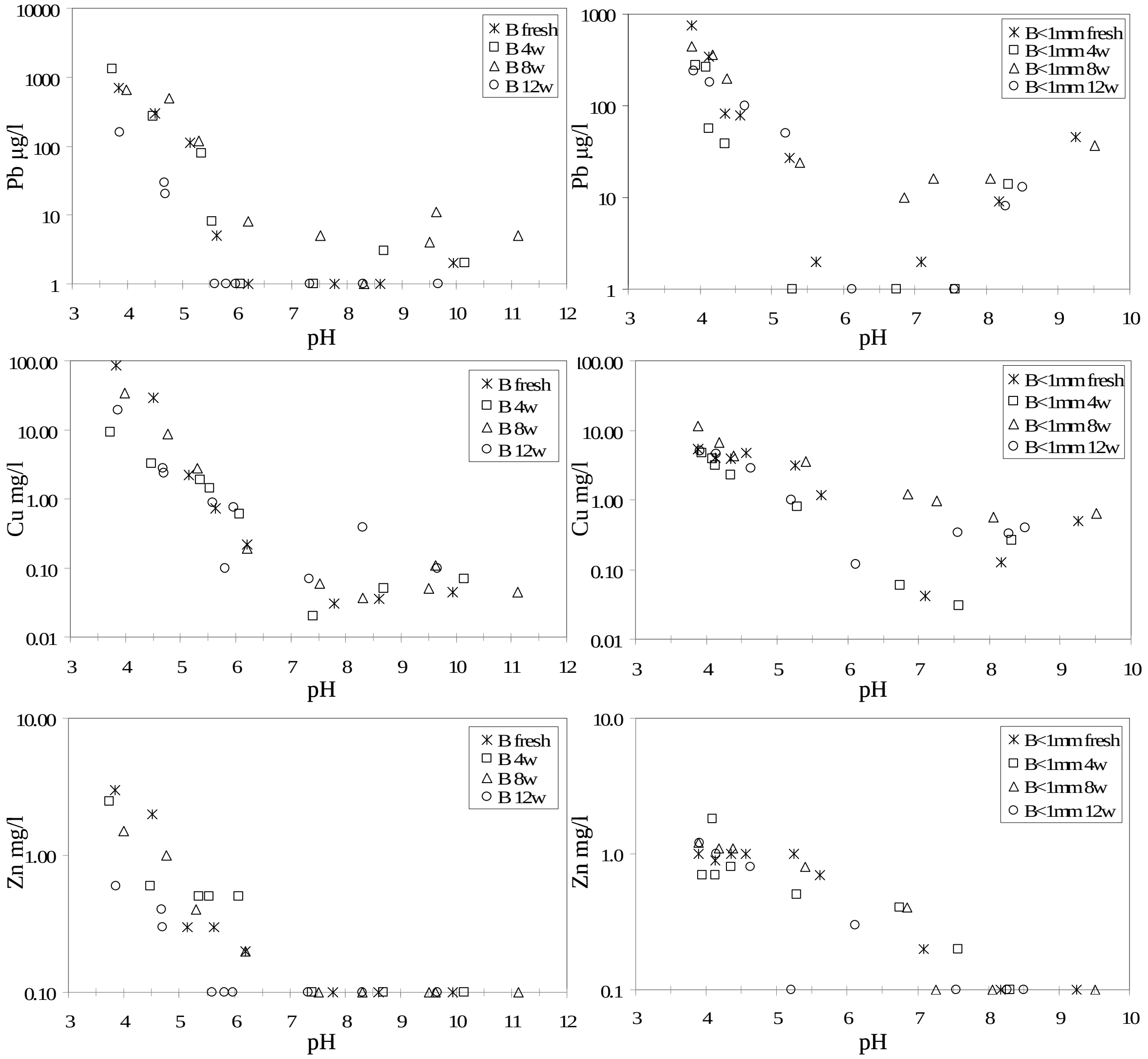


Fig. 6: Heavy metals mobility for the whole sample B and the finest fraction (<1mm) at different steps of treatment.

Amphoteric metals such as Pb and Zn exhibit increased solubility under both strongly acidic and strongly alkaline conditions, resulting in a V-shape solubility curve (Sabbas et al., 2003). With reference to Fig. 6, Pb showed a pH range of minimum leaching between 7 and 9 (Van der Sloot et al., 2001, Meima et al., 1999). In this range, the concentration of lead resulted below the 5µg/l detection limit of the instrument for both the weathered samples.

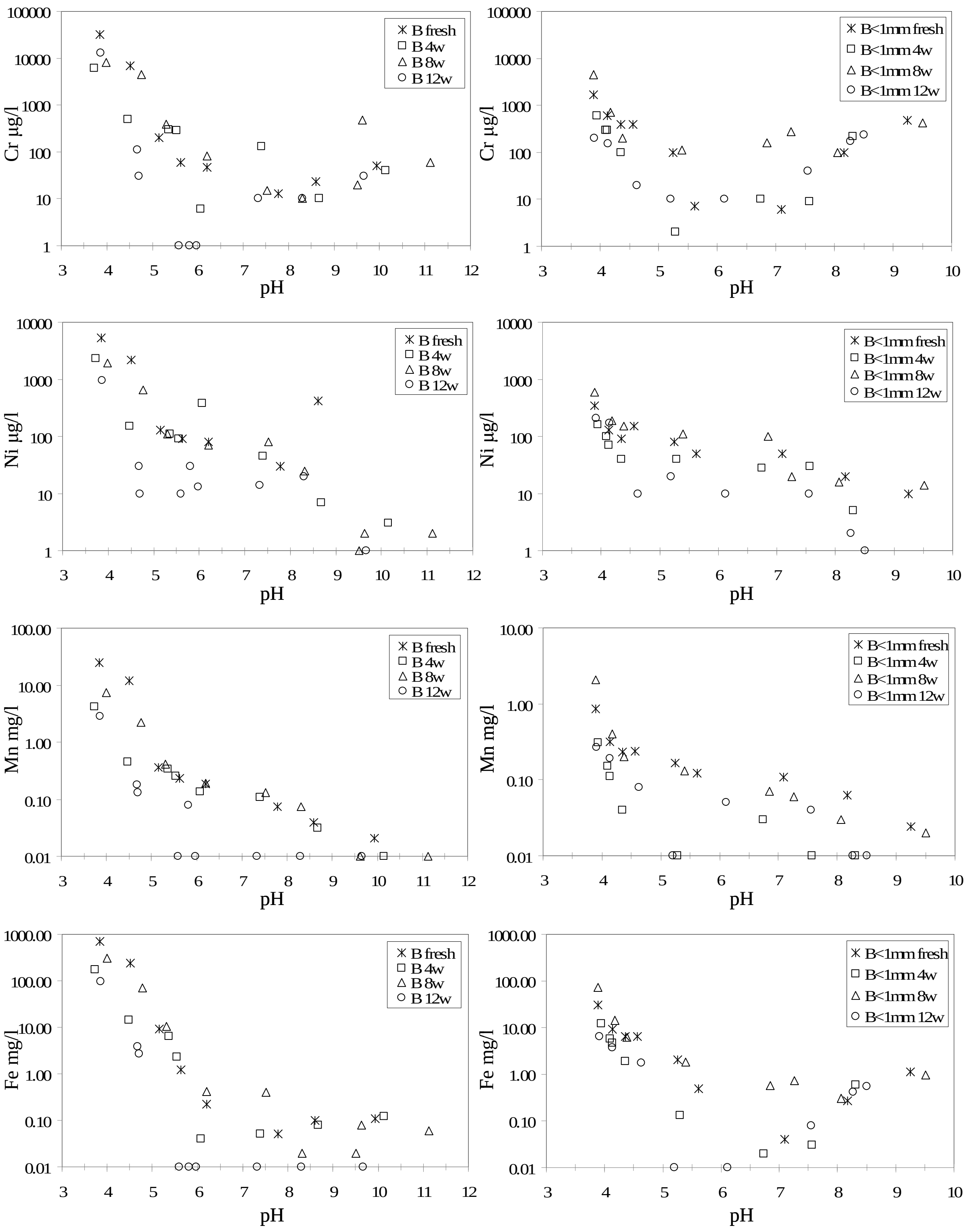


Fig. 7: Heavy metals mobility for the whole sample B and the finest fraction (<1mm) at different steps of treatment

Typical solubility curves for Zn have a minimum at a pH between 10 and 11 (Stumm and Morgan, 1996; van der Sloot et al., 2001). This can explain the absence of an increased solubility in alkaline conditions depicted in fig. 6. Over pH 8 the solubility of Zn resulted below the 0.1 mg/l detection limit of the instrument. In acidic conditions it not possible observe a significant effect on leachability of the ageing treatment.

Cu exhibited a very different behaviour in the two considered samples. Both the analysed materials showed a minimum in leachability for Cu at pH 7 to 8, but in the fraction below 1mm the concentration in the leachate was about ten times higher than in the whole sample. In accordance with the results of the EN 12457-2 leaching test, no beneficial effect on copper release can be observed due to the applied treatment.

Oxyanion forming elements, such as Cr, usually show solubility decrease in alkaline pH (Sabbas et al., 2003; van der Sloot et al., 2001). With reference to Fig. 7, in accordance with the results of 12457-2 leaching test, it is possible to observe that weathering have no beneficial effect on Cr leachability.

Ni leaching was maximum in acidic pH and decreased with the pH increase. The weathered sample showed lower leaching in the whole pH range.

Mn had a solubility curve similar to that of Ni, with a leaching decrease in alkaline conditions. Contrasting with results concerning bulk composition, in acidic pH Mn leaching resulted one order of magnitude higher in the whole sample respect to the finest fraction. However, for pH>5, Mn was never detectable in the eluates from aged sample B, while the applied treatment did not seem to exert any influence on the finest fraction.

Fe leaching curves generally approach a V-shape (Stumm and Morgan, 1996; Dijkstra et al., 2006) with a minimum for about neutral pH values. With reference to Fig. 7, weathered sample B showed Fe concentration always under the instrument detection limit for pH>5.5. By contrast, as already observed for Mn, the finest fraction leaching did not seem to be affected by the weathering treatment.

4.4 Conclusions

The present work concerned the effect of short term natural weathering on chemical properties, with specific attention to leaching behaviour, of RDF high temperature gasification bottom ash.

Results of the EN 12457-2 leaching test showed a one-point pH decrease after 12 weeks for all the considered classes.

Weathering resulted to have a stronger effect on amphoteric elements such as Zn and Pb, while for oxyanion forming elements, such as Cr, it did not exert beneficial effects. After 12 weeks of treatment Cr concentration exceeded the law limits for both inert waste landfilling and reuse, for all the considered fractions.

Cu leaching appeared not to be affected by weathering. Cr and Cu resulted to be the most critical elements in view of recycling or disposal as inert waste.

For the other considered elements no significant effect on leaching behaviour was observed.

Availability test highlighted how the vitrified matrix was able to exert a trapping effect on contaminants: only small fractions of the overall content of heavy metals resulted to available for leaching.

Titration curves from the ANC test showed a fast decrease in pH with increasing acid addition. This shape was explained by degradation of calcite to carbon dioxide and incorporation of CaO into the glassy silicate structures (Selinger et al., 1997; Bethanis et al., 2001; Cheeseman et al., 2003; Cheeseman et al., 2004).

The study of the behaviour of heavy metals at different pH values mostly confirmed the results from EN 12457-2 leaching test.

Chapter 5: Conclusions and perspectives

Physical, mechanical and chemical investigations on BA samples from two RDF high-temperature gasification plants (reported in Chapter 2) showed marked differences in behaviour for this kind of residues if compared with BA from standard MSW combustion plants. Results from physical and mechanical investigations indicated that both samples could be classified as SP (clean and poorly graded sand) according to USCS and as A-1-a (rock, gravel and sand fragments, excellent to good road sub-base) according to HRB. Specific gravity was found to be a little bit higher than characteristic soil values. Standard and modified compaction tests indicated that the dry weight of the materials was not much susceptible to moisture content changes, but it was, instead, sensible to higher compaction energy application. Hazen formula provided an hydraulic conductivity of about $2*10^{-3}$ m/s. Comparing this result with that typical of soils, it was possible to assert the good water drainage of the material.

Chemical characterization showed significant differences between the two considered residues. Since the two gasification plants were very similar, these differences were attributed to the characteristics of the RDFs delivered, but also to the wear of the furnace. In particular, while for a sample metals and anions concentrations were always found below the limits for reuse and inert waste landfilling, for the other sample the release of heavy metals appeared to be a limitation for reuse, but also, for some grain size fractions, for landfilling as inert waste.

The results from the Availability test were representative of glass fraction rich materials, where the vitrified matrix, which is a consequence of high operating temperatures, leads to a reduction of surface area and to the trapping of heavy metals. Significant differences in availability between grain size classes were not noticeable.

ANC test showed titration curves characterized by a fast decrease of pH with increasing acid addition. For all the fractions subjected to analysis, the observed trend was characterized by the increase of heavy metals concentrations with pH decreasing and by a limited release in the alkaline pH range.

Even if it was not possible to identify a clear correlation between heavy metals content (and leaching) and grain size, the possibility of performing a size separation pre-treatment resulted to be feasible for the most contaminated sample. This was true mostly for Cu and Ni, by which the finest fraction resulted to be the most contaminated. For Cr, this kind of treatment would have no effect on the leaching characteristics, which appeared to be almost the same for each grain size, even if chemical composition indicated the finest fraction as the richest in this element.

The effect of short-term natural weathering treatment on the mineralogical, chemical and physical properties of MSW and biomass bottom ash was reported in Chapter 3. Leaching tests (EN 12457-2 and 12457-4) indicated that lead, zinc and copper were the main heavy metals to be released from the considered samples. After 12 weeks of weathering treatment, the concentration of leached zinc fell dramatically, while for lead, it was possible to observe a concentration decrease only for the biomass samples. Lead concentrations seemed to be independent of the pH of the bottom ash and undersaturated if compared to lead hydroxide, anglesite and cerrusite. Solubility of lead seemed to be a result of sorption processes and/or formation of more stable minerals. Cu leaching was well described by complexation processes with dissolved organic C. For the other contaminants studied no beneficial effect for leaching was observed. Availability and column leaching tests confirmed the above mentioned results.

ANC test permitted to carry out a deeper analysis of the weathering process, with particular reference to mineralogical transformations and behaviour of heavy metals.

The results from the experimental campaign indicated that allowing weathering reaction to proceed result in improved stability of the material, even if, contrasting with previous works from other authors, the considered 12 weeks period appeared to be insufficient to comply with leaching law limits, especially for biomass samples.

On the contrary, the treatment resulted to be effective in order to comply with law limits concerning volume stability.

The effect of weathering treatment on RDF high temperature gasification bottom ash was reported in Chapter 4. Concurring with results from Chapter 3, weathering resulted to have a stronger effect on amphoteric elements such as Zn and Pb, while for oxyanion forming elements, such as Cr, it did not exert beneficial effects. After 12 weeks of treatment Cr concentration exceeded the law limits for both inert waste landfilling and reuse, for all the considered grain size fractions.

Cu leaching appeared not to be affected by weathering. Cr and Cu resulted to be the most critical elements in view of recycling or disposal as inert waste, whereas, for the other considered elements, no significant effect on leaching behaviour was observed.

In agreement with results reported in Chapter 2, availability test highlighted how the vitrified matrix was able to exert a trapping effect on contaminants: only small fractions of the overall content of heavy metals resulted to be available for leaching.

ANC test confirmed a fast decrease in pH with increasing acid addition. This shape was explained by degradation of calcite to carbon dioxide and incorporation of CaO into the glassy silicate structures. The study of the behaviour of heavy metals at different pH values mostly confirmed the results from EN 12457-2 leaching test.

In conclusion, this thesis permitted to deep the knowledge about ageing phenomena on BA from MSW incineration, but also on BA from wood waste thermal treatment. In fact, even if utilisation of biomass in heat and power production is common in many countries, few data are currently available about the effect of weathering on the residues from these facilities.

The characterization of residues from high temperature gasification plants highlighted important differences between these materials and the BA from standard combustion plants. First of all, it was not possible to identify a marked enrichment in heavy metals for the finest particle fraction. This makes less effective the possible application of a size separation pre-treatment.

Interesting results have also been derived from the study of the effects of natural weathering on the leaching characteristics of vitrified residues. Further possible investigations could concern the evaluation of long term behaviour of these materials.

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