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SUMMARY

The bottom ash represents the major by-product of the municipal solid waste incineration.

The alkaline properties of the bottom ash and the leaching of heavy metals represent a significant problem for civil/industrial applications. There is, therefore, the need to search new methodologies for its fast stabilization, in order to transform this material in a sustainable product, environmentally safe and low-economic impacting.

The stabilization of this product is a natural (weathering) and proceeds through different processes, including the carbonation. Carbonation is mainly activated by the dissolution of calcium rich minerals (like portlandite) and the consequent leach out of calcium cations in the pore water. Those cations consequently react with the carbon dioxide dissolved in the pore water, leading to the formation of carbonates. The dissolution of alkaline minerals such as portlandite and the formation of carbonates bring the pH to lower values. This decrease in alkalinity, together with the formation of new minerals, lead to a markedly lower mobility of heavy metals, of which the fresh bottom ash is enriched. The carbonation and the total ageing process, however, can be rather long: therefore the research is moving with the aim to find appropriate methods for speeding up these processes.

The laboratory methodologies generally applied for accelerated carbonation are primarily based on the control of certain operating conditions, such as temperature, humidity, the percentage of carbon dioxide in the gas by which the ashes are subjected, and the pressure of this gas.

The accelerated carbonation in general leads to positive results, lowering the time needed for the accomplishment of the ageing period to hours, days or few weeks at most.

The main objective of this master thesis was to verify if the carbon dioxide released by the microbial respiration, enhanced by the adding of several percentages of external organic compounds, could dissolve in the pore water and accelerate the carbonation reaction of freshly quenched bottom ash and of partially weathered ashes.

In the first laboratory phase it has been monitored the microbial activity naturally present in the ashes and the one generated by the adding of external organic matter, with the aim to calculate the quantity of oxygen consumed, and therefore of carbon dioxide produced, during an observation period of four days. In particular has been realized eleven series of respiration tests, among which one was related to the unaltered bottom ash, five in which

SUMMARY

were added increasing amounts of sewage sludge (from 1% to 5% in weight) and five in which were added increasing amounts of crystalline cellulose (from 1% to 5% in weight).

Through the batch leaching test it has been possible, in a second phase, to evaluate the leaching of heavy metals, organic compounds and other elements from the samples of unaltered bottom ash and from the samples where sewage sludge was added.

In the third and final phase where analysed the samples of adsorbing liquid used during the respiration tests. Through this analysis it has been possible to evaluate the quantity of carbon dioxide respectively adsorbed by the ashes and by the adsorbing liquid.

The results show a very relevant microbial activity in the unaltered samples of bottom ashes and in the ones where higher quantities of sewage sludge (4% and 5% in weight) were added. At the contrary are reported a partial inhibition of the activity where lower quantities of sludge and crystalline cellulose were added. The tests conducted on the adsorbent liquid indicate a high adsorbing capacity of the bottom ash of carbon dioxide produced by the bacteria. This capacity increases with the increment of sludge mixed to the ashes. Despite this, however, by the batch leaching test was possible to notice a general increment of heavy metals leaching as higher quantities of sludge were added.

From those results can be assessed that the use of bottom ashes, mixed to external organic compounds is not suggested.

SOMMARIO

Le ceneri pesanti prodotte in fornace al termine del processo di incenerimento dei rifiuti solidi urbani rappresentano il maggiore prodotto secondario di questo trattamento.

Le proprietà alcaline delle ceneri pesanti e la lisciviazione di metalli pesanti, rappresentano un problema rilevante per una loro applicazione diretta in campo civile/industriale; vi è quindi la necessità di ricercare metodologie per una sua veloce stabilizzazione, così da rendere questo materiale un prodotto sostenibile, sicuro per l'ambiente e a basso impatto economico.

La stabilizzazione di questo prodotto avviene in modo naturale (processo di "weathering") e procede attraverso diversi processi, tra cui la carbonatazione. La carbonatazione delle ceneri si attiva, prevalentemente, tramite la dissoluzione di minerali ricchi in calcio (come la portlandite) che lasciano lisciviare cationi calcio nell'acqua presente nei pori: questi cationi reagiscono quindi con l'anidride carbonica disciolta nel liquido e danno origine a carbonati. La dissoluzione di minerali alcalini come la portlandite e la formazione di carbonati portano il pH a valori sempre più bassi. Questo decremento di alcalinità, insieme alla formazione di nuovi minerali dalla dissoluzione di altri in ambiente alcalino, porta a una nettamente minore mobilità dei metalli pesanti, di cui le ceneri pesanti sono ricche. Il processo di carbonatazione, nonché il totale processo di maturazione, possono però essere di lunga durata: la ricerca si sta muovendo nel tentativo di trovare adeguate metodologie per la velocizzazione di questo processo.

Le prove di carbonatazione accelerata sono state maggiormente provate in laboratorio, e solo in pochi casi vi è stata un'applicazione in campo. Le metodologie di laboratorio eseguite fino ad ora riguardano soprattutto il controllo di alcuni parametri operativi, come la temperatura, l'umidità del campione, la percentuale di anidride carbonica a cui le ceneri vengono sottoposte e l'intensità del flusso d'aria arricchita.

La carbonatazione accelerata porta in generale a risultati positivi, abbassando il tempo richiesto per il completamento della fase dalla durata di diversi mesi alla durata di ore, giorni o poche settimane.

L'obiettivo principale di questa tesi magistrale è stato quello di studiare la possibilità di accelerare il processo di carbonatazione sfruttando le reazioni di respirazione aerobica dei batteri presenti in alcuni campioni di sostanza organica esterna: si è verificato se l'anidride carbonica prodotta dai batteri può dissolversi nel liquido interstiziale e quindi facilitare il

processo di carbonatazione sia per le ceneri appena raffreddate che per quelle parzialmente maturate.

In una prima fase di laboratorio è stata monitorata, tramite sistemi in batch, l'attività batterica naturalmente presente nelle ceneri e quella generata dall'aggiunta di materiale organico esterno, al fine di calcolare la quantità di ossigeno consumato, e quindi di anidride carbonica prodotta, in un intervallo di tempo di quattro giorni. In particolare, sono state realizzate undici serie di test di respirazione di cui uno riguardante le ceneri pesanti tal quali, cinque in cui alle ceneri sono state aggiunte quantità crescenti di fango terziario (da 1% a 5% in peso), e cinque in cui alle ceneri sono state aggiunte quantità crescenti di cellulosa cristallina (dal 1% a 5% in peso).

Tramite un test di lisciviazione è stato possibile, in una seconda fase, valutare la cessione di metalli pesanti, materiale organico ed altri elementi dai campioni di cenere tal quale e dai campioni in cui era stato aggiunto fango terziario.

Nella terza ed ultima fase, infine, sono stati analizzati i campioni di liquido adsorbente utilizzati durante il test di respirazione, con lo scopo di valutare la quantità di anidride carbonica rispettivamente adsorbita dalle ceneri e dal liquido adsorbente.

I risultati mostrano un'intensa attività batterica sia nei campioni di ceneri tal quali sia in quelli in cui sono state aggiunte maggiori quantità di fango terziario (4% e 5% di fango in peso), e riportano al contrario un'inibizione della respirazione laddove sono state aggiunte minori quantità di fango e cellulosa cristallina. I test condotti sul liquido adsorbente indicano una elevata capacità di adsorbimento da parte delle ceneri di anidride carbonica prodotta dai batteri, capacità che aumenta con la maggiore aggiunta di fango terziario. Nonostante questo, però, dal test di lisciviazione è emerso, con l'aumentare della quantità di fango aggiunto, un generale incremento della cessione di metalli pesanti.

Da tali risultati è possibile quindi concludere che l'uso di ceneri pesanti mischiate a materiale organico esterno non è consigliato.

INTRODUCTION

Despite the important work undertaken by the European Union to find a match between environmental protection and economic growth (Environmental Action Programmes), the waste generation is in general growing in all EU countries and the pressure on ecosystems and the conservation of habitats and species status is not varied since 10 years ago (EEA, 2010). Those negative indicators, however, are coupled with an increase in positive waste management, an increasing in energy efficiency, the use of renewable energy sources and a reduction in greenhouse gas emissions and with a better water pollution control (EEA, 2010). Nevertheless the number of households is expected to grow up to 20% by 2030, and an increasing in energy consumption, water use and waste generation is anticipated (EEA, 2005; EEA, 2010).

The interest demonstrated by the European Countries for the incineration of waste is growing, as it represents a positive solution for the mass and volume reduction of the treated material (respectively 90% in volume and 70% in mass, Chimenos et al., 2000; Costa et al., 2007; Rougame et al., 2009) and because it offers a complete sanitation of the waste. Moreover, new devices have been engineered to limit the emission of pollutants from those plants (Air Pollution Control systems) and to recover energy from the heat released during the waste treatment in furnace.

The different kinds of furnace give the possibility to burn a wide range of waste typologies (industrial and hospital waste, sludge, municipal solid waste). However with the implementation of the “Waste Directive” the European Countries are required to promote a waste management based on the reuse and recycling of material and to improve the incineration with energy recovery for the waste that cannot be further exploited.

The incineration of waste is a source of secondary waste production, with bottom ash as main by-product formed during the combustion of the waste in the furnace. The municipal solid waste incineration bottom ash, in particular, immediately after its formation is mainly composed by an inert fraction (ferrous, ceramics and other unburned material) and by a new formed fraction (e.g. calcite, ettringite, Al/Fe structures) (Wei et al., 2011). The new formed fraction have been compared to the volcanic ash because of the vitreous neo-formations that characterize the larger grain size and because of the alkaline properties (Zevenbergen et al., 1998) brought by the calcium-rich minerals like portlandite (Yao et al., 2010; Chimes et al., 2000) mainly present in the finest particles size. Moreover, these ashes are enriched in heavy metals that directly derive from the raw waste (Chimenos et al., 2000) and that have the

capacity to leach in greater quantities in the high pH environment (Meima et al., 1999). The ashes are collected at the end of the furnace and are cooled by soaking them in water (quenching); afterward they are stored in external areas or are sent to landfill. Ferrous and non-ferrous materials can be removed by magnets or eddy-current devices (Chimenos et al., 1999).

This secondary product can be exploited for several industrial uses and in civil applications, for example in the concrete production, in the road paving and as a structural material for the landfill covers (Travar et al., 2009; Fernandez-Bertos et al., 2004). However, before any application, the bottom ash needs to be stabilized with a weathering process, that, by the modification of the physical/chemical properties, decreases the alkaline and hazardous characteristics: at the end of this ageing, in fact, the pH is brought from values around 12 to more neutral values, the heavy metals are mostly entrapped in mineral neoformations (Costa et al., 2007; Rendek et al., 2006 a).

The most important process of this stabilization is carbonation. Carbonation starts immediately after quenching and is characterized by a series of reactions that involve the carbon dioxide dissolution in the pore water and the calcium cations that leach out from the minerals (portlandite, ettringite and others) that dissolve in high alkaline conditions (Huijgen et al., 2003).

The dissolution of these minerals decreases the pH of the heap and the reaction between carbon dioxide and calcium cations leads to the formation of carbonates. The heavy metals, that were entrapped in spinels or in the minerals structure and that leached out in form of cations or oxyanions with the dissolution of the hosting formations, are, in great part, bounded in newly formed minerals by substitution or absorption (Wei et al., 2011).

The natural weathering process can have a long duration, from several months to years, and for this reason is considered quite inefficient. In order to speed up the ageing of the bottom ash to promote the use of this material, the researchers are engineering different methodologies to accelerate the process of carbonation. The speeding of carbonation is studied not only to produce a stabilized product to be directly used by the civil industry, but also to convey and entrap the carbon dioxide released from its sources of production (landfills or incinerators).

The parameters that control the accelerated carbonation are mainly moisture, temperature, the partial pressure of carbon dioxide in the gas conveyed through the ashes and the pressure of this gas. Until now it has been recognized that a range of temperatures between 30÷50°C, a

moisture content between 15÷25% (w/w) and an higher quantities of CO₂ in the air flux can speed up the process to hours, days or few weeks at most.

Moreover several researchers (Rendek et al., 2006 b; Zhang et al., 2004; Dugenest et al., 1999), found that the bacteria present in the heap can degrade the unburned organic matter, despite the inhospitable environment, high alkaline and rich in heavy metals. Rendek et al. (2006 b) also demonstrated that the carbon dioxide produced by these bacteria during their activity can be absorbed in the pore water and maybe interact with the calcium elements to form carbonates.

In the light of this knowledge, the aim of this master thesis was to find a new pathway for the accelerated carbonation, exploiting the aerobic respiration of the bacteria present in the heap and in the sewage sludge, In particular in consideration to the fact that the carbonation proceeds faster if the quantity of carbon dioxide present in the pore water is higher respect to the one that can be naturally present in the heap. Thus it has been analysed if the carbon dioxide produced by the microbial activity of the sewage sludge and cellulose added to the ashes can dissolve in the pore water and the carbonation process can become faster.

This work is subdivided as follow: The first part of this thesis is widely dedicated to the current knowledge on bottom ashes, with particular attention on the physical/chemical characteristics of the ashes from their production to the changes to which they undergo during the weathering process; on the most applied techniques for accelerated carbonation and which are the effect on the bottom ash respect to the natural weathering; on the understanding of processes of bacteria activity in the bottom ashes; and on the most common industrial/civil application of this material (Chapters 1, 2 and 3). The third part is finally dedicated to the laboratory analysis, and in particular to the methodologies of investigation and the material used in this research; to the respiration test conducted on the partial weathered bottom ashes and on the fresh ashes where sewage sludge was added and to the respirometric tests conducted with the crystalline cellulose (Chapters 4, 5, 6 and 7); finally Chapters 8 and 9 presents the results obtained from the analysis on the carbon dioxide absorption capacity of the bottom ashes and the leaching beahaviour of several heavy metals. At last the appendix describes breathily the waste production and management in the European countries, with a particular attention on the Italian and Swedish situation, and introduce the incineration techniques, by listing which are the main characteristics of the raw waste that drive to the choice of the best incineration typology and by describing the most applied furnaces and the energy recovery systems

CHAPTER 1

MUNICIPAL SOLID WASTE INCINERATION BOTTOM ASH: FROM PRODUCTION TO STABILIZATION

1.1 Introduction

Bottom ashes represent the main byproduct of the incineration process, covering the 85% to 95% (Rendek et al, 2006, Saffarzadeh et al, 2011) of all the residues, but can be reused in several applications: roads paving, asphalt concrete production, cover of landfills, and others. Nevertheless, since 1979, as reported by Marzi et al. (2012), from a research conducted by Kluge, Saalfeld and Dannecker¹, it was clear that the utilization of fresh bottom ashes used as construction material for a road, were the cause of mechanical deficits. In authors' opinions those deficiencies were derived by the formation of swell-able aluminum hydroxides from oxidation of elementary aluminum and could have been prevented by applying an aging process. This weathering process could have enhanced the ashes stabilization and have positive effect in the leachate behavior.

1.2 Characteristics of freshly quenched bottom ash

The fresh bottom ash, immediately after quenching, presents very high alkaline pH (around 12), that is possible to associate to the saturation of portlandite (Yao et al., 2010; Polettini et al., 2004).

Several researchers (Freyssinet et al., 2002; Wei et al., 2011; Saffarzadeh et al, 2011) have analyzed ashes anatomy from the petrographic and chemical point of view, in order to understand their weatherability and their role on heavy metals mobilization, and all of them agree with the subdivision of the material in three different categories: melt glass phase, calcium-rich minerals phase and refractory phase. The coarse fraction seems to be mainly composed by glass and silicate minerals, while calcium-rich minerals are more numerous in the finest one (Freyssinet et al., 2002, Baciocchi et al., 2010). The composition of the waste flow, that can change daily, is an important factor on the slag structure, in particular for what

¹ Gerold Kluge, Horst Saalfeld and walter Danneker: "Untersuchungen des Langzeitverhaltens von Müllverbrennungsschlacken beim Einsatz im Straßenbau". Umweltbundesamt, 1981.

concern the quantity of hazardous compounds (Chimenos et al, 2000; Wei et al, 2011, Rendek et al., 2007 b).

1.2.1 Melt glass phase

This phase, that is the dominant product of the melting material demixing in the furnace (Zevenbergen et al., 1998; Wei et al., 2011, Chimenos et al., 1999), presents a vitreous banded texture and irregular vesicles (due to the entrapment of gas and air bubbles). These large inorganic fragments (>1mm), mainly composed by silicon, calcium and aluminum elements, show the coexistence with other elements, like silicate mineral phase, developed minerals, and metal-rich associations that are entrapped in the melt (Figure 1.1).

The most important silicate-based group of minerals present in the melt phase is the group of melilites (general formula $(\text{Ca},\text{Na})_2(\text{Al},\text{Mg},\text{Fe}^{2+})[(\text{Al},\text{Si})\text{SiO}_7]$) that forms crystal aggregates in the melt (Gehlenite $\text{Ca}_2\text{Al}_2\text{SiO}_7$ was found in particularly high quantities by Baciocchi et al., 2002), and wollastonite that shows, in some cases, an enrichment in Na, Al and Mg at the expense of Ca and Si. Both this minerals are produced at high temperature (over 1100°C). Other well developed silicon-rich elements, like quartz and feldspars, are encapsulated in the melt and their occurrence is derived directly from the waste burned (Wei et al., 2011 a).

As shown in the pictures below (Figure. 1.1) the vitreous phase is able to incorporate also metal elements that seems to derive from two different sources: the first are the large metallic scraps in the waste stream, that during combustion disaggregate in smaller fragments (from 10 μm to few mm) and persist until the 3% in volume of the all material; the second source is the incineration process itself that is a good environment for the formation of primary metal-rich minerals that are present until 7% in volume in the bottom ash. The first category directly derived from the burned waste, is both present in the melt and in the fragile zone and is mainly composed by Fe, Al and Cu alloys with minor insertions of metals and non metals (Pb, Sb, Ni, Si, S, P) (Saffarzadeh et al., 2011). The second, instead, lead to the formation of two phases: one is constituted by minerals in the form of spinels and the other is characterize by metallic inclusions that form groups of minerals encapsulated in the melt glass matrix (Wei et al., 2011 a).

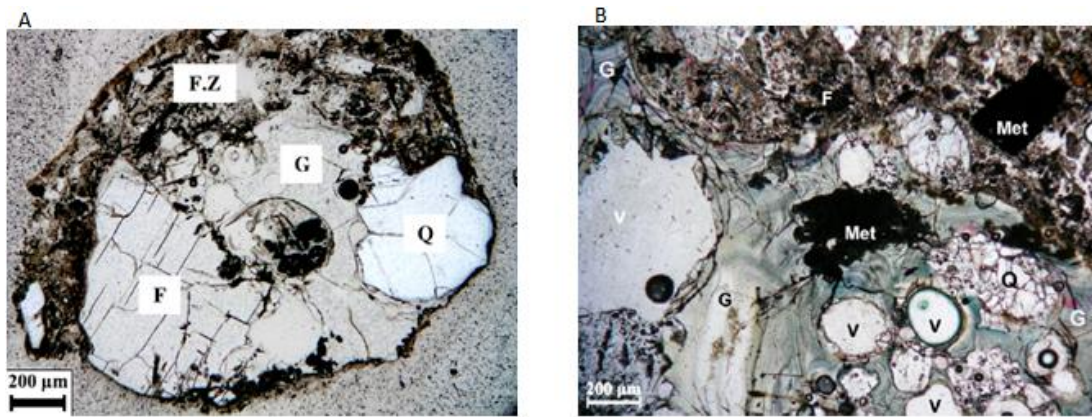


Figure. 1.1. Two examples of internal structure of melt glass phase under PPL. Picture A):

G= glass, Q=quartz, F=feldspar, F.Z.=fragile zone (Saffarzadeh et al., 2011).

Picture B): G=glass, V=vesicle, Met= metallic, F=fragile zone (Wei et al., 2011).

The most relevant minerals from the spinel group are magnetite (Fe_3O_4) and hematite (Fe_2O_3) (Wei et al., 2011; Baciocchi et al., 2010; Freyssinet et al., 2002). The capacity to incorporate cations like Pb^{2+} , Mg^{2+} , Cr^{3+} and others, determine the chemical composition and the shape characteristics of each spinel (Wei et al., 2011 a).

As for the metallic inclusions, they represent an important heavy metal-bearing phase because of their capacity to form new combinations like Fe-Cu, Cu-Zn, Cu-Pb and others. Rendek et al. (2007 b) found that the presence of Al and Fe in the bottom ash don't depend directly on the waste composition but depend on the treatment of separation of those elements from the heap before the weathering process.

The vitreous coarse material is wrapped by a hundred micron thick layer of fine material that is composed by metals, organic matter and scraps of sulphates and carbonates. The circulating fluids can take advantage of the porosity of this non-compact layer and contribute to the weathering process (Saffarzadeh et al., 2011; Freyssinet et al., 2002).

1.2.2 Calcium-rich minerals

The presence of calcium in the bottom ash is linked to combustion MSW containing calcite (CaCO_3), anhydrite (CaSO_4), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) (Chimenos et al., 2000), paper, cartons and food waste (Rendek et al., 2007 b) that, in the furnace, are calcinated to generate lime (CaO) and CO_2 or SO_2 . After the quenching process, lime is hydrolyzed to portlandite $\text{Ca}(\text{OH})_2$ by an exothermic reaction (Reaction. 1.1, Wei et al., 2011; Chimenos et al., 2000; Rendek et al., 2007 b). The presence of those calcium-rich elements, thus, is important for the alkalinity properties of the bottom ash (Saffarzadeh et al., 2011; Rendek et al., 2007 b).



Ettringite is formed by the reaction between calcium and aluminum cations that dissolved from the binding minerals (Reaction. 1.2). This mineral is very sensible to the weathering process (Polettini et al., 2004).



1.2.3 Refractory phase

The material belonging to this category is composed by chippings waste that are not burned in the furnace, like pieces of glass, ceramics, unburned metallic waste, concrete and others (Figure. 1.2) (Chimenos et al., 1999; Wei et al., 2011). Those materials are inert and don't have any influence on the weathering process (Wei et al., 2011).

The refractory minerals, like quartz, feldspars, plagioclase don't contribute to the heavy metals mobilization, and preserve their original chemical composition (Wei et al., 2011).



Figure. 1.2. Photo of coarse refractory material found after quartering and sieving in a sample of MSWI bottom ash. Is possible to recognize some pieces of ceramics, metallic material and construction-demolition waste.

1.2.4 Heavy metals and other elements

The concentration of heavy metals in the bottom ash depends on the characteristics of the incinerated waste and can vary daily. Moreover those compounds, together with the soluble inorganic salts, seems to be contained in greater proportion in the finest fraction of the ashes (< 2mm) (Chimenos et al., 2000; Meima et al., 1999). Wei et al. (2011 a) reported that they are better absorbed in the non silicon-minerals embedded in the vitreous structure. The most distributed heavy metals are lead, zinc and copper (Chimenos et al., 2000, Meima et al., 1999).

Cu is widely present in the raw waste (pigments, electrical and kitchen tools, and others) and its concentration in the bottom ash can vary from $0.3 \frac{g}{kg}$ (Yao et al., 2010) and 1.7 to $2.5 \frac{g}{kg}$ (Wei et al., 2011(a); Meima et al., 1999). It is often found as metal inclusion in form of element, alloys (Cu-Fe, Cu-Pb) and, more rarely, as oxide. (Wei et al., 2011 (a))

Pb, that derives from the presence of batteries, inks and other waste materials, presents a great affinity with Fe and Cu compounds, even if its chemical characteristics (radius and charge) make it unstable at natural conditions when sorbed in the bottom ash metallic spinels (Wei et al., 2011). The Pb concentrations in the freshly quenched bottom ash are around $1.6 \frac{g}{kg}$ (Meima et al., 1999).

The presence of chloride ($3 \frac{g}{kg}$, Meima et al., 1999; $0.34 \div 0.84\%$, Rendek et al., 2007 b) in the leachate depends on the reaction between hydrochloric acid (formed from the combustion of waste rich in halogen materials, e.g. PVC) and alkaline materials (Chimenos et al., 2000).

Sulphates, originated from the reaction between sulphur oxides and alkaline materials and present in noticeable amount in the ashes ($5.7 \frac{g}{kg}$, Meima et al., 1999; $0.29 \div 0.47\%$, Rendek et al., 2007 b), can be linked to the oxidizing reaction of the organic materials (Chimenos et al., 2000). Rendek et al. (2007 b) found that the presence of sulfur in the bottom ash is correlated to the addition of industrial waste and building material in the raw waste.

1.3 Weathering

Weathering is a process that, if developed naturally, may take a long duration. It has been estimated, in fact, that a natural MSWI bottom ash weathering of 2 or 3 months is enough to decrease the release of heavy metals and allow the reutilization of the material or to permit the final disposal (Chimenos et al., 2000), but studies conducted on disposed material monolandfill (Saffarzadeh et al., 2011; Wei et al., 2011) have demonstrated that the reactivity of the ashes is still effective also for the piles deposited for years.

Weathering can change the mineralogical structure and the chemical properties of the materials by the developing of several reactions, like carbonation, hydrolysis/hydration, precipitation of hydroxides and salts, formation of new minerals from the vitreous phase, oxidations and reductions (Costa et al., 2007; Saffarzadeh et al., 2011).

Meima et al. (1997, 1999) identified three main stages of weathering:

- (A) unweathered (grate siftings and unquenched bottom ash) with $pH > 12$;
- (B) quenched non carbonated (freshly quenched and 6-weeks old bottom ash) with $pH 10 \div 10.5$;

(C) carbonated bottom ash (1.5÷12 years old bottom ash) with pH 8÷8.5.

The main advantages brought by this process are the decreasing in leaching of heavy metals, due to the decreasing of alkalinity, the formation of more stable minerals and the decrease in DOC leaching (Meima et al., 1997).

The reactions that are involved in this process have demonstrated to be exothermic (Table 1.1) and the highly increase in temperature is registered in the first months of storage (Klein et al., 2003).

Table. 1.1: Exothermic reactions in bottom ash material. Klein et al., 2003.

| <i>Reaction</i> | <i>Entalphy of reactions [$\frac{kJ}{mol}$]</i> |
|---|--|
| $2Al + 6H_2O \rightarrow 2Al(OH)_3 + H_2$ | -422 |
| $FeS + \frac{9}{4}O_2 + \frac{5}{2}H_2O \rightarrow Fe(OH)_3 + H_2SO_4$ | -921 |
| $CaO + H_2O \rightarrow Ca(OH)_2$ | -65 |
| $Ca(OH)_2 + H_2CO_3 \rightarrow CaCO_3 + 2H_2O$ | -111 |
| $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$ | -120 |
| $Ca(OH)_2 + SiO_2 \rightarrow CaH_2SiO_4$ | -140 |
| $CaH_2SiO_4 + CO_2 \rightarrow CaCO_3 + SiO_2 + H_2O$ | -25 |

1.3.1 Carbonation

Carbonation, that starts immediately after quenching and occurs naturally, causes the alteration of the calcium and magnesium-rich phases. This process has not been completely explained: the source of CO_2 , as several studies have demonstrated, can be atmospheric (the dissolution of carbon dioxide in water, as Rendek et al., 2005, demonstrated, represent the slowest step in the reaction) or may have a biological source (the bacteria can use the not incinerated organic matter as substrate and, in aerobic condition, produce CO_2 that can contribute to the carbonation development. Rendek et al., 2005, Zhang et al., 2004; Dugenest et al., 1999).

The attention on this process is increasing among the researchers, that are experimenting several methods to accelerate the carbonation in order to stabilize the bottom ash on a timescale of hours or days. The methodologies developed by different studies, as will be further explained in chapter xx, involves the use of gasses with higher percentage of CO_2 , at higher pressure than the atmospheric one and at higher temperature than the ambient. A debate is open between the researchers (Arickx et al., 2006; Van Gerven et al., 2005) around the possibility to facilitate a faster carbonation by the use of the CO_2 from its source of

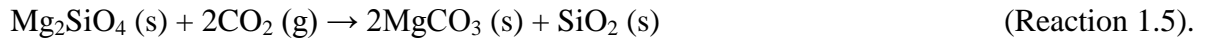
production, and in particular from the stacks of the MSWI facilities, with the purpose to decrease the carbon dioxide emissions as required from the Kyoto Protocol.

Carbonation interests several elements, like portlandite, wollastonite, ettringite, steel slag and others. The carbonation process can proceed naturally by two routes: through the gas-solid interface and in the aqueous phase.

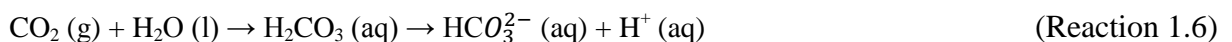
The *gas-solid carbonation* transforms the calcium-rich elements (oxides or silicates) in carbonates. The rate of those reaction is generally low at ambient conditions, but can be improved increasing the system temperature or pressure; at too high temperatures, instead, is registered an increment in released CO₂ caused by the calcinations process (Huijgen et al., 2003). The reactions of dehydroxylation of the calcium hydroxide (Reaction 1.3) and carbonation of the calcium oxide (Reaction 1.4) are fast at ambient conditions in the first layers of the heap, but are inhibited in the deepen part by difficult diffusion of H₂O and CO₂, caused by the calcite layer that deposits on the external stratum of the material (Bacocchi et al., 2010; Aricks et al., 2010).



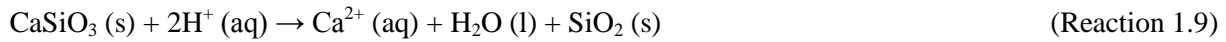
The following reaction (Reaction 1.5) represents the gas-solid carbonation of olivine that, reacting with carbon dioxide, returns magnesite and quartz (Costa et al., 2007).



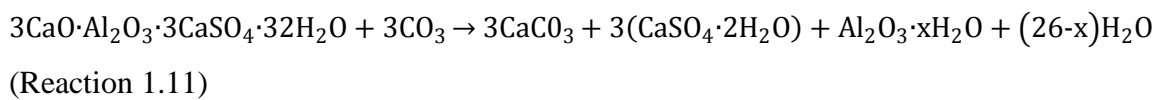
The *carbonation through the aqueous phase* is faster than the previews one and is characterized by the dissolution of carbon dioxide in water (Reaction 1.6) and the leaching of the reactive cation from the mineral (Huijgen et al., 2003). This reaction steps represents a reason why the moisture content in the MSWI bottom ash should be monitored: the alkaline conditions of the matrix, in fact, are controlled by the portlandite solubility capacity and by its ability to react with the carbon dioxide dissolved in the boundary water film that surrounds the ash particles (respectively Reaction 1.7 and Reaction 1.8) (Chimenos et al., 2000; Arickx et al., 2006; Uliasz-Bochenczyk et al., 2010). For this reason is important to ensure a constant moisture in the pile subjected to the weathering process (Rendek et al., 2006, suggests a moisture of 15%).



Silicon minerals, for example wollastonite, can react with dissolved carbon dioxide, leading to the formation of quartz and carbonate in two stages (Reaction 1.9 and Reaction 1.10, Costa et al., 2007):



Ettringite is also submitted to carbonation when the calcium ions leach into solution (at pH > 9, Polettini et al., 2004), and lead to the formation of calcite, gypsum and alumina gel: the general reaction (Reaction 1.11) is reported (Saffarzadeh et al., 2011; Uliasz-Bochenczyk et al., 2010):



As mentioned above, the carbonation of portlandite plays the primary role on the buffering capacity of the bottom ash. Nevertheless the pH trend depends on the formation of calcite (Figure 1.3), that is formed not only from portlandite but also from other calcium-rich compounds: Yao et al. (2010) have demonstrated that when the $\text{Ca}(\text{OH})_2$ is consumed, the pH still shows a decrement caused by the carbonation of other alkaline materials. Carbonate is the secondary mineral produced in greater quantities (Piantone et al., 2004), presenting the possibility to duplicate its weight during the weathering process (Van Gerven et al., 2005).

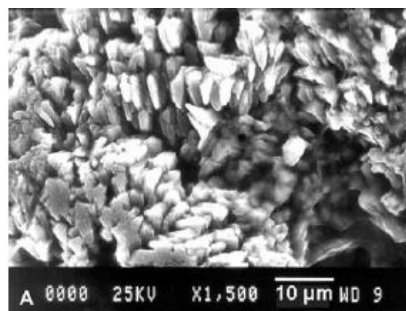


Figure 1.3: Crystallized calcite formed during the weathering of MSWI bottom ash, primary electron image. Piantone et al., 2004.

1.3.2 Secondary minerals generation

Several reactions take place during the weathering phase which transform the primary minerals into secondary minerals (“neoformations”) with different physic-chemical properties and with the capability to interfere in the heavy metal behavior. These neoformations improve

the mechanical properties of the ashes because of the mineral encrustations and pores reduction, which produce hardening (Saffarzadeh et al., 2011).

The neoformations can have two different structures: mineral and gel-like. The minerals represent the most abundant species and they are mainly composed by Al, Ca, Si and SO_4^- (Meima et al., 2002): calcite, ettringite, quartz, gypsum, in fact, are reported to be the most numerous species found in different studies (Piantone et al., 2004, Yao et al., 2010; Zevenbergen et al., 1998; Wei et al., 2011). Most of the crystalline phases seems to be preserved from the original waste composition (as, for example, the refractory minerals; Wei et al., 2011), while the secondary minerals neoformations (e.g. ettringite) present an up-take heavy metals capacity (Piantone et al., 2004).

1.3.2.1. Melt glass alteration

Because of its silicate structure, glass is one of the most weatherable element in the bottom ash and is subjected to dissolution/hydrolysis and to cations exchange (for example showing loss of Na, Si, and Ca in favor of Fe inclusion) at the interface between glass and the circulate fluids (Wei et al., 2011; Saffarzadeh et al., 2011). This process, enhanced by the high pH (faster hydration reactions) and higher temperature (higher glass solubility), is linked to the presence of microfractures that can develop in the vitreous structure and may lead to the embedded heavy metal release (Saffarzadeh et al., 2011). Wei et al. (2011) reported that the glass phase, at $pH > 9$, evolves in a gel-like phase that assumes a reddish color caused by the included Fe-rich precipitates. In particular the dissolution of metallic inclusions (e.g. Fe-S), that depends on the contact with the circulating fluids that enters through the glass porosity, causes the invasion of iron elements deposited in the inner part of the glass at the expense of the vitreous constituents (Si and Ca) that are leached out.

The absence of glass in the raw waste, thus, can negatively affect the metals retention capacity of the weathered bottom ash: Si, in fact, is an important constituent of the secondary crystalline phases that can absorb the metals (Rendek et al., 2007 b).

1.3.2.2. Aluminum-rich neoformations

The aluminum-rich elements, that are present in the ashes in metallic form, are directly derived from the waste stream and are sensitive to high alkaline conditions. The most common products neoformations are Al-hydrate structures and hydrocalumite and ettringite-like species. In particular the anions Cl^- and SO_4^{2-} , present in the pore solution, seem to have a great influence on the Al-species corrosion and on the formation of the hydrocalumite and ettringite-like species (Saffarzadeh et al., 2011; Piantone et al., 2004). The Al-hydrate

structure, instead, can derive both from ettringite destabilization (Reaction 1.11) and from aluminogels precipitated in forms of hydroxide when the solubility of Al is inhibited by the pH, that moves from high alkaline properties to values around 8-8.5 (Meima et al., 2002; Piantone et al., 2004). Arickx et al. (2010) found that the Al-(hydr)oxides can increase up to $5.7 \frac{gAl(OH)_3}{kg}$ for a pile subjected to natural weathering.

Amorphous aluminosilicates (that are the first product of glass weathering and deposit in form of flakes on the glassy particles surface, Zevenbergen et al., 1998) and gibbsite represent the most common forms of solid precipitate of the Al-rich materials group (Meima et al., 2002), but don't show any influence on the pH trend of the ash pile (Chimenos et al., 2000). It has also been documented (Zevenbergen et al., 1998) that long weathering periods of vitreous material and aluminosilicates neoformations, with the contribution offered by the bottom ash environment (e.g. pH), can result on the formation of clay-like minerals (like illite).

1.3.2.3 Iron-rich neoformations

In the weathered bottom ash the iron-rich compounds exist mainly in three different phases: hydrate, oxide and gel-like.

The Fe-hydrate phases (e.g. goethite $Fe^{3+}O(OH)$) are formed from the oxidation of minerals as magnetite and siderite that, at high pH values, are dissolved from the more external layers of the glassy constituents (Wei et al., 2011 b). Goethite is the most abundant compound from the Fe-hydrate group.

The oxide species (secondary magnetite and hematite) are the most abundant mineral phases in the older heaps .

Magnetite, in particular, is supposed to be formed by dehydration/reduction of secondary Fe-hydrate products (Reaction 1.12) where the ferric oxyhydroxide ferrilydrite undergo to a hydrolysis reaction in presence of dissolved Fe^{2+} , returning magnetite as secondary product) possibly under biological-controlled process (through Fe reducing bacteria, Wei et al., 2011 b) and in a long time (Saffarzadeh et al., 2011).



1.4 Influence of carbonation on heavy metals

A natural weathering period of 3 months seems to be enough to register an important decrease on the hazardous elements leaching: lead, zinc and barium, in particular, shows a fast drop in

the first 60 days of weathering, while copper leaching proceeds for longer time (Chimenos et al., 2000). A 1.5 years old bottom ash contains unweathered Pb, Cu and Zn minerals, that are stable under atmospheric conditions. (Meima et al., 1999). Those trends are linked to the capacity of neoformations to sorb this elements in their structure: carbonates can uptake Pb and Zn (Chimenos et al., 2000; Piantone et al., 2004, Wang et al., 2009) with an average content of respectively 100÷6300 ppm and 100÷1800 ppm (Freyssinet et al., 2002), ettringite can sorb Pb, Cr^{III} and Cr^{VI}, Fe-oxides presents particular affinity for As (Piantone et al., 2004) and Pb (Meima et al., 1999). This affinity is correlated with the large interaction surface that is frequent for the neoformations (goethite surface can range from 8 to 200 m² while magnetite from 4 to 100 m²) and to the capacity to substitute isomorphously their cations with other elements that are available in the matrix (Saffarzadeh et al., 2011).

Meima et al. (1999) found that the leaching of those compounds from the heap is dependent on the solubility-control capacity of the minerals in which they are entrapped. In particular Pb leachability is independent from the alkalinity during the first period of maturation, while is linked to its sorption in unstable minerals (e.g. spinels): with the maturation progress, this element is more pH sensible, but its percolation is controlled by more stable mineral (e.g. carbonates). Zn, instead, is more pH dependent and the Zn minerals (present in the freshly quenched bottom ash) are too soluble to stably entrap this elements: the lower leachability of zinc registered in the older bottom ash can only be associated with its embedding in the neoformations.

Cu mobilization seems to be controlled by organic compounds, to which is bounded to form organometallic complexes (Chimenos et al., 2000; Yao et al., 2010; Arickx et al., 2010; Polettini et al., 2004). During weathering, however, the organic compounds can be oxidized or degraded by the bacteria, leading to a new mobilization of Cu: this metal can be transferred to Fe-oxides (Yao et al., 2010), Al-minerals (Meima et al., 2002), Cu-oxides (Chimenos et al., 2000; Meima et al., 2002), to carbonates (Van Gerven 2005; Yao et al., 2010), to exchangeable or residual fractions in form of free ion (Yao et al., 2010). Arickx et al. (2010) found that Cu presents a particular affinity to fulvic acids and to the hydrophilic fraction to which is bounded: those compounds can be absorbed in the Fe/Al (hydr)oxides in grater quantity as the pH decreases. The absorption by oxides, in fact, is enhanced by pH decrement (that promote the active surface increment), the oxides concentration and the ionic strength. It has been demonstrated, however, that the pH evolution is important for the long-term leaching ability of this compound because Cu-oxides (like tenorite, CuO) shows a great solubility when the pH drops to values close to 8 (Meima et al., 2002); Al-(hydr)oxides, also,

show stability in alkaline environment, while enhance the metal leaching in acid conditions (around pH=5; Yao et al., 2010). The Cu-stability can be achieved because of the formation of new sorption sites after long-term weathering (Meima et al., 2002; Wei et al., 2011), especially secondary neoformations of hydrous iron oxides, to which this metal show high affinity (Wei et al., 2011 b; Saffarzadeh et al., 2011).

Chromium, during natural weathering, presents an high leaching behavior (Van Gerven et al., 2005; Hyks et al., 2009). This characteristic is linked to the fact that the leachability of this metal is controlled by barium chromate (BaCrO_4) (Van Gerven et al., 2005; Cornelis et al., 2008) and by its capacity to replace sulphate (SO_4^{2-}) as oxyanion (CrO_4^{2-}) in ettringite formations (Van Gerven et al., 2005; Piantone et al., 2004; Cornelis et al., 2008). When, during weathering, pH decreases, ettringite dissolves and this metal enters into solution. Sulphates, then, precipitates with barium ($\text{Ba}_{0.5}\text{Ca}_{0.5}\text{SO}_4$, Hyks et al., 2009) and chromium enters in solution in higher quantities in form of oxyanion, to be subsequently absorbed into amorphous Al/Fe oxides as the pH becomes more acidic (Van Gerven et al., 2005)

Moisture and storage conditions can also play a role on the heavy metal retention: zincite and some sulphate minerals (chromates, vanadates), in fact, can be found in poorly drained heaps, while are negatively influenced in aerated and well drained systems, where they can trap heavy metals only temporary. Carbonates and Fe-oxyhydroxides, instead, seems to be stable at high L/S values and atmospheric conditions (Piantone et al., 2004).

CHAPTER 2

POSSIBLE APPLICATIONS OF MSWI BOTTOM ASHES AND ACCELERATED CARBONATION METHODOLOGIES

2.1 Possible applications of municipal solid waste incineration bottom ashes: introduction

The larger use of incineration as treatment of the solids wastes in the European countries and in several worlds countries, introduced the problematic of the bottom ash disposal. Moreover the European legislation is promoting the recycling and reuse of waste materials. The bottom ashes, that physically are similar to the natural sand and gravel material, can be used to realize civil or industrial manufacturing, without exploiting the natural resources. However the leaching of toxic compound and their initial reactivity represent an issue for the fast application of the ashes, that, for those reasons, are more commonly disposed in mono-landfills.

The most common applications of bottom ashes and fly ashes are: roads paving, concrete structures, embankments fill, parking areas, noise barriers and others.

In the following paragraph are described briefly some possibilities for the secondary application of MSWI bottom ash

2.1.1 Road paving

Road paving by the use of incinerator ashes is a common practice in European countries like Denmark, Germany, France and others, but in the last years a greater attention have been spend in order to identify the possible emissions that can derive by those structures.

The possible sources of risks that may generate from the paving of roads with bottom ashes-derived materials are the leakage of heavy metals and toxic compounds that can come into contact with the environment through different pathways: air (inhalation and dermal contact) and soil/groundwater (irrigation and food chain) (Shish et al., 2011).

Brigisdóttir et al. (2006) found that the quantity of emissions that can generate from a road paved with common material and from a road paved with bottom ash are similar (in particular for what concern the leaching of salty elements and some heavy metals like As (from 76 to

120 $\frac{mgAs}{kg}$) and Ni (from 11 to 200 $\frac{mgNi}{kg}$). Moreover the use of bottom ash required 20% less of gravel material, avoiding an ulterior leaching of metals (2.8 $\frac{mgAs}{kg}$ and 8.1 $\frac{mgNi}{kg}$).

A similar result was reported by Lind et al. (2008) that, by analyzing the heavy metals behaviour and their interaction with environment in a short observation time, found that the bottom ash (maturated in a pile for a period of 8 months) leaching capacity is comparable with the natural environment weathering and leaching.

From the structural point of view, it has been assessed that the evenness, the rutting and the bearing capacity of a road realized with bottom ashes is similar to the one realized with common road paving material, while lower permeability demonstrated by the ashes represents an issue for the streets that require a quick drainage (Phil, 1997).

2.1.2 Bottom ash in construction and ceramics materials

The reactions that occur during the unavoidable initial weathering process of the bottom ashes have several effects on the concrete durability. The swelling capacity, in fact, can negatively impact the concrete strength properties (Ginés et al., 2009), while the presence of reactive chemical elements can have several effects on both on the concrete material itself and on the reinforcing elements that are often coupled with his construction material, like steel or iron (Berg and Neal, 1998).

The addiction of fly ash (FA) to the bottom ash for the production of cementitious materials brings two main positive benefits on the compressive strengths: the first is that the improves the formation of an hydrate phase and the second in that compensates to the lack of fines grain size of the BA (Gines et al., 2009; Bouikni et al., 2009). However the maximum advisable quantity of FA should not exceed the 15%, because a greater percentage of FA would increase the water-cement ratio and reduce the compressive strength (Ginés et al., 2009).

The shrinkage behaviour after drying-wetting cycles has been assessed by Pera et al. (1996) that reported a positive response of BA on the durability the concrete made with this material if the metallic aluminium reactions were avoided.

Bottom ashes were also added to stabilize wastewater treatment sludge (respectively 20% and 80%) to create environment-friendly products, like bricks, to be used in public facilities. With a high sintering temperature (around 1000 °C), the compressive strength of the sewage sludge is enhanced by the addiction of bottom ashes. However the benefits on the porosity of this material are limited: the ashes, in facts, promote the formation of a beehive structure that

creates more voids in the brick. However this problematic can be avoided by increasing the sintering temperature: this procedure can create a permeability of 0.016 cm/s and a water absorption ratio of 2.8% (Lin et al., 2006).

Ceramic materials are widely used for many applications, not only industrial but also domestics, depending on their composition. The high temperature (higher than 1000 °C) adopted for the formation of those materials promote the homogeneous incorporation of the all elements that are used as ingredients. Recently have been investigated the possibilities to use both untreated bottom ash and vitrified bottom ash as main components of the ceramics elements. In particular it has been assessed that the use of non treated bottom ash have, from the point of view of the material durability, the same characteristics of the ceramics constituted by vitrified ashes (Siddique, 2010 and Rambaldi et al., 2010). From the chemical point of view, however, the vitrification have the potentiality to reduce the heavy metals release and to destroy the organic contaminants (Siddique, 2010 and Rambaldi et al., 2010), making them more suitable for several common applications, like the construction of decorative materials and pavements bricks.

2.1.3 Use of bottom ash as top cover construction material

A landfill cover is a multilayer system that is used as a barrier between the waste body and the external environment, with the main purpose to limit the landfill gas emissions and to control the infiltration of water through the waste (Travar et al., 2009).

Bottom ash can be used as mineral material for the construction of the top cover, however should be coupled with a finest grain size material (like fly ash or clay) in order to decrease its permeability in the liner (Travar et al., 2009). The protection layer, instead, can be realized by mixing the both fly ash and bottom with sewage sludge from anaerobic digestion (Travar et al., 2009).

The release of heavy metals from the ash is higher if the ashes underwent to a short weathering periods, however, in the long term, the precipitation on new clay-like minerals from the ash and the formation of absorptive sites can reduce the leaching of this compound through the barrier.

2.2 Accelerated carbonation of MSWI bottom ash: introduction

Carbonation represents an important step for the weathering process because of the physical-chemical changes that brings to the bottom ash. The duration of this process, however, represents a limiting factor for a secondary use of this material and a economical burden at the incineration plant expense, that should reserve an external area for the bottom ash weathering for the duration of months.

In the last decade several studies, mentioned in the following paragraphs, focused on the possibility to accelerate the carbonation process, not only to promote a fastest secondary use or to ensure a safe disposal, but also to evaluate the carbon dioxide sequestration capability of this material, in order to meet the necessity to control the CO₂ emissions.

2.2.1 *Parameters that affect the process*

The parameters that most of all affect accelerated carbonation are: moisture and grain size of the heap, temperature, carbon dioxide partial pressure in the system. The operating conditions have a great importance on the effects of treatment because the physical/chemical changes strictly depend on the environmental conditions.

2.2.1.1 Moisture

The presence of water in the heap porosities should be controlled because, as already demonstrated, it represents an important media for the interaction between CO₂ and calcium compounds: dissolved CO₂ can in fact interact with leached Ca²⁺. However too high water quantities represent an obstacle for CO₂ diffusion through the matrix (Costa et al., 2007; Baciocchi et al., 2010).

Rendek et al. (2006, a) found that a moisture content of 15 % (w/w) gives the highest results of carbon dioxide absorption ($25 \div 30 \frac{l}{kgDM}$) for a 4 mm-sieved sample of MSWI bottom ash at the CO₂ pressure of 2 bar (corresponding to a CO₂ solubility in pore water of $68 \frac{mol}{m^3}$ at a temperature of 20°C). Lower values were achieved for higher moisture contents, confirming that the dissolved CO₂ may experienced more difficulties to interact with the ash particles.

2.2.1.2 Ash grain size

It has been demonstrated that the highest proportion of Ca-based compounds are present in the finest part of the bottom ash (Freyssinet et al., 2002; Costa et al., 2007), and so it is

expected to be more reactive with CO₂. Baciocchi et al. (2010), in fact, found that at the same operating conditions (pressure 2 bar, L/S $0.3 \frac{l}{kg}$, T 30°C) the finest fraction (from 0.425 mm to less than 0.150 mm) could show a carbon dioxide uptake from 9 to 14 %, while the coarse fraction (from 12 mm to 0.425 mm) showed a lower interaction capacity (around 4% of carbon dioxide absorption) after a treatment of 8 hours.

2.2.1.3 Temperature and CO₂ partial pressure

The operating temperature can have an effect both for the solubility of carbon dioxide in water and on the elemental dissolution of minerals in the bottom ash matrix.

The CO₂ solubility is described by the Henry's law:

$$[CO_2] = K_{CO_2} \times P(CO_2)$$

Where :

[CO₂] is the CO₂ concentration in water ($\frac{mg}{l}$)

K_{CO₂} is the Henry's constant ($\frac{mg}{l atm}$) that depends on the gas-solvent characteristics and on the temperature

P(CO₂) is CO₂ partial pressure (atm).

The Henry's constant values decrease with the increase of temperature, but the concentration of the gas in the liquid solution is also directly proportional to the partial pressure of the gas. In particular Rendek et al. (2006 a) showed that by increasing the carbon dioxide partial pressure from 2 bar to 17 bar (Figure 2.1) the carbonation process developed much more faster: higher pressures, in fact, lead to an increase in the concentration of carbon dioxide in the pore water, providing an higher rate kinetic. However, for a given quantity of bottom ash, is not possible to obtain higher quantities of carbonates by increasing the CO₂ partial pressure.

Temperature can play a role on what concern the carbon dioxide absorption: Baciocchi et al. (2010), in fact, found that increasing the temperature from 30 to 50°C at the same pressure and moisture conditions (P=10 bar and L/S $=0.3 \frac{l}{kg}$) the CO₂ uptake increased of 5% for each grain size fraction. The results is linked with the leachability of cations Ca and Mg that are liberated during silicate dissolution that starts at this temperatures.

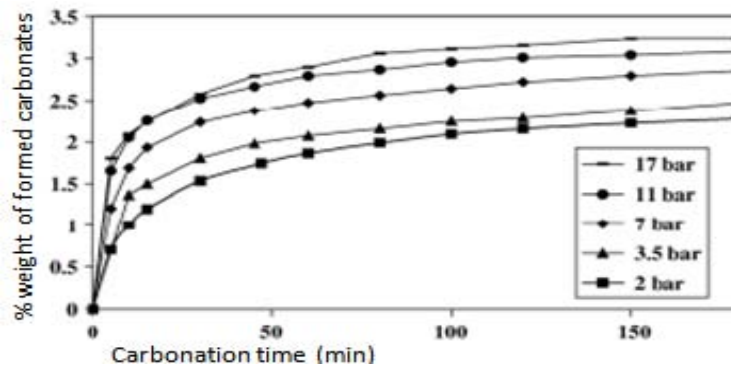


Figure 2.1: Gain of carbonate content as a function of carbonation time for five different CO_2 pressures ranging from 2 to 17 bar (moisture content: 20% w/w), (Randek et al. 2005).

2.3 Effects of accelerated carbonation on the heavy metals leaching behavior

The effects consequent to the artificial carbonation are similar to the one registered with the natural weathering, with the positive aspect that those results are achieved in much lower time. In particular the pH undergoes to a rapid decrement within the first hours of treatment: Arickx et al. (2006), at the operating condition of $T=50^\circ\text{C}$, 10% CO_2 enriched air and moisture 26% (w/w), found that the pH decreased from very alkaline values (around 12) to 8.5 within the first day of experimentation, while, to reach the same results at the same temperature and CO_2 percentages but with atmospheric humidity, the required time was 48 h (Arickx et al., 2010). Similar results were achieved by Baciocchi et al. (2010) in the first 2 hours at the operating conditions of 30°C , CO_2 pressure of 10 bar and $L/S = 0.3 \frac{\text{l}}{\text{kg}}$. Those results have been obtained by applying the accelerated carbonation to the finest fraction of bottom ash ($< 2 \text{ mm}$).

This fast pH drop has an important influence on metal leaching, like Pb and Zn, which concentration in the leachate can decrease of more than one order of magnitude in the same period of time (Baciocchi et al., 2010; Aricks et al. 2006). Poletini et al. (2005) and Poletini et al. (2004) associated the Pb and Zn reduction to the sorption of this metal onto calcite or onto oxides of Al or Fe formed during carbonation in slurry phase condition ($L/S=10$).

Todorovic et al. (2006) registered an increase in Pb and Zn availability in the leachate by treating the bottom ash samples in a bag with technical-grade CO_2 gas (“moderate carbonation”), while couldn’t record any effect on those elements by treating the ash with a excess of CO_2 in suspension (“severe carbonation”).

Meima et al. (2002) found that Cu-leaching ability was reduced after accelerated carbonation (bubbling $5 \frac{l}{h}$ of moistened air through the ash suspension for 3-4 days), even if presented higher leaching values respect to natural weathering: this can be associated, as above mentioned, to the secondary neoformations that can develop after long weathering periods and that can bound the heavy metals (Meima et al., 2002). Van Gerven et al. (2005), however, registered a high Cu leaching reduction in the first days of treatment by applying 10% CO₂ enriched air, the temperature of 30÷50°C and humidity under 25%. Similar results were achieved by Arickx et al. (2010) that reported a decrease of 30% in Cu release in the first 48 h of carbonation. The decrease in Cu mobilization can be linked to the complexation to Fe/Al neoformations that are formed in higher quantities respect to ne natural weathering (Polettini et al., 2004). In particular (Arickx et al., 2010) found that Al-(hydr)oxides increased to $7.86 \frac{gAl(OH)_3}{kg}$ during the accelerated carbonation, a slightly higher value than the one registered during natural ageing.

Chromium is considered ad a critical contaminant because, during carbonation, its mobilization is enhanced in greater proportion respect to the natural weathering (Baclocchi et al., 2010; Van Gerven et al., 2005), especially in the finest grain-size (Baclocchi et al., 2010). This behavior can be linked to the competitiveness that exist between oxyanions in sorption or precipitation reactions in alkaline environment: because SO_4^{2-} and CO_3^{2-} that are present in higher quantities, this may cause the greater Cr, Sb and Mo leaching (Van Gerven et al., 2005; Cornelis et al., 2008).

Arickx et al. (2010) found also that accelerated carbonation can have a role on the organic matter decrease in the bottom ash, reporting TOC (especially the hydrophilic fraction) decrement of 55% in the solid phase and a decrement of 26% in the leachate. However Todorovic et al. (2006) registered a very high increment of DOC leaching during severe carbonation

The interaction between the carbon dioxide flux with the other operating conditions should be monitored in order to limit the leaching behavior of some elements: in particular Todorovic et al. (2006) found that Cu, S and Sb mobility was reduced when the temperature and the treatment time was increased; DOC mobilization also shows a decrement with a longer treatment.

Polettini et al. (2004) induced the accelerated carbonation also by blowing a N₂ flux and a atmospheric oxygen in the reactor. The anoxic conditions created with the nitrogen flux leaded to a decrement of the pH respect both the fresh and weathered bottom ash, but always in the alkaline range of values. However the increasing of treatment time showed a positive

influence. The forced aeration, instead, reproduced, in 2÷4 days the same conditions created by the natural weathering.

2.4 Examples of field scale accelerated carbonation

2.4.1 Use of incinerator flue gas

The stack gas from incinerator contains 10% of CO₂ and the treatment of bottom ash with this gas can give positive results not only for the bottom ash stabilization but also to decrease the carbon dioxide emission in atmosphere (Arickx et al., 2006; Van Gerven et al., 2005). Arickx et al. (2006) addressed the stack flux through a pipe packed with almost 500 g of bottom ash sand fraction. The greater technical problem was related to the condensate that formed from the high percentage of humidity of the flue gas (21 %vol): the water that reaches the bottom ash, in fact, leads to an high initial leaching of heavy metals and so to waste water volumes to be treated. The result is similar to the one reach in laboratory scale with accelerated carbonation, giving a totally stabilized material. Anyway the maximum carbon dioxide sequestration potential is equal only to the 2% of the total emission, and, for this reason, the utilization of bottom ash for pollutants emissions control seem not to be feasible (Bacocchi et al., 2010).

2.4.2 Accelerated carbonation in industrial plants

In order to promote a fast carbonation of several tonnes of bottom ashes, Steketee et al. (2009) applied two industrial methodologies: the use of silos equipped with blowers (1.2 m³ CO₂/ton h), gas mixing units and heat exchangers, and the use of composting methodologies, divided in a first indoor phase, where the ashes are turned with a revolving machine, that promoted the interaction with the atmospheric CO₂, and an external maturation phase to promote the complete mineralization. During the tests were treated 3000 tons of bottom ashes for a total observation time of 11 weeks.

In both cases it has been observed a lowering leaching of heavy metals, in particular of copper, aluminium and antimony, and a fast decrease of the leaching of DOC.

CHAPTER 3

ORGANIC MATTER IN THE MUNICIPAL SOLID WASTE INCINERATION BOTTOM ASH

3.1 Introduction: organic matter composition in the bottom ash and bacteria activity

Due to the inhomogeneous combustion that can develop in the combustion chamber, certain quantities of unburned organic biodegradable material can be collected with the bottom ash (Zhang et al., 2004; Ferrari et al., 2002). Some carbonaceous waste, in particular, seems to be more resistant in the combustion process: cotton and bone fragments, banana and orange skins (Chimenos et al., 1999), and total organic content in the freshly quenched bottom ash can accounts to a value around 4% (Zhang et al., 2004; Chimenos et al., 2004; Rendek et al., 2007). Rendek et al. (2007 b) found that the increment of unburned material can be directly linked to the waste fuel composition and to the methodology of combustion. Separate collection and the consequent removal of inerts, in fact, decrease the LHV of the raw waste, with the consequent necessity to add more material to the furnace to maintain an high HV. This facilities the formation of non homogeneous combustion areas. The rotary kiln incineration device seems to provide less efficient combustion, because the greater quantities of TOC in the bottom ash. However the percentages of elemental carbon are greater respect to the soluble and degradable, due to the areas of pyrolysis that may develop during the waste mixing. (Rendek et al., 2007 b).

The quantity of organic carbon present in the bottom ash can be evaluated by the loss of ignition (LOI) by heating the sample at 550°C for 2 hours (Chandler et al., 1997). This parameter, in fact, corresponds to the quantity of total unburned material. The total carbon composition has been found to be greatly composed by organic carbon (around 70%) and the remaining by inorganic carbon (around 30%) (Chandler et al., 1997; Van Zomeren and Comans, 2009)

The principal organic compounds that are more common in the fresh ash are carboxylic acids, n-alkanes, steroids, phthalates, PAH, carbohydrates, amino acids and hexosamines (Zhang et al., 2004; Dugenest et al., 1999). The acids are present in longer chains; n-alkanes presents some analogies to the natural petroleum paraffines; steroids are mainly present as cholesterol and sitosterol; phthalates are toxic but stable compounds, resistant to

biodegradation; PAH are formed in pyrolysis conditions and are also toxic, however are present in much lower quantities than the other elements (Dugenest et al., 1999); carbohydrates, and especially glucose, can be obtained by thermal decomposition of cellulose and successive acid hydrolysis (Zhang et al., 2004).

Ferrari et al. (2002) found that the most abundant organic carbon species that can be extracted (DOC) is mainly composed by low molecular weight and very polar organic acids, that derives from thermal decomposition of lignin and cellulose like materials. Van Zomeren and Comans (2009) reported that the most abundant fraction of extractable organic carbon is composed by fatty acids and hydrophilic acids, while only the 1% of the DOC consists of humic acids. The non extractable organic carbon, instead, derives from the non chemically deteriorated organic carbon and represents the most abundant fraction (70%) in the organic carbon speciation. This fraction is directly linked to the presence of very hydrophobic substances, like plastic material in the raw water (e.g. PS) (Ferrari et al., 2002; Van Zomeren and Comans, 2009)

The microorganisms present in the bottom ash are able to degrade the organic matter and to resist to the inhospitable environment that the bottom ash offer: in particular Dugenest et al. (1999) found that bacteria show a fast growth during the first month of weathering ($T=30^{\circ}\text{C}$) and continue to multiply for the first 5 month of natural treatment, while a decrement was registered between the months 5 and 17 of weathering. A similar result was found by Zhang et al. (2004) that, in the first 5 months of observation could register a decrease of glucose and a dominance of ribose concentration in the stored up ashes, confirming an increase of microbial biomass. The carboxylic acids (Dugenest et al., 1999) and, above all, aminoacids and hexosamines (Zhang et al., 2004), are the most degraded and can experience the 60% of degradation (Dugenest et al., 1999; Zhang et al., 2004).

However the bacteria activity in the bottom ash can be improved with higher moisture (Rendek et al., 2006 b) while an increment of temperature between 30°C and 70°C decreases the rate of degradation (Dugenest et al., 1999). Moreover the highest grade of activity is registered in the finest fraction, where the organic matter concentration seems to be greater (Zhang et al., 2004).

3.2 Influence of bacteria activity on the bottom ash

The influences that bacterial activity can have on bottom ash during the degradation of the organic compounds has not been deeply studied. However Rendek et al. (2006 b) found that the carbon dioxide produced by the bacteria during the aerobic respiration can interact with

the bottom ash matrix. In particular it has been demonstrated that, during respiration tests with OxiTop, an high quantity of carbon dioxide that should have been released during the test, was entrapped in the fresh ash pore water (Figure 3.1).

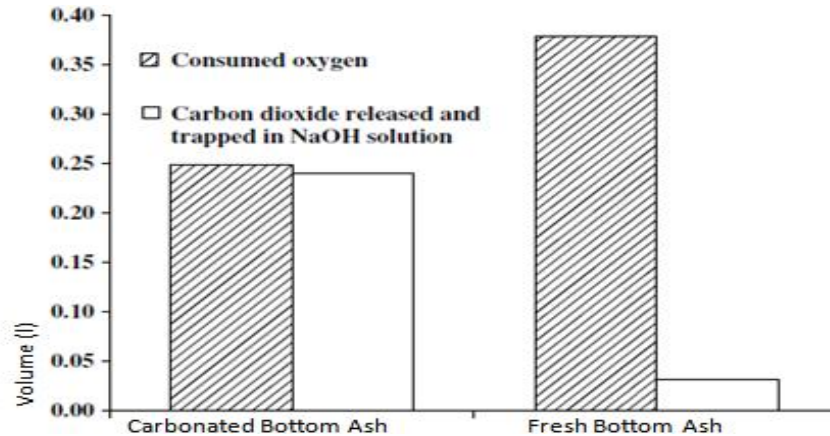


Figure 3.1: Comparison between volumes of consumed O_2 and CO_2 in NaOH solution for fresh and carbonated ash at 23% (w/w) moisture after one week at 30°C (Rendek et al, 2005).

The interaction between the bottom ash matrix and the CO_2 produced by bacterial can lead to the formation of carbonates (Rendek et al., 2006 b)

Moreover Aouad et al. (2008) found that, in acid conditions (pH 6.7), bacteria are able to exploit the release of oligoelements (Fe and Mg) from the mineral dissolution and to produce a biofilm that covers and cements the bottom ash grains together. A comparison between the leaching behavior of sterile bottom ash and biotic bottom ash showed that the heavy metal retention capacity of the biofilm can range between 31% to 53%, depending on the element. The alteration rate of bottom ash also experiences a decrement in a biotic environment.

3.3 Organic carbon leaching from bottom ash

The availability of mobilized organic matter in the bottom ash can be impactful for the environment (Rendek et al., 2007 a; Guimaraes et al., 2006) because can increase the BOD and COD in the leachate (Guimaraes et al., 2006).

Guimaraes et al. (2006) found that the DOC leaching is correlated to pH and to Ca leaching. In particular, at alkaline-neutral conditions the DOC dissolution is independent from Ca leaching, while, at acidic conditions DOC behaviour is dependent to Ca dissolution and can form DOC-Ca complexes. This trend can be controlled by the raw waste composition:

when the percentages of paper is higher respect to the percentages of plastics the DOC is likely to leach at more acidic conditions, at the contrary if the quantities of burned plastics are higher respect to the papers, the DOC dissolves at more alkaline values. Moreover if calcium hydroxide is added during the incineration process can also play a role on the organic carbon leaching behavior because promotes the formation of DOC-Ca complexes.

Nevertheless Zhang et al. (2004) found that the microbial degradation is determinant for the extractable dissolved organic carbon, and reported a TOC decrease from 1.17% in fresh ash to 0.76% in carbonated ash.

CHAPTER 4

MATERIAL AND METHOD

4.1 Material collection and conservation methodologies

In the following paragraph are described the plants where the materials have been collected, the sample preparation and the storage conditions. The information related to the wastewater treatment plant and the incineration plant has been directly derived from the web sites of the organizations that manage those plants, and respectively VASYD and SYSAV.

4.1.1 Sewage sludge

The sludge have been selected from the Källby Wastewater Treatment Plant, that treats the wastewater from the city of Lund (75000 residents and 120000 population equivalents). This plant is managed by the municipal joint authority “VA SYD”, in charged for the water and sewage management for the Burlöv, Eslöv, Lund and Malmö departments.

The wastewater, after the mechanical, biological and chemical treatments it passes through a pond system, and then discharged into the stream Höje å. This sludge is obtained from the primary clarifiers, the secondary clarifiers and from the post precipitation. The water content of this material is very high and some treatments are required:

1. mechanical thickening, by the use of 3 drum thickeners;
2. digestion under anaerobic conditions, in mesophilic environment for the duration of 20 to 30 days. The biogas formed is firstly depleted of carbon dioxide, water and hydrogen sulphide to obtain mainly methane, and then is reused as vehicle fuel;
3. dewatering in centrifuges with the addition of polymers, to better separate the solid from the liquid phase.



Figure.4.1: Källby wastewater treatment plant, aerial view. Google Earth, 2008

The wastewater treatment, and consequently the characteristics of the sludge, is controlled by the “ReVAQ” certification system, run by the Swedish Water and Wastewater Association. This system monitors the reduction of heavy metals in the wastewater and controls the amount of nutrients in the sludge, in order to obtain a high quality product usable as agriculture fertilizer. The most common applications of this material are reported in Table 4.1.

Table 4.2 and 4.3 respectively lists the physical and pH characteristics of the sludge and the elemental concentration in the eluate evaluated for a sewage sludge sample subjected to 4 days of respiration test and to a batch leaching test (the characteristics of those tests are described in the following paragraphs).

Table 4.1: Sludge production, storage and main uses from the Källby wastewater treatment plant in the year 2011. Source: Tobias Hey, Lund University.

| <i>Stored, produced, main uses</i> | <i>Quantities (Ton)</i> |
|------------------------------------|-------------------------|
| Stored in Värpinge (01-01-2011) | 4945 |
| Produced in 2011 | 6968 |
| Agriculture fertilizer | 6477 |
| Soil production | 454 |
| Landfills top cover | 677 |

Table 4.2: Moisture content, dry density and pH of the sewage sludge

| | |
|-----------------|----------------------|
| <i>Moisture</i> | 74% |
| <i>Density</i> | $264 \frac{kg}{m^3}$ |
| <i>pH</i> | 8.5 |

Table 4.3: Elemental composition of the wastewater sewage sludge after 4 days of respiration tests, evaluated in the leachate obtained with the batch leaching test.

| <i>Heavy metals</i> | <i>Concentration</i> ($\frac{\mu g}{l}$) |
|-----------------------|--|
| Cr | $1.6 \pm 20\%$ |
| Cu | $24 \pm 10\%$ |
| As | $26 \pm 20\%$ |
| Cd | $0.18 \pm 10\%$ |
| Hg | $0.07 \pm 15\%$ |
| Pb | $<1.5 \pm 10\%$ |
| Zn | $35 \pm 30\%$ |
| Mo | 50 |
| Sb | $5 \pm 10\%$ |
| Fe | $3.5 \pm 10\%$ |
| <i>Other elements</i> | <i>Concentration</i> [$\frac{mg}{l}$] |
| Al | $0.13 \pm 10\%$ |
| Si | $2.6 \pm 10\%$ |
| Ca | $11 \pm 5\%$ |
| Mg | $6.9 \pm 5\%$ |
| S | 84.8% |
| Na | $9.9 \pm 5\%$ |
| K | $25 \pm 5\%$ |
| N _{tot} | $180 \pm 10\%$ |
| Chloride | - |
| TOC | 300 |

The sludge has been always stored in PP containers since the day of sampling and it has been always preserved in the fridge at the temperature of 3.5°C.

4.1.2 Bottom ash

The bottom ash used for those experiments have been collected by the Sydvästra Skåne Avfallsaktiebolag (SYSAV) incinerator, located in Malmö, Sweden. This incinerator, designed in 1974 and renewed with a new line operative since the year 2000 and corresponding to the new EU-standards in relation to the emissions from waste incineration plants, is owned by nine municipalities in the Skåne district: Burlöv, Kävlinge, Lomma, Lund, Malmö, Staffanstorps, Svedala, Trelleborg and Vellinge.

The system is able to treat a total of 550000 ton of waste per year and is equipped with two hot-water boiler to produce hot water for the district heating network, and with two steam boilers that produce electricity and heating (Figure 4.2).

The waste, collected from residential, businesses and recycling centers, is incinerated without further pretreatment in a reverse acting grate furnace. The temperature in the furnace is normally over the 1000°C and the waste is firstly dried and then combusted.

The products of this process are slag, fly ashes, wastewater and gypsum. The slag production is estimated to be roughly 15% to 20% in weight, while the fly ashes are the 3% in weight of the combusted waste. Bottom ash and fly ash are collected separately and moved to a waste site (Spillepeng, Malmö). Bottom ash are deprived of iron and inert materials and are stored in heaps to neutralize the chemical properties. Fly ash, instead, are moved to the definitive disposal. The wastewater is treated in situ while the gypsum slurry is dewatered and sent to the landfill.

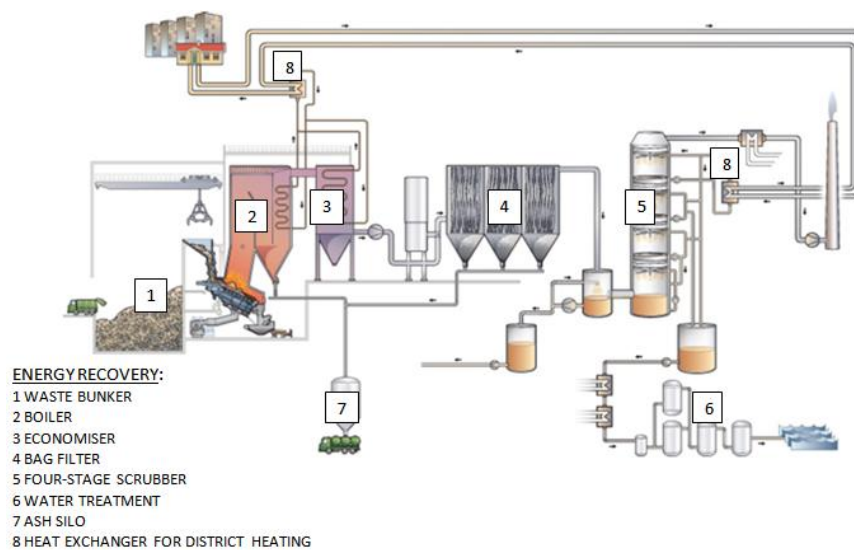


Figure 4.2: Sysav waste-to-energy plant scheme, Malmö. Sysav 2009.

The bottom ash samples have been collected in two differed stages of weathering: a first 35 kg sample was collected after 8 months of ageing and it has been stored inside a jar at laboratory temperature and atmospheric condition for almost 10 months (“carbonated ash” sample); the second heap, instead, have been taken from the plant 15 hours after quenching (“fresh ash” sample) and it has been always preserved in a PE bag inside the freezer (T=-18°C).

The ashes samples have been obtained by a quartering procedure: the whole quantity of ash (the fresh ashes have been taken from the freezer one day before to have a thawed material) have been disposed on a plastic sheet on the ground and it have been mixed up. Secondly the heap has been divided in four parts (Figure 4.3) and two opposite sections have been returned to the container. This procedure was repeated for three times.

The obtained quantity has then been sieved with a 4 mm sieve.



Figure 4.3: Sample preparation steps: quartering procedure and sieving.

The sieved quantity of carbonated ash (2 kg) have then been stored in a PE bags in the fridge, while the fresh ashes have been divided in smaller quantities of 400 g and stored in PE bags in the freezer.

Because of the necessity to have a ambient temperature material for the experiments, the material preserved in the fridge have been always taken out one hour before any usage, while the one preserved in the freezer have been taken out at least two hours before the test starting.

4.1.2.1 Carbonated ash characteristics

Moisture, density and pH have been evaluated, and the results are summarised in the following table (Table 4.4). Moisture have been obtained by drying a sample in the oven for 24 hours at the temperature of 105°C; the density is correlated to the sample dry weight, non-compacted.

Table 4.4 Moisture, dry density and pH evaluated for the carbonated ash.

| | |
|-----------------|--------------------------|
| <i>Moisture</i> | 15.4% |
| <i>Density</i> | 1147.42 $\frac{kg}{m^3}$ |
| <i>pH</i> | 9.7 |

As for the sludge, the chemical composition has been analyzed after 4 days of respiration test and by measuring the elements concentration in the leachate obtained by the batch leaching test. The following table (Table 4.5) lists the chemical composition of this material.

Table 4.5: Elemental composition of the carbonated ashes after 4 days of respiration tests, evaluated in the leachate obtained with the batch leaching test.

| <i>Heavy metals</i> | <i>Concentration</i> ($\frac{\mu g}{l}$) |
|-----------------------|--|
| Cr | $5.6 \pm 20\%$ |
| Cu | $45 \pm 10\%$ |
| As | $1.6 \pm 20\%$ |
| Cd | $0.18 \pm 10\%$ |
| Hg | $<0.05 \pm 15\%$ |
| Pb | $21 \pm 10\%$ |
| Zn | $160 \pm 30\%$ |
| Mo | 13 |
| Sb | $16 \pm 10\%$ |
| Fe | $0.05 \pm 10\%$ |
| <i>Other elements</i> | <i>Concentration</i> [$\frac{mg}{l}$] |
| Al | $2.4 \pm 10\%$ |
| Si | $1 \pm 10\%$ |
| Ca | $104 \pm 5\%$ |
| Mg | $0.62 \pm 5\%$ |
| S | 105% |
| Na | $66 \pm 5\%$ |
| K | $21 \pm 5\%$ |
| N _{tot} | $2.2 \pm 10\%$ |
| Chloride | $76 \pm 5\%$ |
| TOC | < 3 |

4.1.2.2 Fresh ash characteristics

The physical and chemical characteristics of this material are reported in the following tables (Table 4.6 and Table 4.7).

Similarly in the other cases, the elemental composition has been analyzed after the 4 days of respiration tests and after the batch leaching test procedure.

Table 4.6 Moisture, dry density and pH evaluated for the fresh ash.

| | |
|-----------------|-----------------------|
| <i>Moisture</i> | 18.1% |
| <i>Density</i> | $1055 \frac{kg}{m^3}$ |
| <i>pH</i> | 10.64 |

Table 4.7: Elemental composition of the fresh ashes after 4 days of respiration tests, evaluated in the leachate obtained with the batch leaching test.

| <i>Heavy metals</i> | <i>Concentration ($\frac{\mu g}{l}$)</i> |
|-----------------------|---|
| Cr | $49 \pm 20\%$ |
| Cu | $520 \pm 10\%$ |
| As | $3.8 \pm 20\%$ |
| Cd | $0.3 \pm 10\%$ |
| Hg | $0.084 \pm 15\%$ |
| Pb | $24 \pm 10\%$ |
| Zn | $213 \pm 30\%$ |
| Mo | 65 |
| Sb | $18 \pm 10\%$ |
| Fe | $0.15 \pm 10\%$ |
| <i>Other elements</i> | <i>Concentration [$\frac{mg}{l}$]</i> |
| Al | $9.1 \pm 10\%$ |
| Si | $2.1 \pm 10\%$ |
| Ca | $68 \pm 5\%$ |
| Mg | $0.17 \pm 5\%$ |
| S | 58.7% |
| Na | $154 \pm 5\%$ |
| K | $46 \pm 5\%$ |
| N _{tot} | $3.1 \pm 10\%$ |
| Chloride | $210 \pm 5\%$ |
| TOC | 46 |

4.1.3 Conservation methodology after the tests

After the respiration tests the solid samples have been stored in PE bags in the freezer. The sodium hydroxide, instead, have been moved with a syringe in 20 ml PE containers and preserved in the fridge.

The leachate samples have been aspirated by syringes from each glass bottles and have been moved to PE containers and preserved in the freezer.

4.2 Tests description

4.2.1 Respiration tests

For the respiration tests it has been used an WTW OxiTop Control B6M (the laboratory is equipped of 6 bottles with a volume of 1000 ml each), completed of the following main accessories:

- a “OC controller 110”, to monitor the activity of the samples in the measuring container;
- the measuring heads, that are able to transmit to the controller the measurement data by means of the infrared interface: by calling up the data is possible to see on the controller display the graphic trend of the samples;
- The CO₂ absorber container that is possible to screw to the measuring heads.



Figure 4.4 Photo of one of the OxiTop bottles complete of measuring head and controller used in the laboratory.

The evaluation period starts after the lag phase and it has a duration of 4 days. The data, once the test is completed, are sent from the controller to the computer and can be analyzed by a Microsoft Excel spreadsheet: is therefore possible to see the values of pressure change recorded every 20 minutes. The negative pressure values that are showed in the spreadsheet are linked with the fact that while the oxygen is consumed by the microorganism in the organic substance, the carbon dioxide is released as a product of their respiration. This carbon dioxide is absorbed by the reagent (sodium hydroxide) and a depression in the bottle is registered (Figure 4.5).

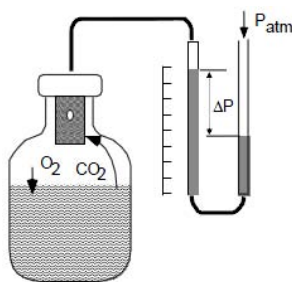


Figure 4.5: Schematic working model used by the OxiTop system. S. Marsili-Libelli: *Fondamenti di bioenergetica cellulare*

From those values and applying the ideal gas law, it has been possible to evaluate the quantity of oxygen consumed, and, assuming that the number of moles of consumed oxygen are equal to the number of mole of carbon dioxide produced, is possible to calculate the CO_2 released both for wet weight and dry weight of the sample; moreover, by a chemical analysis, is possible to evaluate the actual quantity of CO_2 that the sodium hydroxide has been able to absorb.

By monitoring the trend of the process curves, is possible to notice when, inside the bottles, there is a depletion of oxygen, because the curve starts to move from a regular proceeding. This situation is linked to the fact that at the beginning of the tests in the bottle there is the atmospheric pressure (1013.25 hPa) with an oxygen partial pressure of 210 hPa: when the OxiTop registers a negative pressure equal to this value, it means that the O_2 has been completely consumed and the bottles should be aerated. During the tests described in the next chapter the bottles have been aerated even if the pressure didn't reach the negative value of 210 hPa because the registered activity in many cases was low and the proceeding of the pressure curves was not regular. In some cases, highlighted in the following chapters, the pressure curves presented positive values. This is not in line with normal functioning of the OxiTop. The main reasons of this malfunctioning could be correlated to a problem of the sensors, to a low absorption capacity of the sodium hydroxide or to the development of anaerobic conditions in the bottles. From the previews, the low absorption capacity of the NaOH seems to be the last probable because, as alkali solution, can easily react with carbon dioxide (Peng et al., 2012). For those experiments the sodium hydroxide solution was 0.1 M for the CA samples and 1 M for the FA samples

When the trends presented positive values of pressure, the curves have been rearranged maintaining the same trend but shifting down the values in the negative axes. In particular in some situations at the beginning of the test the curve showed an increment in the positive axis followed by a decrement in the negative axis. The rearrangements have been done considering

the increment in the positive part as an initial non absorption or non-sensor detection, and so those growing values have been considered equal to zero. The positive peak, thus, was considered as the starting point on the analysis and the followed decrement curve was shifted in the negative axis of the same value of the peak gap, to which it was given the value zero.

During the tests, furthermore, it has not been possible to maintain a constant temperature (the bottles were subjected to the daily temperature variations in the laboratory) and moisture.

4.2.1.1 Tests preparation

The respiration test have been running for the with the following typologies of samples: carbonated ash; carbonated ash + 1%, 2%, 3%, 4%, 5% of anaerobically digested sewage sludge; carbonated ash + 1%, 2%, 3%, 4%, 5% of cellulose; fresh ash; fresh ash + 1%, 2%, 3%, 4%, 5% of anaerobically digested sewage sludge; fresh ash + 1%, 2%, 3%, 4%, 5% of cellulose.

For each test it has been produced at least 3 replicates, for a total of 66 samples analyzed. However, in few cases, for the data analysis described in the following chapters, only two replicates for each test have been considered.

Samples of around 120 g of bottom ash have been weighted on a precision balance and, in the case of sludge or cellulose adding, the required percentage in weight is mixed to the ashes. Afterwards the prepared samples have been watered with controlled quantities of distilled water, in order to get the needed moisture (23% w/w).

The following table (Table 4.8) summarizes the material composition of each sample composed by bottom ash and bottom ash with the addition of sewage sludge (SL). Table 4.9 lists the samples characteristics composed wy ashes mixed with cellulose crystalline (MC). For any sample is reported the moisture content, the external organic matter content and the ash content

Table 4.8: Samples composition, series number of each sample, moisture content achieved, sludge content and ash content

| <i>Sample</i> | <i>Series number</i> | <i>Moisture</i> | <i>SL</i> | <i>Ash</i> |
|---------------|--------------------------|-----------------|-----------|------------|
| | | % | g | g |
| CA | 14 | 23.57 | 0 | 120.72 |
| | 15 | 23.51 | 0 | 120.13 |
| CA+1% | 56 | 23.06 | 1.29 | 120.28 |
| | 57 | 22.98 | 1.49 | 120.23 |
| | 58 | 23.22 | 1.29 | 120.59 |
| CA+2% | 17 | 23.37 | 2.56 | 120.42 |
| | 18 | 23.43 | 2.8 | 120.75 |
| | 19 | 23.30 | 2.65 | 121.08 |
| CA+3% | 20 | 22.80 | 3.8 | 122.78 |
| | 21 | 22.90 | 3.77 | 120.1 |
| | 22 | 22.94 | 4.05 | 121.49 |
| CA+4% | 23 | 23.19 | 5.17 | 124.32 |
| | 24 | 23.52 | 5.5 | 120.35 |
| | 25 | 23.37 | 4.9 | 120.85 |
| CA+5% | 27 | 23.52 | 6.31 | 125.42 |
| | 28 | 23.37 | 6.41 | 122 |
| FA | 35 | 23.27 | 0 | 123.47 |
| | 36 | 23.17 | 0 | 127.25 |
| | 37 | 23.05 | 0 | 128.05 |
| FA+1% | 38 | 22.94 | 1.47 | 133.99 |
| | 39 | 22.81 | 2.16 | 127.83 |
| | 40 | 22.68 | 1.39 | 137.5 |
| FA+2% | 41 | 22.89 | 3.06 | 129.62 |
| | 53 | 23.17 | 2.64 | 127.5 |
| | 54 | 23.01 | 2.6 | 127.2 |
| FA+3% | 44 | 22.96 | 4.07 | 129.93 |
| | 45 | 22.98 | 4.1 | 127.44 |
| | 46 | 23.12 | 3.97 | 127.22 |
| FA+4% | 47 | 23.08 | 5.22 | 127.68 |
| | 48 | 23.25 | 5.24 | 127.66 |
| | 49 | 22.94 | 5.43 | 127.89 |
| FA+5% | 50 | 22.98 | 6.52 | 127.73 |
| | 51 | 23.16 | 6.44 | 127.4 |
| | 52 | 23.23 | 6.45 | 127.22 |
| | 59 | 23.11 | 6.36 | 127.48 |
| | 60 | 23.59 | 6.46 | 127.45 |

Table 4.9: Samples composition, series number of each sample, moisture content achieved, cellulose content and ash content

| <i>Sample</i> | <i>Series number</i> | <i>Moisture</i> | <i>MC</i> | <i>Ash</i> |
|---------------|----------------------|-----------------|-----------|------------|
| | | % | g | g |
| CA+1% | 61 | 22.8 | 1.2 | 120.12 |
| CA+2% | 62 | 22.43 | 2.41 | 120.3 |
| CA+3% | 63 | 22.25 | 3.62 | 120.5 |
| CA+4% | 64 | 21.72 | 4.81 | 120.22 |
| CA+5% | 65 | 21.77 | 6.01 | 120.15 |
| FA+1% | 67 | 22.02 | 1.31 | 120.27 |
| FA+2% | 66 | 21.89 | 2.36 | 120.15 |
| FA+3% | 68 | 21.41 | 3.8 | 120.34 |
| FA+4% | 69 | 21.14 | 5.03 | 120.47 |
| FA+5% | 70 | 20.96 | 6.38 | 120.78 |

Once the three bottles are filled with this samples, by the use of the measuring heads is possible to associate each bottle to the controller and to monitor the trend day by day.

The tests ran at ambient temperature ($22\pm0.5^{\circ}\text{C}$) and an average value is considered in the results.

4.2.2 Batch Leaching tests

The leaching tests are important in order to assess the possible impacts that a certain kind of material, like a waste, can have on the environment, and in particular on the soil and on the groundwater for a short or a long period of time: those tests, in fact, are performed in order to simulate the effect that natural dilavation, for example caused by the rain, can have on the waste material disposed in a landfill (Fällman et al., 1996; Allgaier and Stegmann, 2005).

For this work it has been followed the standard procedure EN 12457-2:2002: one stage batch test at a L/S of $10 \frac{\text{l}}{\text{kg}}$ applied to the matrix with a particle size below 4 mm.

The batch leaching test is based on the concept that at the starting there is a concentration gradient between the free water volume, the material and the pore water. In relation to the diffusion coefficient of each substance present in the matrix, during the test time the gradient tends to decrease because of the increase of the concentration of those species inside the free water volume. At the end it should be reached a chemical equilibrium between the solid material, the pore water and the deionized water added (Fällman et al., 1996).

The test is performed by the use of a machine (Figure 4.5) provided of a network of springs linked to a rotating platform and a thermometer: the machine is filled of water (in order to

maintain the temperature constant and to produce a more soft shacking) and the temperature is rinsed to the required one (in this work the temperature have been fixed to the ambient one). The bottles, blocked through the springs, are moved by the rotating platform with a velocity of 60 revolutions for minute for 24 hours.

The agitation system is used in order to decrease the boundary layer around particles and increase the rate of leaching (Fällman et al, 1996).

After the shaking period is possible to observe the formation of two distinct phases: the solid on the bottom and the liquid one (Figure 4.6)



Figure 4.6: Batch Leaching process steps and equipment.

As reported above, the $\frac{L}{S}$ ratio was chosen equal to 10. In the term “liquid” is included not only the quantity of deionized water added in the test bottle, but also the quantity of pore water present in the matrix; on the other side “solid” represents the dry weight of the sample.

The choice of this value is correlated to the necessity to study the characteristics of the material in order to address it to the right disposal facility: higher values of this ratio, in fact, are used to assess the long term impacts of the disposed waste. In the practical scenario the L/S can be expressed by the following formulation (Equation 7.1) (Quina et al., 2011):

$$\frac{L}{S} = \frac{I \cdot T}{\rho \cdot H} * 10 \quad (\text{Equation 7.1}), \text{ where}$$

I= infiltration rate $\frac{cm}{y}$

T=time of interest (y)

ρ = material density ($\frac{g}{cm^3}$)

H=fill depth (m)

10= conversion factor ($\frac{10l}{cm \cdot m^2}$)

From the above equation is possible to see that, to predict the impacts on a long period of time, like 100 years, is necessary to impose a L/S equal to 10.

4.3 Applied modalities for the evaluation of the carbon dioxide absorption capacity of the bottom ashes.

In order to verify if the ashes have the capacity to absorb the carbon dioxide generated by the bacteria, both indigenous and external, is possible to analyze the quantities of carbonates, and in particular sodium carbonates, that are present in the absorber used during the respiration tests. The reaction between the sodium hydroxide and the carbon dioxide (Reaction 4.1) requires 2 moles of NaOH and one of CO₂ to obtain one mole of sodium carbonate and one of water.



Thus, by evaluating the quantities of Na₂CO₃ that are present in the solution and by considering the theoretical quantities of CO₂ produced by the microorganisms, is possible, by making the difference, to evaluate the possible amount of carbon dioxide absorbed by the ashes.

The analysis on the absorber liquid has been completed by Professor T. Olsson at the department of biology of the University of Lund, Sweden.

From a stochiometric point of view, considering the moles of CO₂ produced and the moles of NaOH present in the absorber liquid, is clear that the solution was saturated by the sodium carbonate, because the number of CO₂ moles produced were, in all cases, greater than the number of moles of sodium hydroxide present in the absorbent liquid. The analysis of the respiration curves, however, showed a continue decrement of the pressure inside the Oxitop bottle, a decrement that should have been registered only if the carbon dioxide would have been absorbed by an absorbent material. Thus, taking in account the complete saturation of the absorbent is possible to consider that the ashes played an important role on the CO₂ absorption during the four days of observation for the all samples analyzed.

For all the tests, the absorbent liquid volume was equal to 0.0011 l and was composed by sodium hydroxide diluted into distilled water.

The calculation passages are the following:

1. The concentration of inorganic carbon (IC) in the samples have been detected and reported as milligrams per liter of absorbent and thus transformed in grams of sodium carbonate per liter.
2. By considering the molecular weight of Na₂CO₃ (105.99 g/mol) it has been possible to evaluate the quantities of moles per liter, and subsequently, the number of moles present in

the sample of absorbent liquid. Finally, considering the reaction 10.1 and the stochiometric relationships, the quantities of carbon dioxide absorbed were calculated.

3. The moles of CO₂ released were analytically calculated by taking in account the oxygen consumed during the respiration tests and the quantities of CO₂ that can be released by the volume of one liter of material.
4. As last, was evaluated the difference between the carbon dioxide released and the carbon dioxide absorbed by the sodium hydroxide and the absorption capacity showed by the bottom ash has been expressed by a percentage.

The analysis has been made with the samples of FA and CA where no sludge was added and were the 3% and 5% in weight of sludge was added.

CHAPTER 5

CARBONATED ASH RESPIRATION TESTS: RESULTS AND DISCUSSION

5.1 Introduction

In this chapter are described and discussed the results registered in the four days-respiration tests and the chemical analysis of the leachate produced from the solid samples after the respiration tests.

The following paragraphs have been subdivided in relation to the typology of sample applied to each respiration test (Carbonated ash and carbonated ash plus 1%, 2%, 3%, 4%, 5% of sewage sludge).

The results of the chemical analysis performed on the leachate extracted from the carbonated ash sample and from the carbonated ash plus 3% and 5% are reported in chapter 10, where are also compared with the fresh ash results.

5.2 Carbonated ash

As described in the previews chapter (Chapter 7, Table 7.2), the pH value was equal to 9.7, one grade higher respect to the one reported by Meima et al. (1997), that found that the ashes weathered for 1.5 years the pH should range between 8 and 8.5. The higher value found in our material could be linked to the storage conditions: the ashes, in fact, have been stored inside a non-hermetically closed plastic jar. The carbon dioxide, thus, could have interacted only with the first centimetres of the heap. A similar consideration was given by Chimenos et al. (2000) that found that the pH of a sample of fresh ash stored in a hermetically closed container didn't change for 3 months of observation. A second reason could be linked to the grain size of the ashes. The material used for this tests, in fact have been sieved to a grain size < 4mm. Costa et al. (2009) found that the pH of 1 year weathered bottom ash with a size distribution between 12 mm and 0.425 mm was equal to 9.88.

The pressure trends (Figure 5.1 A) and the grams of O₂ consumed respect to one kg of dry bottom ashes (Figure 5.1 B), shows an initial fast activity (first 6 hours) followed by a decrement (subsequent 18 hours) and a last phase of slower growth (from hour 30 to hour 72)

that led to an almost stable non-growth phase (plateau from hour 72 to hour 96). The estimated pressure gap is equal to an average value of 11 hPa and the bottles have been aerated twice (at the hours 21 and 67).

The TOC evaluated with the leaching test at the end of the experiment was lower than $3\frac{mg}{l}$, indicating that the all biodegradable matter was degraded. This assumption is confirmed by the plateau reached at the hour 72: a similar trend has been reported in the case of zero growth rate, characterized by the total degradation of nutritive compounds and the accumulation of toxic elements (Cossu, 2011).

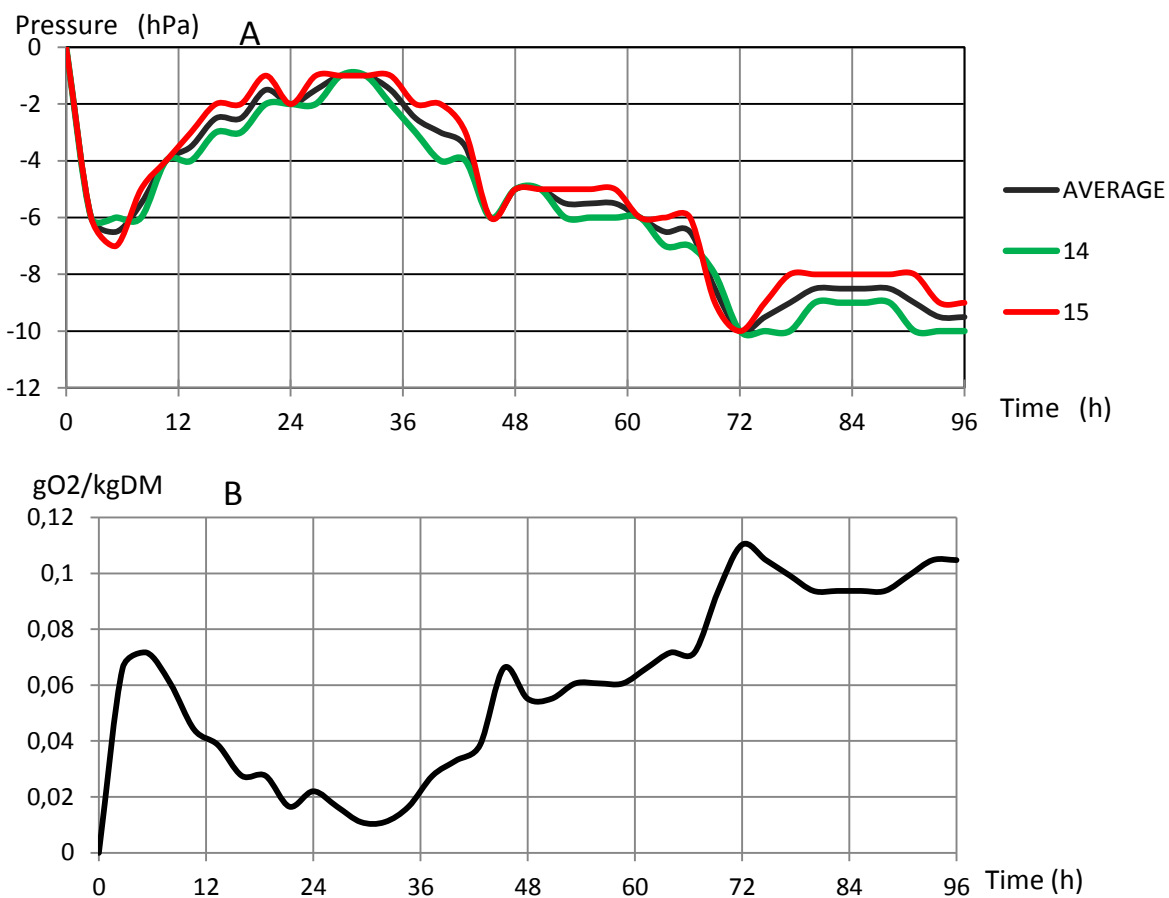


Figure. 5.1: Average pressure and oxygen consumption trend for the carbonated ash sample.

5.3 Carbonated ash plus 1% sewage sludge

A small percentage of sewage sludge was added to the carbonated ash samples. The activity registered in those tests was higher than the one registered during the CA test (Figure 5.2 A and B). In this case the bottles have never been aerated for the all duration of the test.

The trend is regular and shows a general increasing in the oxygen consumption (ΔP was 14.33 hPa). This result can be linked to a good adaptation of the bacteria in the bottom ash and to the presence of a greater quantity of nutrients brought with the sludge.

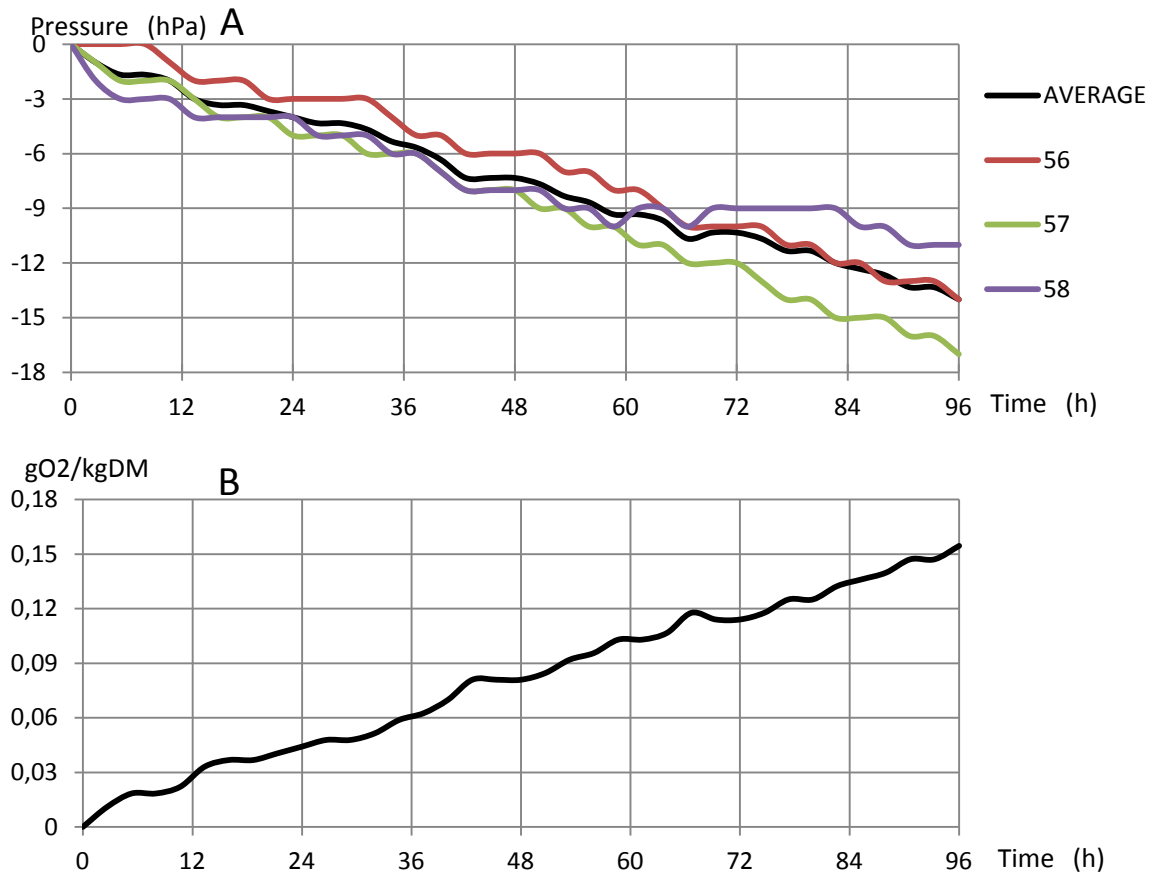


Figure 5.2: Average pressure and oxygen consumption trend for the Carbonated Ash sample + 1% of sludge.

5.4 Carbonated ash plus 2% sewage sludge

As expected from the results obtained from the CA+1% tests, the registered activity showed an increment during this experiment (Figure 5.3.). The final average ΔP , in fact, was equal to 17.66 hPa.

The bottles have been aerated only once, at the hour 72. During those experiments the sensor registered a positive pressure during the first 12 h and during the last 12 h.

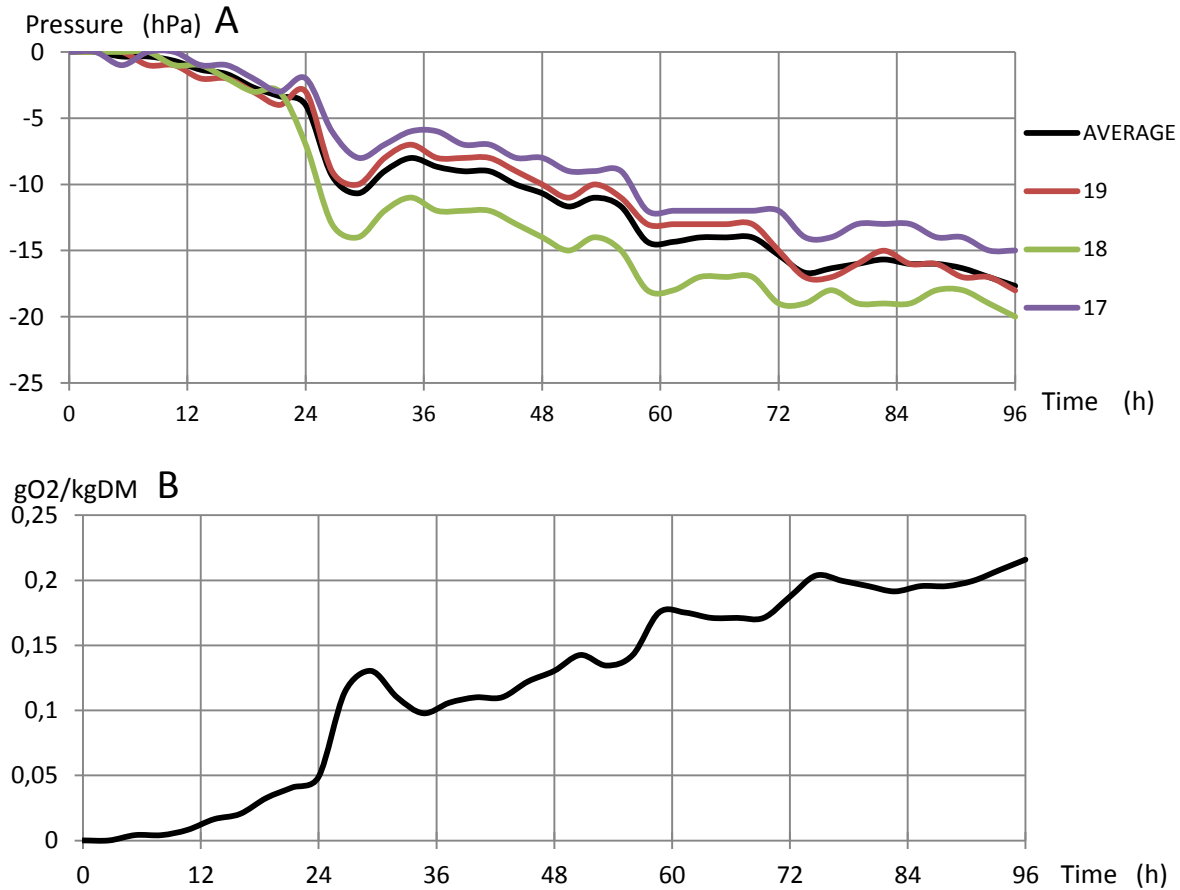


Figure 5.3: Average pressure and oxygen consumption trend for the Carbonated Ash sample + 2% of sludge.

5.5 Carbonated ash plus 3% of sewage sludge

The increasing percentage of sludge added to the ash promoted the microorganisms activity during the test. Figure 5.4, in fact, shows a total average pressure gap of 18.66 hPa. The TOC at the end of the test was equal to $4.3 \frac{mg}{l}$ and, if comparing with the CA experiments, is possible to assess that the nutritive substrate have not been totally consumed in the 4 days of observation.

The bottles have been aerated once, at the hour 63, and the curves presented positive values of pressure (for 2 of the 3 replicates only in the first 6h, while for the third in the first 12 h).

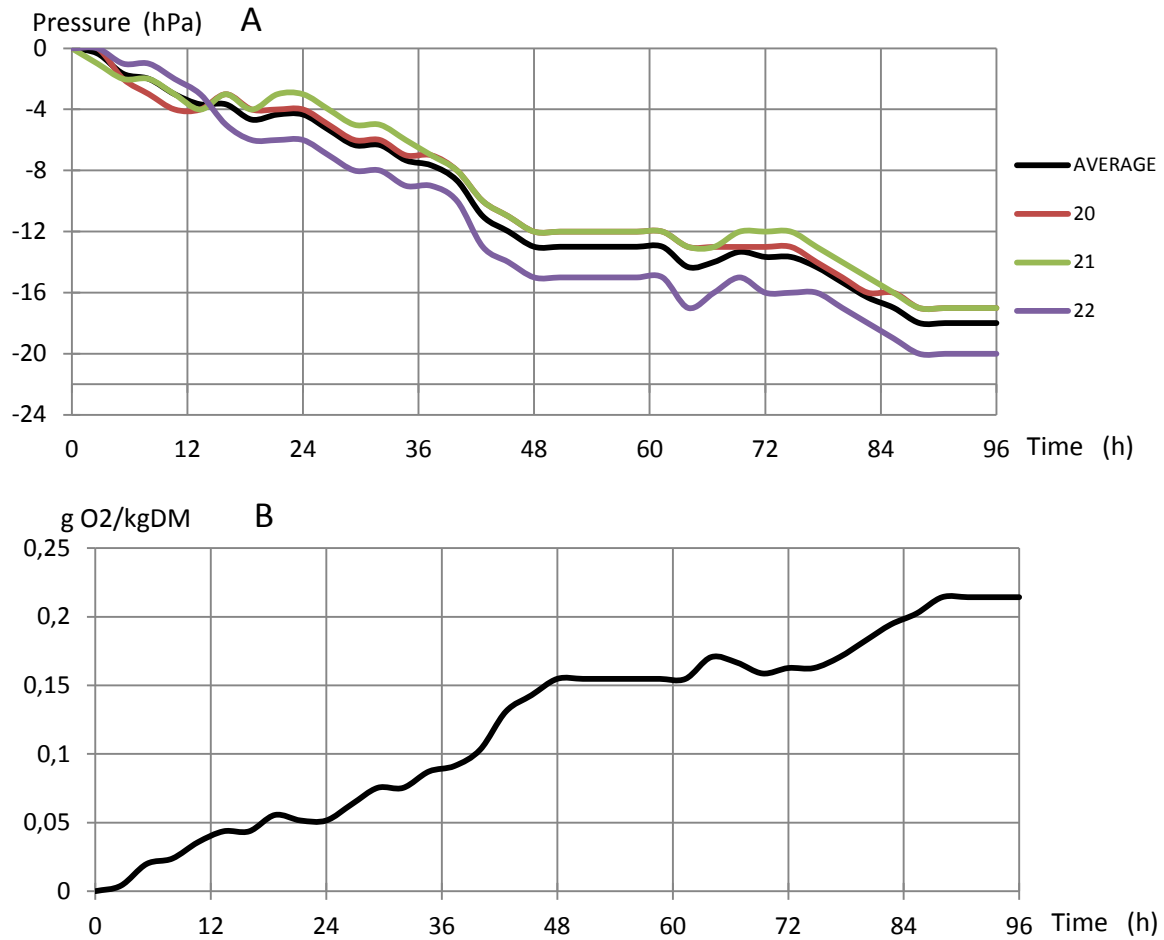


Figure 5.4: Average pressure and oxygen consumption trend for the Carbonated Ash sample + 3% of sludge

5.6 Carbonated ash plus 4% of sludge

The activity shown in those tests experienced a fast increase, and the registered linear rate (Figure 5.5) indicate that the activity in the samples was still growing at the end of the observation days.

The pressure gap ΔP was equal to 36 hPa, nearly doubled respect to CA+3% and triplicate respect to the CA samples. This increment resulted also in the estimated volumes of carbon dioxide released (Table 5.1), that triplicate respect to CA. The bottles have been aerated twice (at the hours 23 and 74) and that the sensors reported positive values of pressure in the first 12 hours of the second day of test.

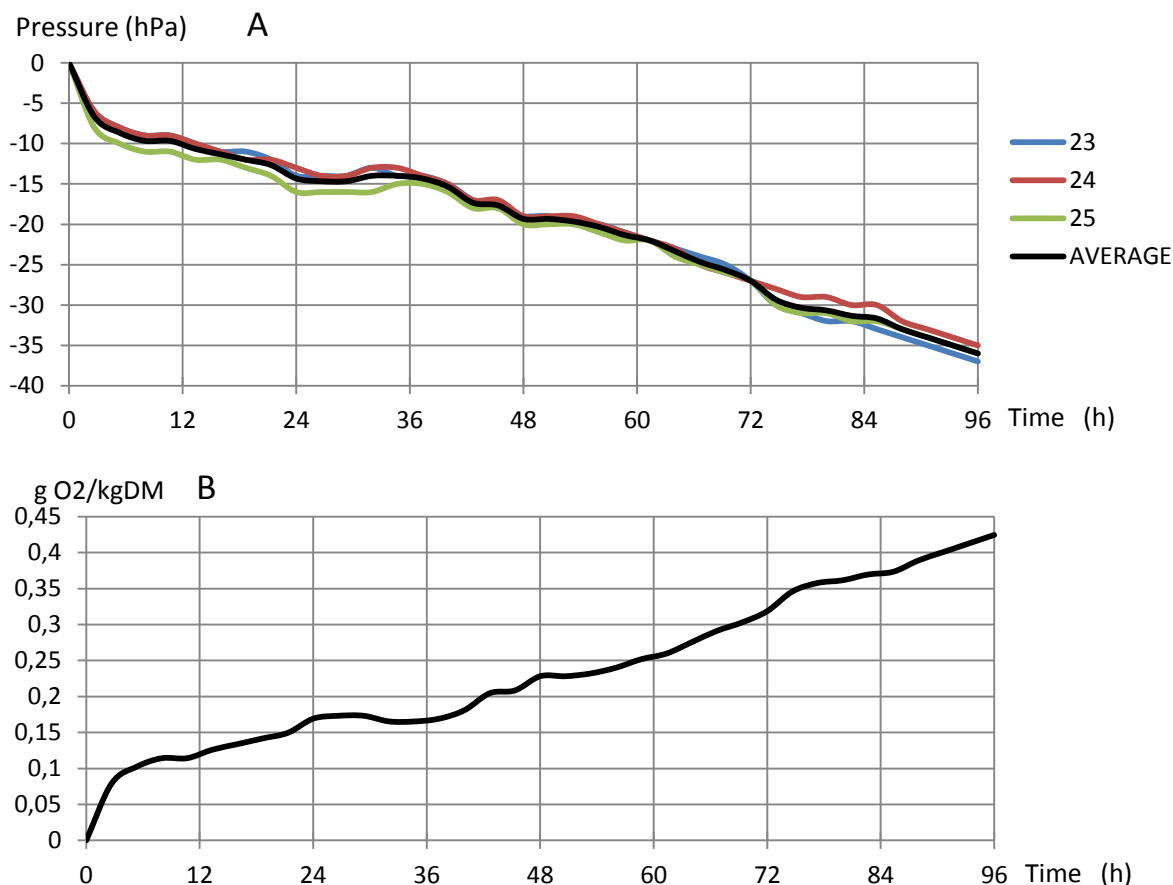


Figure 5.5: Average pressure and oxygen consumption trend for the Carbonated Ash sample + 4% of sludge

5.7 Carbonated ash plus 5% sludge

In this test, where 5% of sewage sludge was mixed to the ashes (6.2 g), is possible to see that the rate of activity is higher respect all experiments previously analysed (Figure 5.6). In particular the final pressure gap was equal to 52.5 hPa (almost triplicate respect to CA+3%) and the released carbon dioxide was the 36% greater respect to CA+3% (Table 5.1).

The final TOC was equal to $4.6 \frac{mg}{l}$, only $0.3 \frac{mg}{l}$ higher respect to the one found at the end of the CA+3% test, where 3.8 g of sludge were mixed to the ashes. The velocity of degradation of the organic matter brought by the sewage sludge has been more intense respect to the other cases.

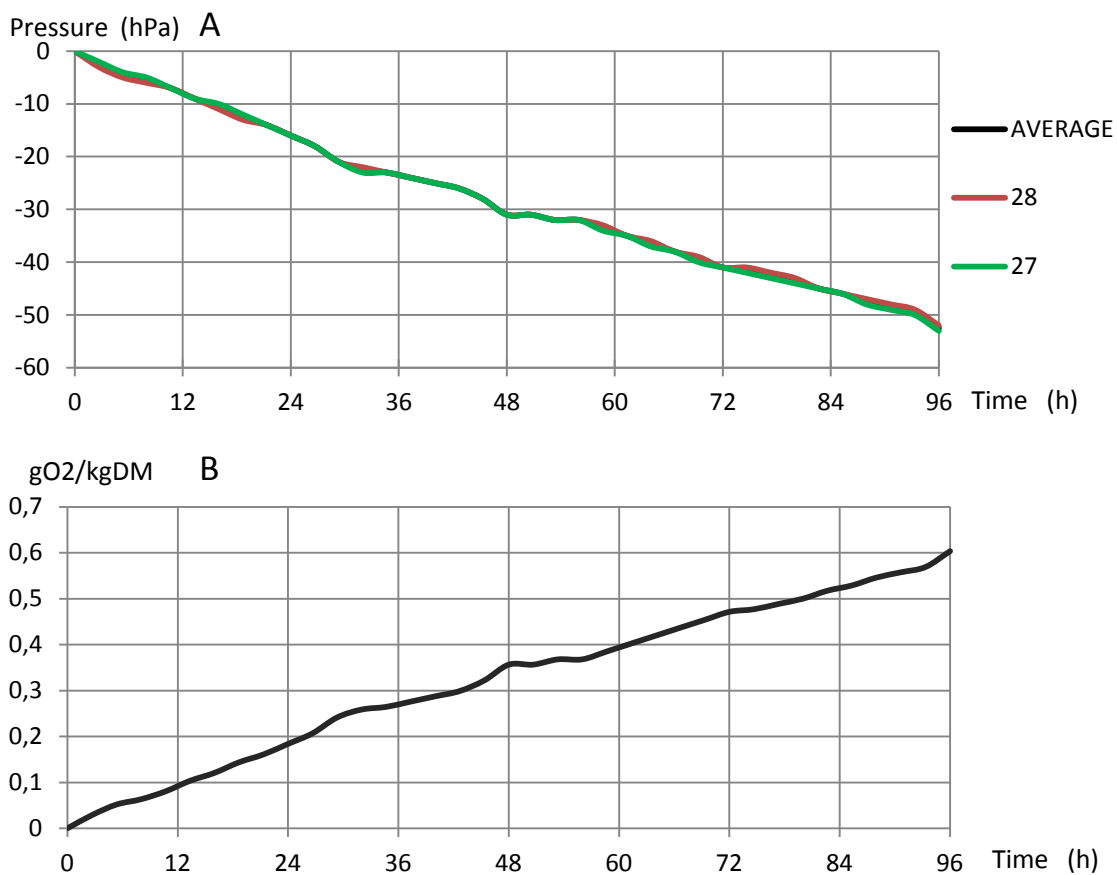


Figure 5.6: Average pressure and oxygen consumption trend for the Carbonated Ash sample + 5% of sludge

5.8 Carbon dioxide generation

The following table (Table 5.1) summarizes the average CO₂ production expected for one kilogram of dry matter at the temperature of 22°C and atmospheric pressure (101325 Pa), for the all samples analysed during the 4 days of observations.

Table 5.1: Volume of CO₂ produced for kgDM of weathered bottom ash at the temperature of 22°C and pressure of 101325 Pa.

| <i>Sample</i> | <i>Volume of CO₂ produced per kg of dry matter lCO₂ kgDM</i> |
|---------------|--|
| CA | 0.092 |
| CA + 1% | 0.12 |
| CA + 2% | 0.146 |
| CA + 3% | 0.153 |
| CA + 4% | 0.293 |
| CA + 5% | 0.42 |

For what concern the CA sample, the result differ significantly from the ones found by Rendek et al. (2006 b), that presented pressure gap of 261hPa with an oxygen consumption of $2.5 \frac{lO_2}{kgWM}$ at T=25°C and atmospheric pressure. Those differences may be linked to the different operative conditions at which the test have been completed and to the characteristics of the utilized samples. Rendek et al. (2006 b) respiration tests, in fact, have been running at the controlled temperature of 30°C, while in our tests the temperature was the ambient one (22°C) with possible daily oscillations ($\pm 0.2^\circ\text{C}$): the higher temperatures may have enhanced the microbial activity (Barja et al., 1997; Cossu, 2001). Moreover Rendek et al. (2006 b) samples were obtained from artificially accelerated carbonation: this treatment preserved the TOC in the ashes (Rendek et al., 2006 b), that was totally available during the tests and was ~120 mg/l; in the weathered bottom ash (as the one used in our experiments) the organic carbon material can undergo to a decrement of 60÷70% (Arickx et al., 2010).

As expected, the increment of sewage sludge brought to the samples improved the quantities of carbon dioxide released by the microorganisms. In particular the quantity of CO₂ produced in the CA+5% sample was 5 times greater than the CA sample and almost the double respect to the CA+4%.

CHAPTER 6

FRESH ASH RESPIRATION TESTS: RESULTS AND DISCUSSION

6.1 Introduction

In this chapter are reported and commented the results obtained by the respiration tests on the fresh ash samples, where several percentages of sewage sludge were added. The respiration curves trends differ significantly from the ones obtained for the carbonated ashes, thus the curves are compared in the figures present in the following paragraphs.

The quantities of organic carbon present in the fresh ash were very relevant, and the oxygen consumed was almost equal to the one consumed for the test where 5% in weight of sewage sludge was added to the ash samples. Moreover a partial inhibition of the microorganisms' activity was registered.

The initial pH of the fresh ash was 10.64, in line with what Meima et al. (1999) reported for the freshly quenched-6 weeks weathered bottom ash.

6.2 Fresh ash

As is possible to see from the following figure (Figure. 6.1), the average pressure decrement was 57hPa: the registered activity was low in the first 60 hours while experienced a fast improvement for the last 36 hours, as showed by the tail of the curve. This particular trend can be referred to a lag phase suffered by the bacteria followed by a exponential growth and an high activity.

Despite the more inhospitable environment that the FA can offer (e.g. high pH) the presence of higher quantities of organic compounds respect the CA samples can explain this trend. In this test, in fact, the final TOC was equal to $46 \frac{mg}{l}$.

The high activity registered in the last part of incubation time is typical of fresh ashes in the first five months of ageing (Dougenest et al., 1999).

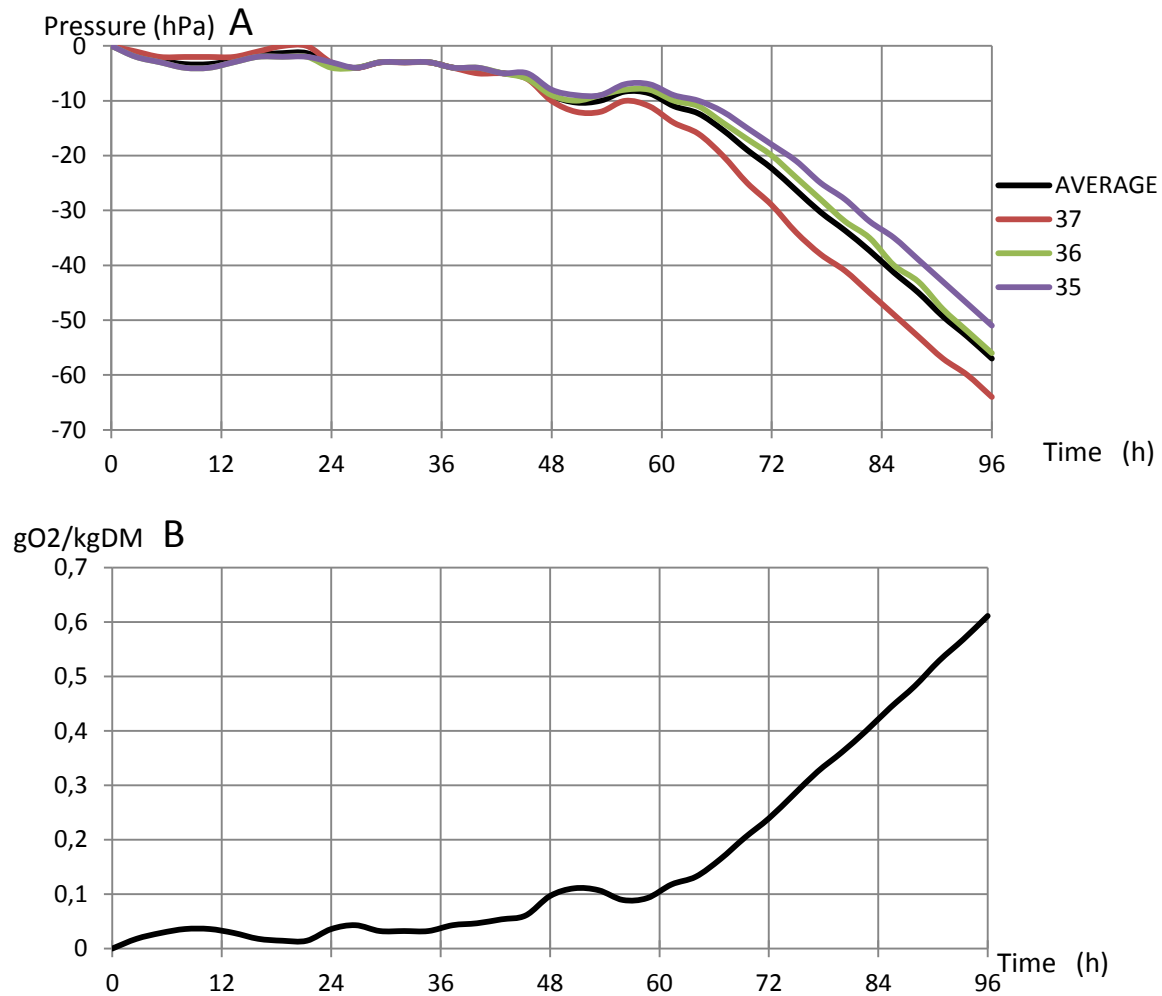


Figure. 6.1: Average pressure and oxygen consumption trend for the fresh Ash sample.

The comparison between FA and CA is shown in Figure 6.2. The trends underline a very similar development until hour 56, followed by a great diversion of the curves since this moment to the end of the test. From this analysis is possible to assess that in both situations the bacteria suffered an initial period of lag phase, that, as for the CA samples was followed by a stationary phase, because of the total degradation of some nutritive compounds.

The FA curve, instead, was followed by an exponential phase with maximum growth of bacteria and oxygen demand. Those results are in agreement with what Dugenest et al. (1999) found: while the fresh ash are characterized by an intense bacterial activity that lasts for the first 5 months of ageing, the carbonated ash suffers a regression of activity rate, reaching a plateau after 11 months of weathering.

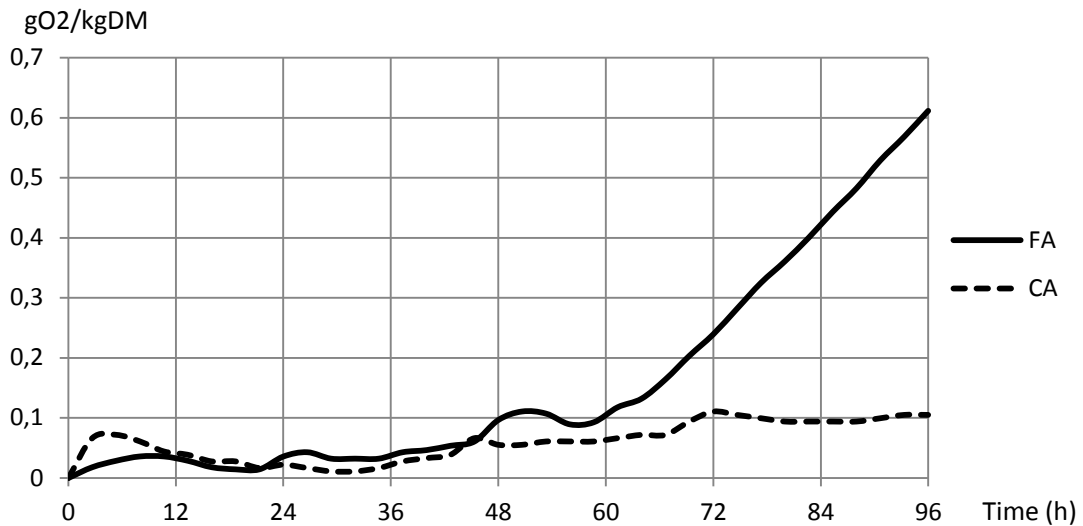


Figure 6.2: Comparison of the oxygen demand trends between the fresh ash and the carbonated ash samples.

6.3 Fresh ash plus 1% of sewage sludge

Figure 6.3 shows the trend of pressure decrement and oxygen demand for this test. As is possible to see the pressure trend is parallel for the first three days of test, showing a good adaptation period, while is discordant for the last 12 hours of experiment. In those last hours of test, in fact, sample 40 experienced a faster growth of activity (reaching the decrement of 60 hPa) respect to the other samples (that registered an average decrement of 47 hPa). This difference can be linked to the distribution of organic matter in the samples, and therefore to a different adaptation time: samples 40, in fact was prepared with 137 g of fresh ash, while sample 38 with 133 g and sample 39 with 127 g. Nonetheless those results seem to be not correlated with the addition of sludge. In sample 39, in fact, it has been mixed 2.16 g of sludge respect to the 1.27g that should have been added, but the final pressure decrement is lower respect to the other samples, where the right quantity of sludge was added. The activity, thus, seems not to have taken advantage from the adding of new substrate.

This partial inhibition could be correlated to the presence of calcium hydroxide in the ash. Portlandite, in fact, that is present in high quantities in the freshly quenched bottom ash, have the property to stabilize the sewage sludge and is used in the industrial application to destroy pathogens, prevent odours and to dehydrate the sewage sludge (Czechowski et al., 2006). The leakage of heavy metals, moreover, may have played an important role on this longer adaptation time.

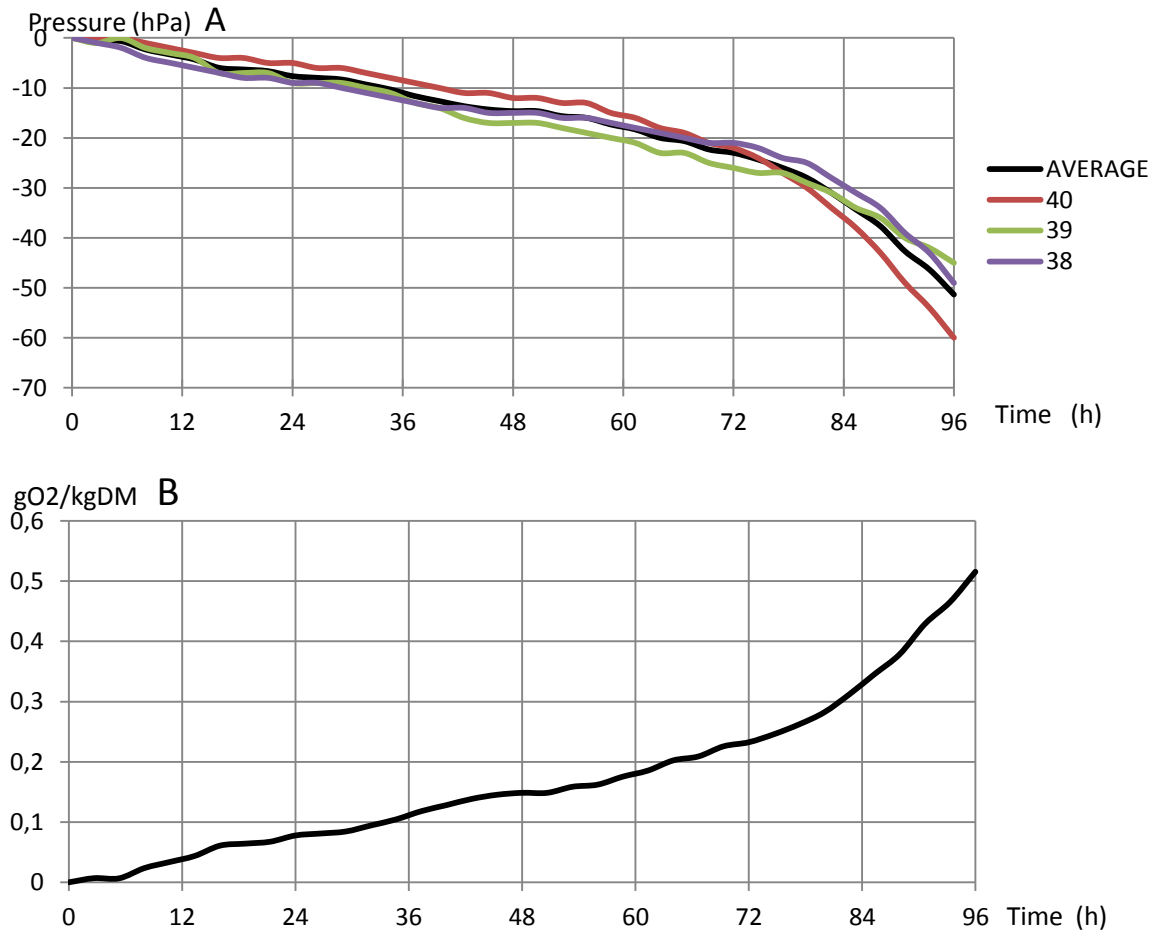


Figure 6.3: Average pressure and oxygen consumption trend for the fresh ash +1% sludge.

The difference between this tests and the one related to the carbonated ash plus 1% of ash are evident from the following figure (Figure 6.4) where is possible to see a gap between the trends, with a particular division between the curves since the last 24 hours. The higher activity observed for the FA+1% samples is clearly correlated to the greater presence of organic matter respect to the CA samples, and in particular to the organic matter already present in the ashes. This assumption is confirmed by the statistical analysis that linked, with a higher Pearson coefficient, the activity trend to the ashes content.

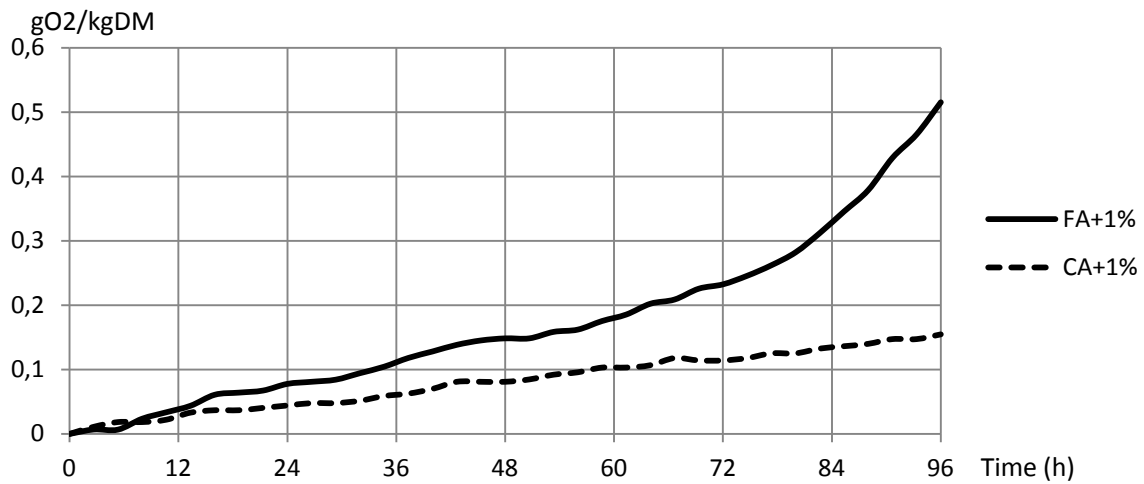


Figure 6.4: Comparison of the oxygen demand trends between the fresh ash+1% sludge and the carbonated ash samples +1% sludge.

6.4 Fresh ash plus 2% of sewage sludge

The tests conducted with the fresh ash plus 2% of sewage sludge showed an average decrement of activity respect the FA and FA+1% tests. As is possible to see from Figure 6.5, the maximum ΔP was equal to an average of 33 hPa. Moreover the weight of the samples was equal to 127 g: this, again, proves that the activity in the sludge may be inhibited by the presence of portlandite and alkaline digestion.

In order to better understand this trend, other three replicates have been prepared and, incrementing the weight of the samples of 2 (41), 8 (42) and 9 (43) g, and maintaining constant the weight of added sludge (2.65 g). While the sample 41 showed a very similar trend, sample 42 showed a decrement up to 67 hPa and sample 44 registered a depression of 85 hPa.

The increment of activity, doubled for sample 42 and 2.5 times higher for sample 44, seems to confirm that the greater activity depend on the distribution of organic matter in the fresh ash. A non homogeneous distribution in the sewage sludge can be also possible, but is improbable that, for all the 8 samples analyzed until now (3 for FA+1% and 5 for FA+2%), the concentration of biodegradable organic matter and bacteria was too low to interact with the fresh ash microbial respiration.

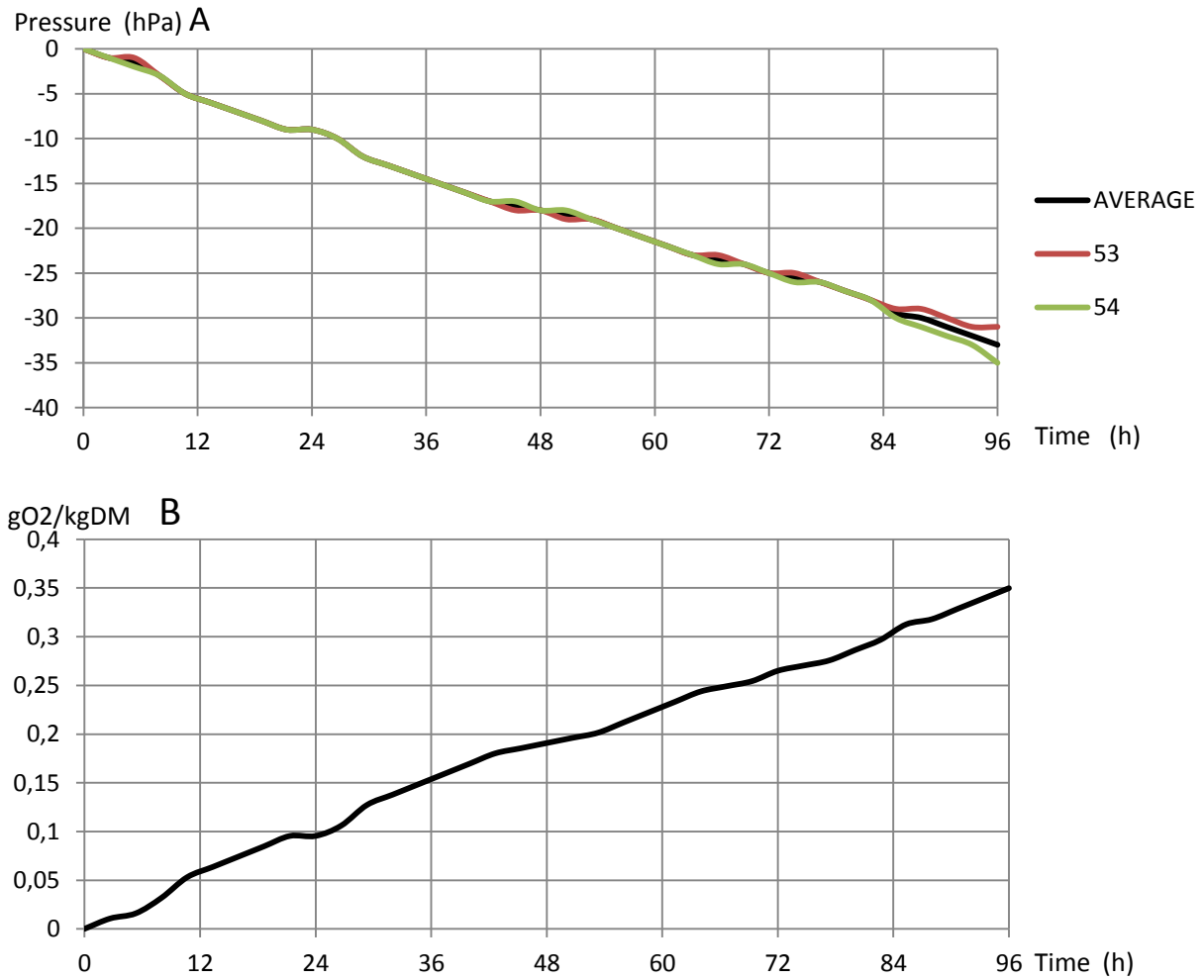


Figure 6.5: Average pressure and oxygen consumption trend for the fresh ash +2% sludge.

For the two cases analyzed, the difference between the carbonated ash tests was still marked, even if in lower proportion respect to the previews examples. In this case, in fact, is not possible to see the exponential growth that characterized the last 24 hours of the FA and FA+1% examples (Figure 6.6).

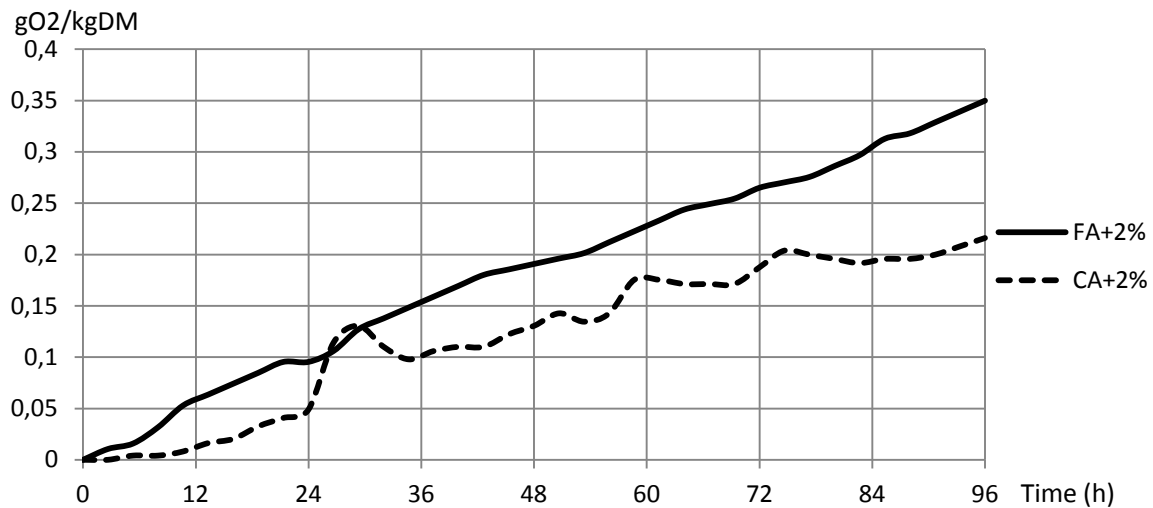


Figure 6.6: Comparison of the oxygen demand trends between the fresh ash +2% sludge and the carbonated ash samples +2% sludge.

6.5 Fresh ash plus 3% of sewage sludge

Those tests, where the 3% of sewage sludge was added to the fresh ash, started with the same rate as the previews (for FA+1% and FA+2%, in fact, is possible to see a decrement of circa 15 hPa in the first 36 hours) (Figure.6.7). After this point, however, the activity rate suffered a regression. This momentary regression, that can be associated to a longer lag-phase, compromised the following trend, even if is possible to foresee that, with a longer time of observation, the activity would have been intense as in the previews examples in consideration to the fact that the final TOC content was equal to $89 \frac{mg}{l}$. The organic matter, in this case, may have been preserved because of the inhibition the microbial population growth (Wong et al., 2000)

The average ΔP , in fact, was 27 hPa, the lowest registered for all the test where the fresh ash have been used.

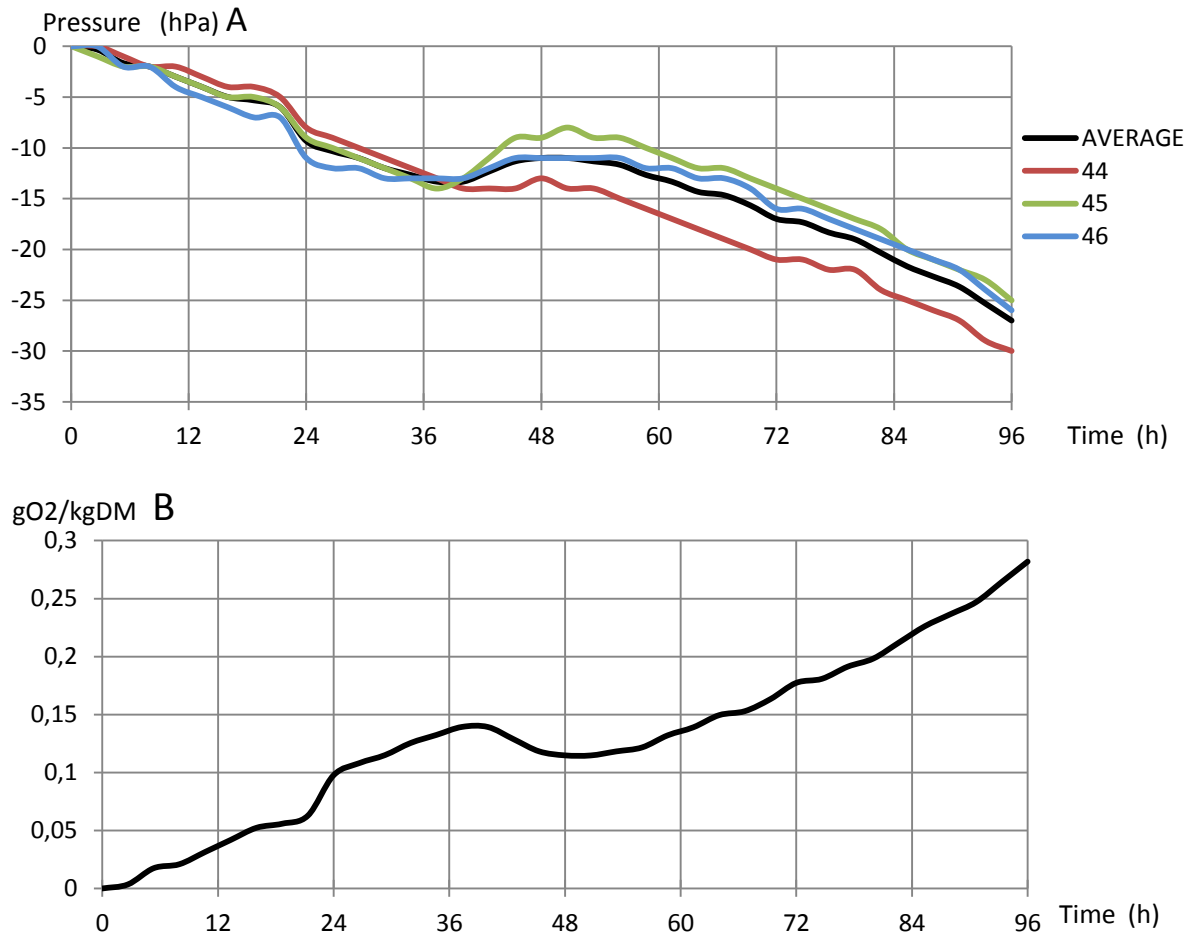


Figure 6.7: Average pressure and oxygen consumption trend for the fresh ash +3% sludge.

Despite the period of regression experienced between the second and the third day of observation, the comparison with the trend registered with the CA+3% confirms that the activity, at the end of the fourth day, was still growing (Figure 6.8). The FA+3% and CA+3% curves, in fact, proceeds with no particular differences until the minute 5040. After this point, while for the CA+3% is possible to see that the trend tends toward a plateau (final TOC= $4.3 \frac{mg}{l}$), the FA+3% sample the growth is still linear.

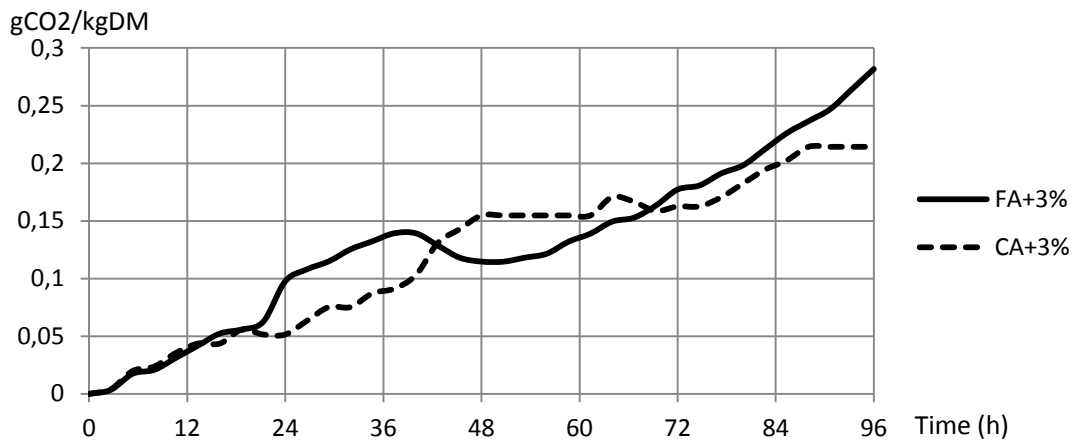


Figure 6.8: Comparison of the oxygen demand trends between the fresh ash+3% sludge and the carbonated ash samples +3% sludge.

6.6 Fresh ash plus 4% of sewage sludge

Figure 6.9 represents the pressure and oxygen consumption trend achieved in this test, where 3% of sewage sludge was added to the fresh ash. The activity experienced an increment respect to the FA+2% and FA+3% tests, even if not with the same rate as FA and FA+1%. The ΔP was, in fact, equal to 46.3 hPa with an equal moisture content (23% w/w) and weight (127 g) for all the 3 replicates.

Similar to the case described in the previews paragraph (FA+3%), the trend suffered a period of stasis during the second half of the second day. Despite the fact that this rate decreasing manifested in both cases between the second and the third day, in the FA+4% sample the plateau duration was much shorter and didn't affect in great proportion the following trend. This result may be linked to a greater quantity of sewage sludge that was added to the ash samples (5.3 g respect to the 4 g added in the FA+3%) that could supply to the inhibition of alkaline digestion.

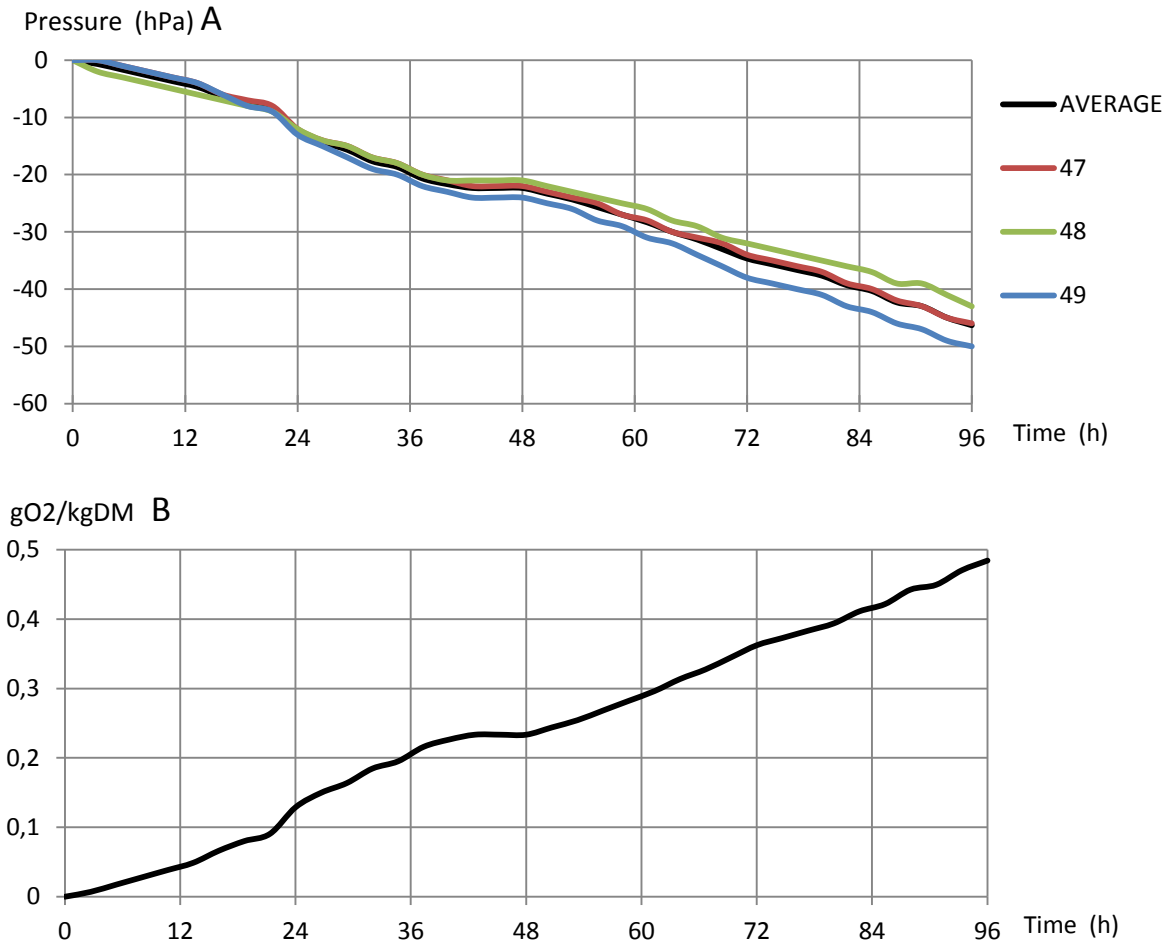


Figure 6.9: Average pressure and oxygen consumption trend for the fresh ash +4% sludge.

By analyzing the comparison between the FA+4% and CA+4% (Figure 6.10) is possible to assume that an higher quantity of sludge promoted the activity within the ashes, even if the the test was affected by a lower adaptation velocity respect to CA+4% and by a possible inhibition of the bacteria: this issue led to a almost equal performance of the FA+4% sample to the CA+4%, even if the amount of easily degradable organic matter was surely higher in the FA sample.

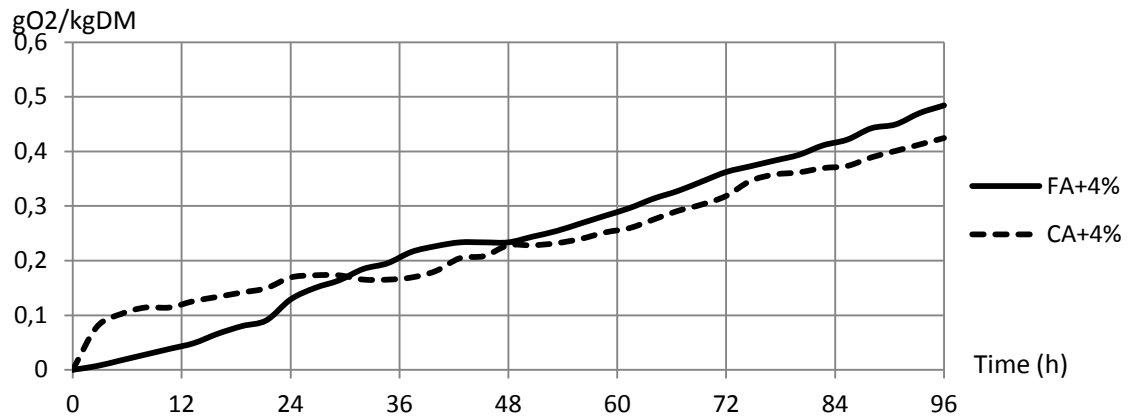


Figure 6.10: Comparison of the oxygen demand trends between the fresh ash+4% sludge and the carbonated ash samples +4% sludge.

6.7 Fresh ash plus 5% of sewage sludge

The respiration trend afterwards reported (Figure 6.11) shows a slightly higher oxygen consumption respect to the one observed for the FA sample: 0.61 gO₂/kgDM consumed for the FA sample and 0.69 gO₂/kgDM consumed for the FA+5% sample. The final TOC leached from the two samples, however, is respectively equal to 46 mg/l and 74 mg/l. From those results is possible to assess a high difficulty suffered by the bacteria in the FA+5% samples, that, consumed the oxygen in the Oxytop bottle without taking advantage of the abundance of organic matter in the samples.

The reported results in Figure 6.11 show an average final pressure decrement of 66.5 hPa, the highest registered among the all previews tests, even if the temperature was slightly lower (22°C).

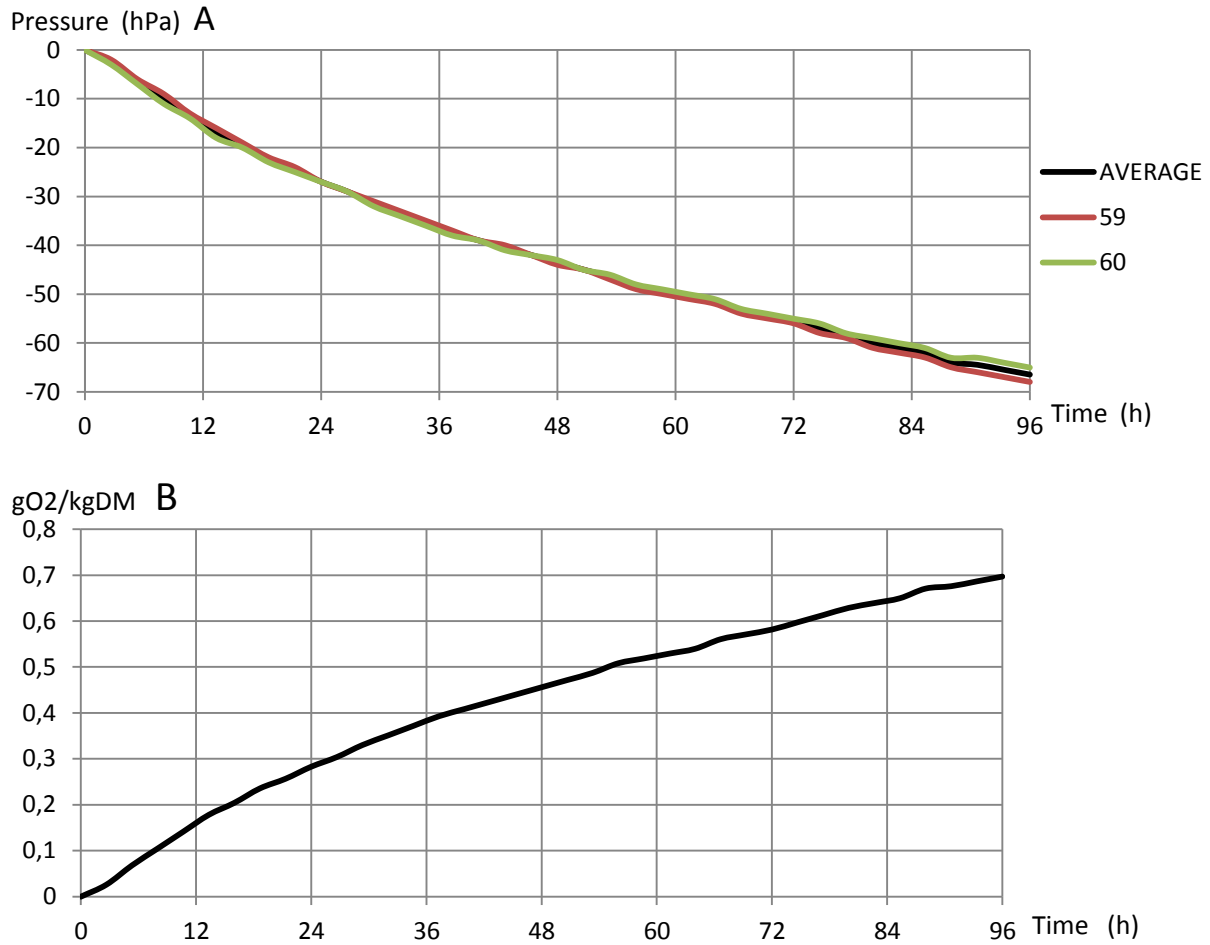


Figure 6.11: Average pressure and oxygen consumption trend for the fresh ash +5% sludge

The comparison between the tests done with the fresh ash and the related test with the carbonated ash is shown in Figure 6.12. From this graph is possible to see that the CA+5% and FA+5% curves are parallel, with lower values for the FA+5%. As previews mentioned, the parallelism of the curves can be associated to the identical quantity of sludge, while the gap can be linked to the inhibitory action of the chemical elements present in the FA+5% samples

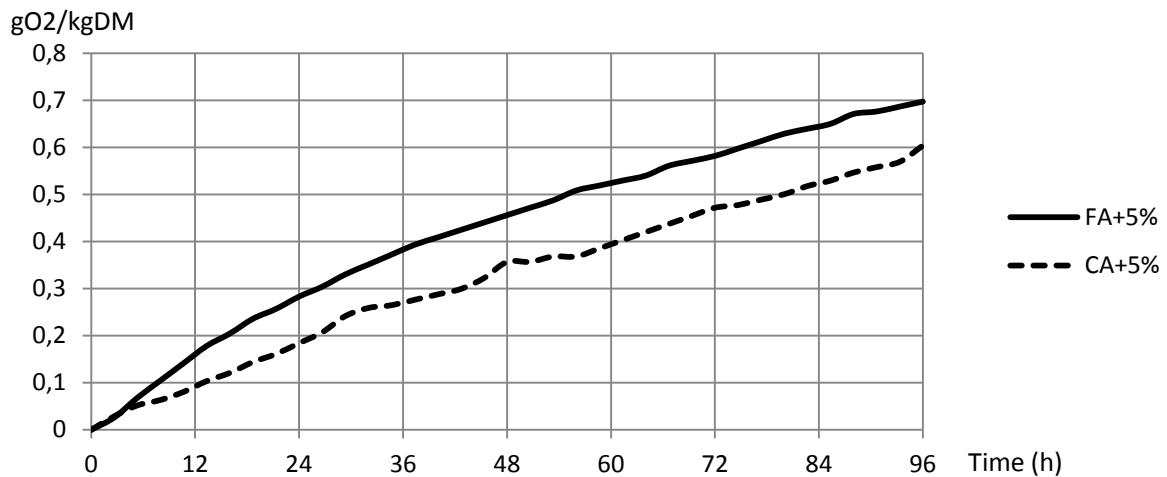


Figure 6.12: Comparison of the oxygen demand trends between the fresh ash+5% sludge and the carbonated ash samples +5% sludge.

6.8 Carbon dioxide generation

The following table (Table 6.1) represents the estimated average quantities of carbon dioxide generated during the four days of observation for the all considered samples.

From the reported data is clear the partial activity inhibition registered for the samples FA+1% up to the samples FA+4%, with a negative peak for the sample FA+3%. The biological activity, with and increment in external organic matter addition for the FA+4%, increases again, even if reaches lower trends respect to the FA+1% samples. This fact can be correlated to the negative acclimation of the sludge's bacteria in the ashes and the greater release of toxic compounds that may had played a role in the partial inhibition of the ashes bacteria as well.

Table 6.1: Volume of CO₂ produced for kgDM of fresh bottom ash at the temperature of 22°C and pressure of 101325 Pa.

| Sample | Volume of CO ₂ produced per kg of dry matter |
|--------|---|
| | $\frac{lCO_2}{kgDM}$ |
| FA | 0.464 |
| FA+1% | 0.391 |
| FA+2% | 0.265 |
| FA+3% | 0.214 |
| FA+4% | 0.368 |
| FA+5% | 0.527 |

Respect to the ashes, the sewage sludge utilized was particularly abundant in several elements. In order to assess the elements concentration, a respiration test of the duration of days was run with the sewage sludge. The collected material, after this test, undergone to the batch leaching examination and the heavy metals concentration in the leachate were examined.

The arsenic concentration was equal to 26 µg/l, several time higher respects to the CA and FA arsenic concentration (respectively 1.6 µg/l and 3.2 µg/l). The molybdenum, that for the sludge was equal to 50 µg/l, may had influenced only the carbonates ashes, that presented an concentration of only 13 µg/l, while the concentration of this heavy metals in the fresh ash was equal to 65 µg/l. Finally the iron content in the sludge leachate was also important, in consideration to the fact that its concentration was equal to 3.5 mg/l, while in the CA leachate and in the FA leachate was respectively equal to 0.05 mg/l and 0.15 mg/l.

CHAPTER 7

CARBONATED ASH AND FRESH ASH PLUS CELLULOSE RESPIRATION TEST: RESULTS AND DISCUSSION

7.1 Introduction

Those tests had the aim to assess the feasibility of promoting carbonation by exploiting the aerobic respiration reactions of bacteria in a different material, like wood or vegetable fibers.

At this purpose, different percentages (1%, 2%, 3%, 4% and 5%) of microcrystalline cellulose have been mixed to samples of fresh ash and carbonated ash. The results of the respirometric tests, discussed in the following paragraph, demonstrate that this material can be applied at this scope. However the carbonation velocity would be longer, because of the lower kinetic of degradation respect to the sewage sludge.

In this discussion it has been made a comparison of the experiments with 3% and 5% of cellulose with the respective results obtained for the carbonated ash and fresh ash respirometric tests that ran with the same percentages of sewage sludge. The choice to omit from the discussion the results obtained with the other samples where 1%, 2% and 4% of cellulose was added is linked to the fact that the 3% and 5% results were considered sufficient to describe in an appropriate way the behaviour of the cellulose crystalline mixed with bottom ashes.

7.2 Carbonated ash plus cellulose

7.2.1 Carbonated ash plus 3% of cellulose

In this test, where the 3% of cellulose was mixed to the carbonated ash, the rate of activity increased almost linearly and the final pressure gap registered in this test is equal to 15 hPa.

The following figure (Figure 7.1) shows the comparison between the results obtained with the adding of 3% in weight of cellulose to the carbonated ashes and the ones obtained with the adding of the same percentage of sewage sludge. As is possible to see, the lines proceed almost parallel. The gap between them can be correlated to the easiest degradable matter present in the sample where sludge was added.

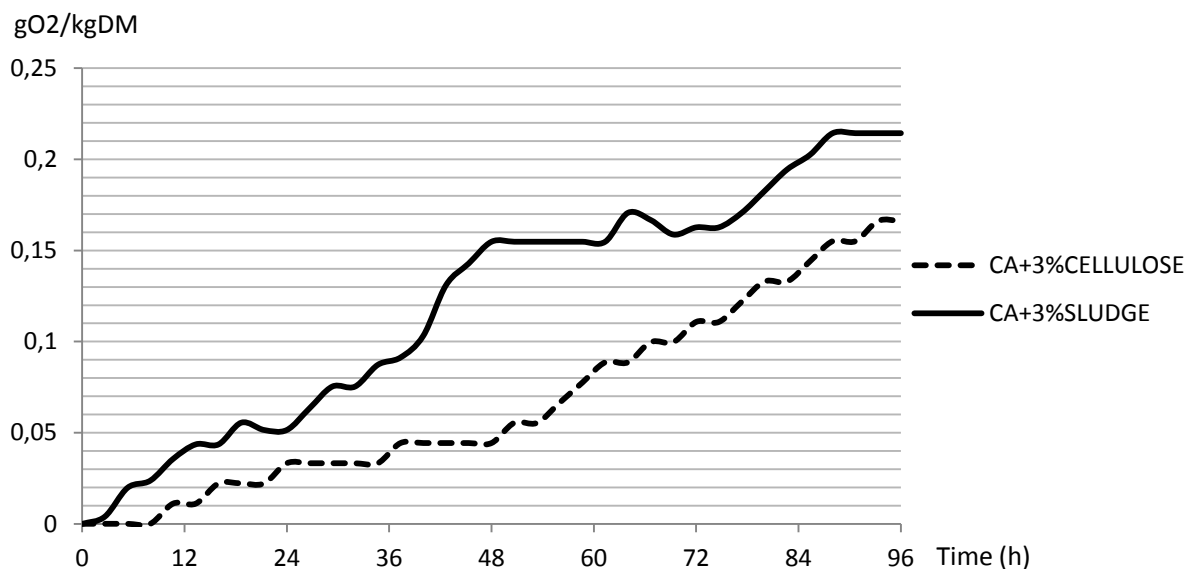


Figure 7.1: Comparison between the oxygen consumption registered during the respiration tests for the samples composed by carbonated ash and 3% of cellulose and for the samples composed by carbonated ash and 3% of sewage sludge

7.2.2 Carbonated ash plus 5% of cellulose

As is possible to see in Figure 7.2, where is shown the comparison between the carbonated ash samples with the 5% of sewage sludge and the carbonated ash samples with the 5% of crystalline cellulose, the cellulose demonstrated a very slow activity, comparable to the one presented in the previews paragraph (Figure 7.1).

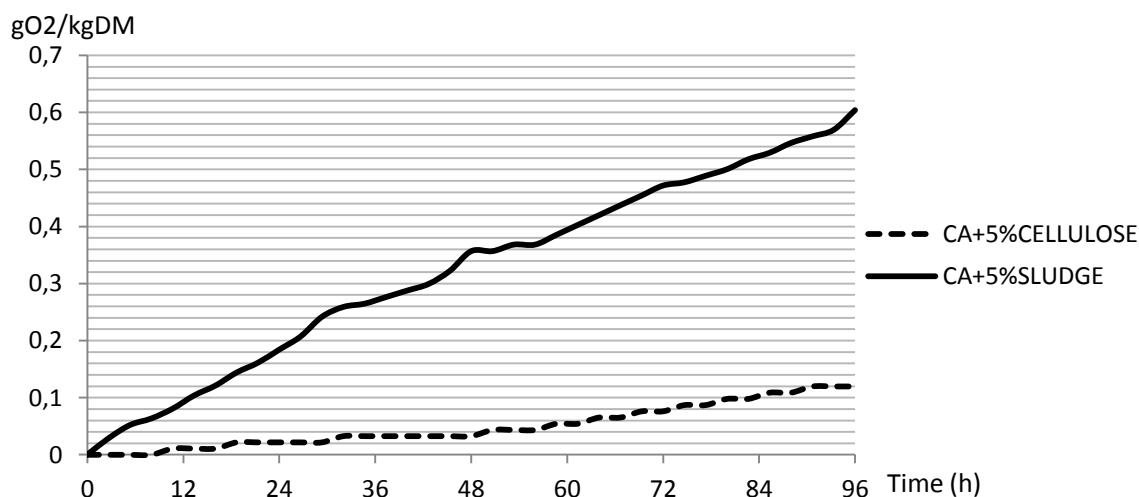


Figure 7.2: Comparison between the oxygen consumption registered during the respiration tests for the samples composed by carbonated ash and 5% of cellulose and for the samples composed by carbonated ash and 5% of sewage sludge

7.3 Fresh ash plus cellulose

7.3.1 Fresh ash plus 3% of cellulose

The tests done on the fresh ash plus 3% in weight of crystalline cellulose showed a total initial absence of activity that interested the first 15 hours of observation. After this initial period, the growth proceeded linearly until the end of the tests.

From this trend, shown in Figure 7.3) is possible to assess that the bacteria had difficulties to degrade the cellulose structure, but also suffered a inhibition: the activity, in fact, is comparable to the CA+3% sample and the presence of an high initial concentration of degradable carbon in the fresh bottom ashes didn't brought any benefits to the bacterial growth.

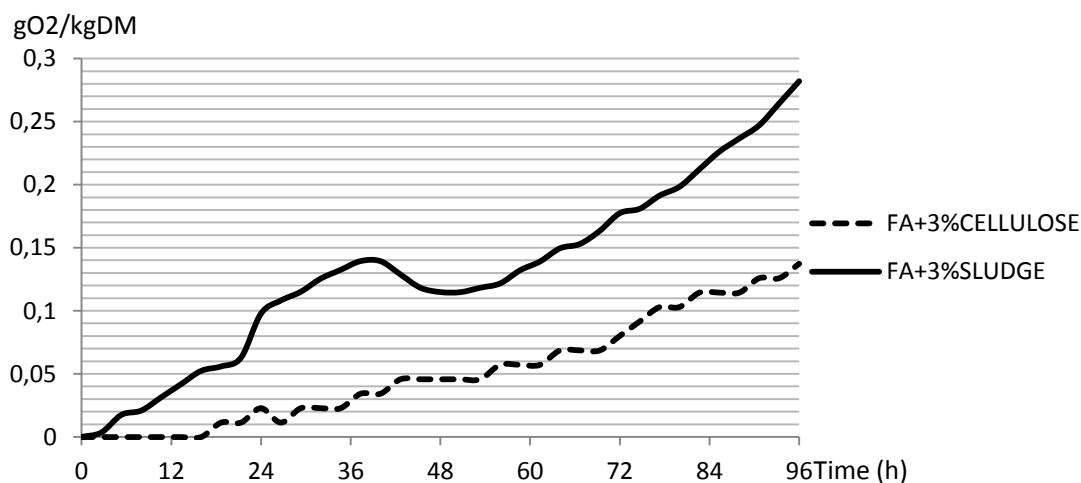


Figure 7.3: Comparison between the oxygen consumption registered during the respiration tests for the samples composed by fresh ash and 3% of cellulose and for the samples composed by fresh ash and 3% of sewage sludge

7.3.2 Fresh ash plus 5% of cellulose

In this last test the graphical result gave an almost horizontal trend proceeded by a linear growth that interested the first 24 hours (Figure 7.4). The reported trend can be correlated to a adaptation period lived by the bacteria: the obtained curve, in fact is similar to the trend shown for the FA sample in the first 60 hours of observation (see Chapter 6, figure 6.1 B).

In that case, in fact, the microorganisms required a quite long period of time to adapt to the inhospitable environment, but afterwards degraded the organic substances following an exponential growth trend. In the case of cellulose addition, at the contrary, the bacteria had more difficulties, due to the crystalline structure of the cellulose, to have access to the organic

compounds, and thus to develop a past growth similar to the FA samples, were the organic carbon was more easily attackable.

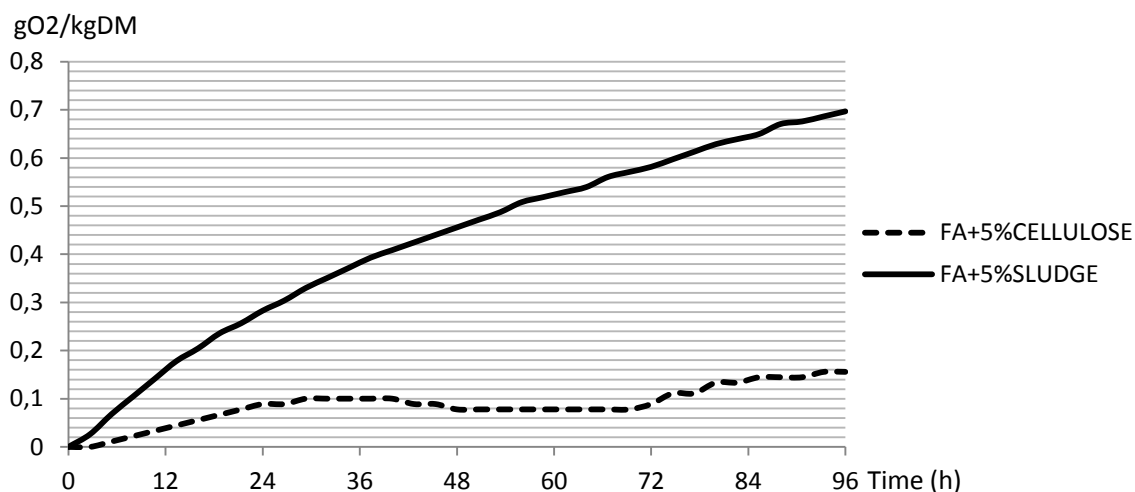


Figure 7.4: Comparison between the oxygen consumption registered during the respiration tests for the samples composed by fresh ash and 5% of cellulose and for the samples composed by fresh ash and 5% of sewage sludge

Cellulose is a polymer of glucose having a D-configuration and connected by β -glycosidic linkages. The crystalline structure is not unique but can show different conformations depending on the inter-molecular hydrogen linkages that the hydroxyl group can form (Perez et al., 2010).

There are several pathways through which cellulose can be degraded: biological, alkaline and radiolytic. The alkaline degradation proceeds mainly through three different stages: (1) initial degradation characterized by the peeling of the end-wise; (2) a slower phase (stopping reaction) where peeling is inhibited and the degradation depends only on the accessibility of the end-group; (3) a termination reaction when the degradation of the polymer chains is completed (Humphreys et al., 2010). The peeling-phase is limited both by the stopping-reaction initiation and by the presence of a crystalline structure. While the peeling rate is fast (half-life of some days), the stopping rate is longer (half-life of months) (Calvini, 2008).

The main products of alkaline degradation are α and β -isosaccharinic acid (3-deoxy-2-C-(hydroxyl-methyl)D-erythro pentonic acid and 3-deoxy-2-C-(hydroxyl-methyl)D-threo pentonic acid) (Knill et al., 2003; Humphreys et al., 2010). The presence of calcium ions (Ca^{2+}), moreover, improves the formation of those two saccharinic acids (Knill et al., 2003; Humphreys et al., 2010) and the total degree of alkaline degradation is reduced because of the enhance of the stopping phase-reaction at the expense of the peeling reactions.

In this series of experiments, furthermore, it has been used a crystalline cellulose, and so the structure of this material could have inhibited the bacterial activity. It has been demonstrated, in fact, that crystalline cellulose is not easily accessible for bacterial enzymes, that degrade firstly the amorphous matrix. Highly crystalline structures are increasingly resistant to hydrolysis (De Coninck-Chosson, 1988).

Finally it has been assessed that some aerobic bacteria have the capacity to degrade isosaccharinic acids in alkaline environments, but this group of bacteria easily develop only when those compound are the only source of carbon (Humphreys et al., 2010).

As discussed in chapter 6, while the carbonated ash were characterized by a low presence of organic compounds and an high leaching of calcium cations, the fresh ash were enriched in TOC while the Ca showed a low leaching behaviour. In the first case, thus, the high presence of calcium could have inhibited the fast peeling reactions, and the bacteria couldn't easily accede to the cellulose matrix. In the second case, instead, the low activity can be linked to the preliminary degradation of amorphous cellulose present in the bottom ash, while the crystalline degradation would have required a longer time respect the duration of the tests.

A further analysis on the carbon dioxide production evaluated for the here reported samples, shows that the cellulose can promote the bacteria respiration in the carbonated ash, but not at the same rate as the sewage sludge.

The released carbon dioxide during the test where 3% of cellulose was added to the carbonated ash was equal to $0.12 \frac{lCO_2}{kgDM}$, slightly inferior respect to the one found for CA+3% ($0.15 \frac{lCO_2}{kgDM}$) but coincident to the volumes evaluated for the carbonated ash with 1% of sludge.

Similarity, the carbon dioxide produced during the respiration test where the 5% in weight of cellulose was added ($0.09 \frac{lCO_2}{kgDM}$) was similar to the CO_2 released during the CA respiration test.

Finally, the hypothesis that the presence of toxic compounds and the alkaline environment played a role on the partial inhibition of microorganisms in the FA samples were cellulose was added, can be confirmed by the theoretical volume of released carbon dioxide during the FA+3% of cellulose respiration tests, that was equal to $0.1 \frac{lCO_2}{kgDM}$; this value is comparable with the CA respiration test.

CHAPTER 8

ANALYSIS OF THE CARBON DIOXIDE ABSORPTION CAPACITY OF THE BOTTOM ASHES

8.1 Introduction

In this chapter are reported and analyzed the data obtained by the chemical analysis on the absorber liquid and the oxygen consumption tends, and thus carbon dioxide production values, obtained through the respirometric curves. The utilized procedure has been described in chapter 4.

At the present state, the only research to which is possible to compare the obtained data is the one conducted by Rendek et al, 2006. In this case, in fact, they used an Oxitop to measure the microorganisms activity and a 0.1 M NaOH solution to evaluate the CO₂ absorption capacity of a sample of artificially carbonated bottom ash and of a sample of fresh bottom ash.

8.2 Analysis on the Carbonated Ashes

The concentration of sodium hydroxide in the absorber liquid during those tests had a concentration of 0.1 M.

As in possible to see from the next table (Table 8.1), the quantities of carbon dioxide absorbed by the ashes and by the absorber experienced an increment parallel with the quantities of sewage sludge added, and so with the amount of biological activity present in the samples.

In particular is clear that the lower activity registered for the CA samples produced a lower quantity of carbon dioxide and thus a lower absorption by both the sodium hydroxide and the ashes. As higher quantities of external organic matter were added, the activity promoted a greater release of CO₂ and thus a faster absorption by the ashes.

The lower absorption capacity showed by the ashes in samples 15 and 28 where, on equal quantity of carbon dioxide released it has been registered a higher entrapping capacity by the sodium hydroxide, can be referred to the ashes composition of those specific samples.

Table 8.1: Carbonates production and analysis on the carbon dioxide absorption for the carbonated bottom ash.

| <i>Samples</i> | <i>IC mg/l</i> | <i>gNa₂CO₃/l</i> | <i>gCO₂/l absorbed by the NaOH</i> | <i>gCO₂/l released by the bacteria</i> | <i>gCO₂/l absorbed by the ashes</i> | <i>% of absorption by the ashes</i> |
|----------------|--------------------|--|---|---|--|---|
| CA (14) | 108 | 0,108 | 0,045 | 0,19 | 0,14 | 76 |
| CA (15) | 157 | 0,157 | 0,065 | 0,19 | 0,13 | 66 |
| CA+3% (20) | 134 | 0,134 | 0,056 | 0,30 | 0,25 | 82 |
| CA+3% (21) | 137 | 0,137 | 0,057 | 0,29 | 0,24 | 81 |
| CA+3% (22) | 167 | 0,167 | 0,07 | 0,36 | 0,29 | 81 |
| CA+5% (27) | 181 | 0,181 | 0,075 | 0,87 | 0,8 | 91 |
| CA+5% (28) | 231 | 0,231 | 0,096 | 0,88 | 0,78 | 89 |

Those results, graphically represented in the following figures (Figure 8.1 A, B and C), are not in line with the results achieved by Rendek et al., (2006). In that case, in fact, the quantities of carbon dioxide released by the bacteria and carbon dioxide entrapped in the absorber were comparable, where in our case there is an important gap between those values. In the Researches case, however, it has been utilized an artificially carbonated bottom ash: as explained in chapter 5, while the organic carbon was preserved, the reactive elements may were almost totally stabilized. This can explain the low absorption capacity experienced by the carbonated bottom ash utilized in that study.

In our research was utilized, as opposite, a material that, after a period of 1.5 years in a plastic jar, was poor in organic carbon but enriched in reactive materials. Thus is possible to accept that the quantities of carbon dioxide produced during the degradation of the organic carbon present in the ashes and the one brought by the external degradable matter could have interacted with reactive elements in the ashes.

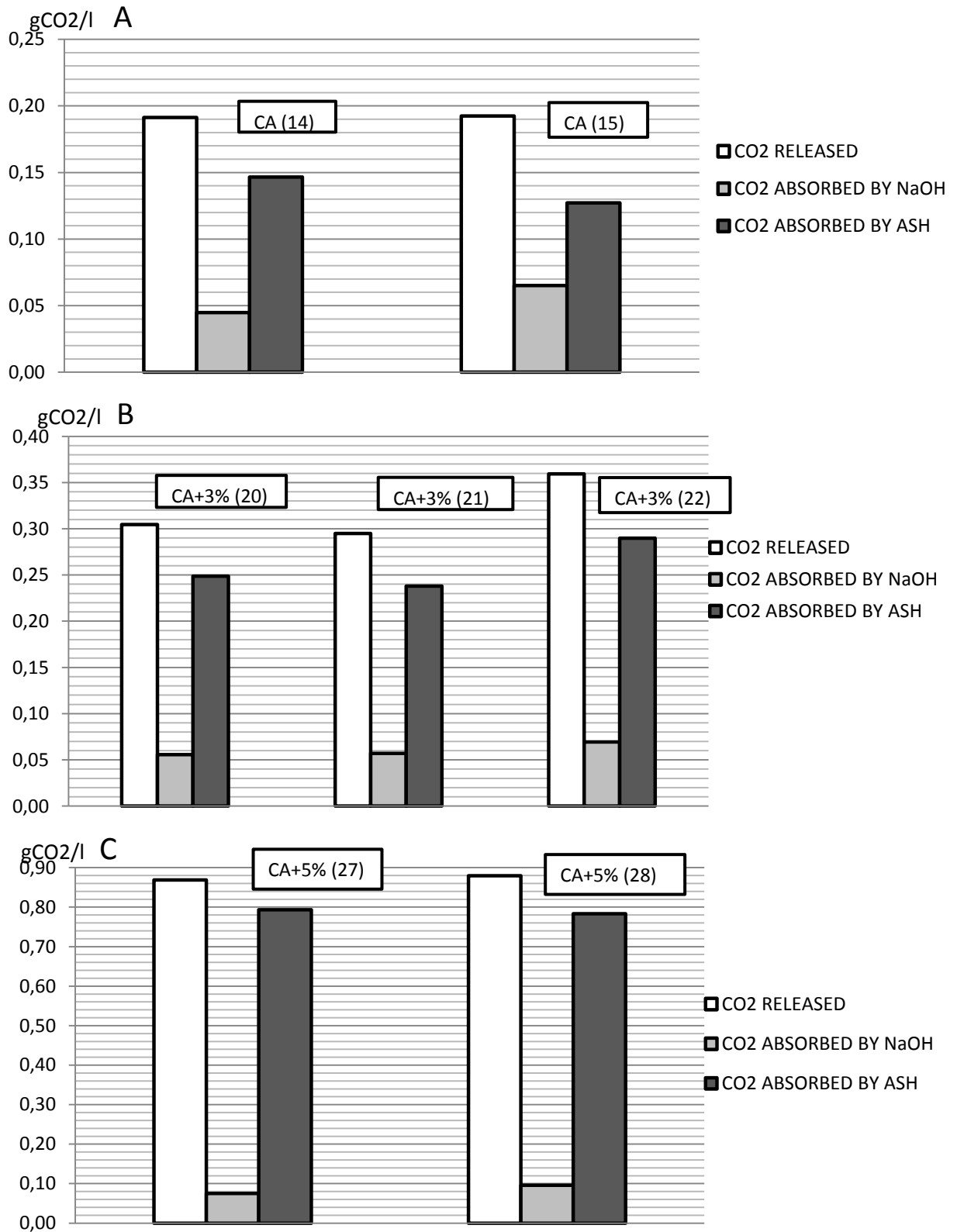


Figure 8.1: Carbon dioxide released by the bacteria, absorbed by the sodium hydroxide and by the ashes for the samples of carbonated ashes (A), carbonated ashes with the adding of 3% of sewage sludge (B) and carbonated ashes with the adding of 5% of sewage sludge (C).

8.3 Analysis on the Fresh Ashes

The concentration of sodium hydroxide in the absorber liquid during those tests had a concentration of 1 M.

From the next table (Table 8.2) is possible to observe a lower carbon dioxide production in the FA+3% samples, directly linked to the partial inhibition suffered by the bacteria during those tests. For the other samples, FA and FA+5%, the CO₂ absorption capacity demonstrated by the ashes was very high and in some cases was greater than the 90%.

Table 8.2: Carbonates production and analysis on the carbon dioxide absorption for the fresh bottom ash.

| <i>Samples</i> | <i>IC mg/l</i> | <i>gNa₂CO₃/l</i> | <i>gCO₂/l absorbed by the NaOH</i> | <i>gCO₂/l released by the bacteria</i> | <i>gCO₂/l absorbed by the ashes</i> | <i>% of absorption by the ashes</i> |
|----------------|--------------------|--|---|---|--|---|
| FA (35) | 233 | 0.233 | 0.10 | 0.81 | 0.72 | 88 |
| FA (36) | 198 | 0.198 | 0.08 | 0.86 | 0.78 | 90. |
| FA (37) | 238 | 0.238 | 0.10 | 0.98 | 0.88 | 90 |
| FA +3% (44) | 170 | 0.170 | 0.07 | 0.45 | 0.38 | 84 |
| FA +3% (45) | 166 | 0.166 | 0.07 | 0.38 | 0.31 | 82 |
| FA +3% (46) | 204 | 0.204 | 0.08 | 0.40 | 0.31 | 79 |
| FA +5% (59) | 179 | 0.179 | 0.07 | 1.03 | 0.96 | 93. |
| FA +5% (60) | 186 | 0.186 | 0.08 | 0.99 | 0.91 | 92. |

The results obtained from those analyses are similar to the ones reported by Rendek et al., (2006), that found that almost the 90% of carbon dioxide produced by the indigenous bacteria of the fresh ashes was entrapped by the ashes themselves.

Thus is possible to hypnotize that the carbon dioxide directly dissolved in the samples pore water and reacted with the reactive elements present in the ashes.

The following figures (Figure 8.2 A, B and C) represents the obtained results. As is possible to see from Figure 8.2 C, where the bacteria experienced a partial inhibition of their activity, a major quantity of carbon dioxide was entrapped in the absorber liquid.

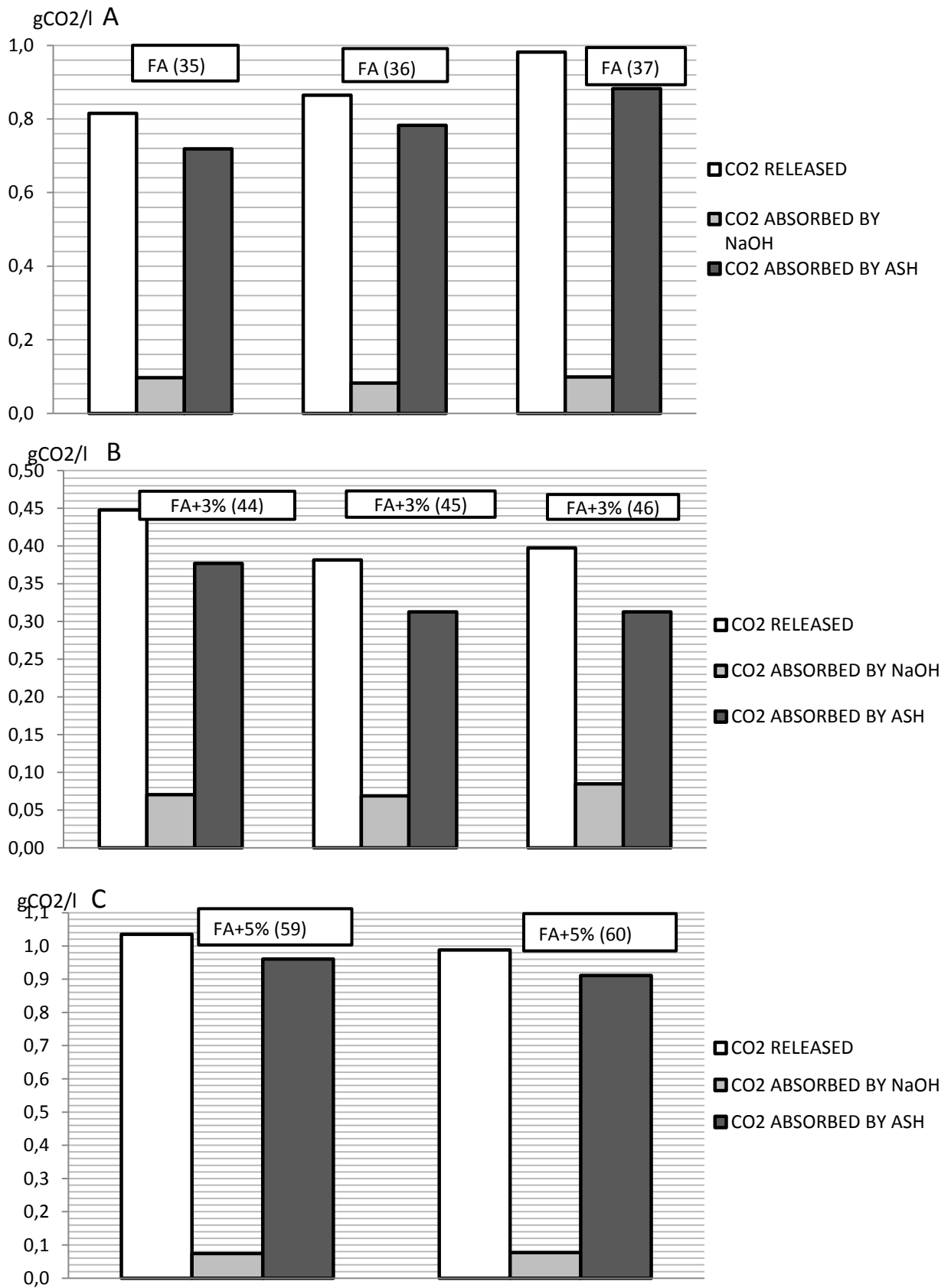


Figure 8.2: Carbon dioxide released by the bacteria, absorbed by the sodium hydroxide and by the ashes for the samples of fresh ashes (A), fresh ashes with the adding of 3% of sewage sludge (B) and fresh ashes with the adding of 5% of sewage sludge (C).

In both the cases analyzed, finally, is possible to assess that the bottom ashes have the capacity to absorb the carbon dioxide produced by the bacteria introduced by the adding of an external organic matter.

Moreover, comparing the rate of absorption demonstrated by the samples where no sludge was added with the rate of absorption shown where the 3% and 5% of sludge was mixed is clear that the CO₂ entrapping velocity of the reactive elements present in the bottom ashes increases with the adding of external organic matter.

The inhibition suffered by the bacteria in the FA samples caused a lower carbon dioxide production and thus a lower absorption capacity experienced by the ashes.

CHAPTER 9

IMPACTS ON THE LEACHING OF HEAVY METALS AND OTHER ELEMENTS

9.1 Introduction

In order to define the material created by mixing the sewage sludge to the bottom ashes as environmentally safe and sustainable, it was necessary to evaluate the leaching capacity of the samples.

In this chapter is described the behavior of Silicon and Calcium, as those two elements describe, through their variation in the leachate, the maturation stage of the bottom ashes. Moreover an analysis on the heavy metals behavior was conducted, in order to evaluate the possible impacts on the environment that the bottom ashes mixed to an external organic matter.

9.2 Silicon and calcium behavior

As is possible to see from the following figure (Figure 9.1), Si and Ca maintained their concentration in the leachate almost constant, independently from the quantities of sewage sludge added to the bottom ashes.

In particular in the CA tests the low Si leaching can be correlated to its precipitation with hydrated phases (Piantone et al., 2004); in the FA tests, instead, where the leaching was slightly higher respect to CA, the Si behavior can be correlated to an initial weathering stage of the glassy components. The relative stability of $\text{Ca}(\text{OH})_2$ validates the hypothesis that the microbial activity in the sludge may have been inhibited by this high alkaline compound.

The high leaching of calcium in the CA examples, instead, can be linked to the solubility of portlandite and other calcium-rich unstable minerals, like ettringite (Meima et al., 1997). The relative high pH, in fact, indicates that the CA weathering was in a medium stage between the completed carbonated bottom ash and the freshly quenched bottom ash, and thus the elements were still concurring for the formation of new stable minerals and the quantities of carbonates was still poor.

In the FA tests, at the contrary, the low leaching behavior of calcium can be associated to portlandite and calcium-rich elements (like ettringite) stability in the freshly quenched bottom ash non subjected to carbonation.

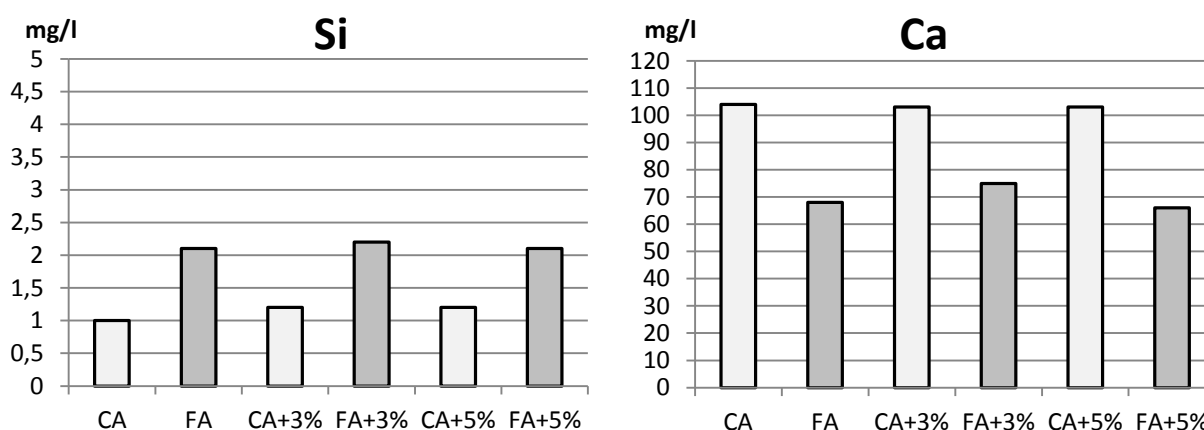


Figure 9.1 Silicon and Calcium leaching capacity after 4 days of respiration test

9.3 Heavy metals behavior

The leaching of heavy metals is described in the following figure (Figure 9.2). As is possible to see, in general the samples experienced an increment of heavy metals leaching with the increment of sewage sludge added to the samples.

The increment of Fe in the leachate may be due to the oxidation of minerals such as magnetite and siderite that, at high pH values, are dissolved from the more external layers of the glassy constituents (Wei et al., 2011). Moreover, it has been reported that ferric oxyhydroxide ferrilydrites undergo to a hydrolysis reaction in presence of dissolved Fe^{2+} , (Wei et al., 2011). However from the statistical analysis, it is possible to correlate the increment of sludge quantities to the increment of Fe in the leachate: this trend may be due to the high presence of this heavy metal in the used sludge (3.5 mg/l), that during aerobic respiration can be subjected to a great mobilization (Peng et al. , 2011). Moreover is possible to assess that the biodegradation of the organic matter in the sludge create a reducing environment (Meima et al., 1997; Aouad et al., 2008) that promoted the leaching of this element from the bearing minerals. The rate increment of Fe leaching is similar both for FA and CA, thus is possible to assess that this leaching behaviour have been promoted by the same cause.

The dissolution of Fe(hydr)oxides caused by reducing environment, could have caused the increment of leaching behaviour of different heavy metals to which shows affinity, like Pb and As (Meima et al., 1999; Piantone et al., 2004). Meima and Comans (1999) found that Pb leaching from bottom ash is dependent on the solubility-control capacity of the minerals in which they are entrapped. In particular Pb leachability is independent from the alkalinity during the first period of maturation, while is linked to its sorption in unstable minerals like

carbonates. This fact may partly explain the increment of leaching behavior experienced by this metal. The rate of concentration increment of Pb in the leachate is more evident for the carbonated bottom ash. When the pH decrease, in fact, this metal becomes more pH sensible and its stability should be controlled by the formation of stable minerals like carbonates (Meima et al., 1999). In our case, as previously assessed, the carbonate formation was not complete and so the Pb was not entrapped in those minerals. Moreover the pH was lower respect to the FA samples, and this may have enhanced the Pb leaching. For both the CA and FA samples, however, the the statistical analysis showed a direct correlation between the Pb trend and the moisture content of the samples.

In case of As, the addition of external organic matter and the subsequent consumption of oxygen can lead to enhanced mobility. Soil organic matter can exert control over arsenic mobility (Klitzke and Lang, 2009), and therefore plays an important role for As adsorption (Warwick et al., 2005). Buschmann et al., (2006) suggested that As forms H-bridges with organic matter and inner- and outer- sphere complexes with functional groups-phenolic and carboxylic (Mukhopadhyay and Sanyal, 2004). Grafe et al., (2002) and Simeoni et al., (2003) have reported As mobility by fulvic and humic acids-components of organic matter. Bauer and Blodau, (2006) demonstrated that the addition of organic acids, from an alkaline peat leachate, resulted in increased mobility of As from iron oxides, soils, and aquifer sediments. Harvey et al. (2002) have reported As mobility, in ground waters, due to degradation of dissolved organic matter.

Cu demonstrated the major increment of leaching behaviour among all the samples (Fig. 9.3.6). Cu have the capacity to bound to organic material and its leaching capacity seems to be controlled by this substances (Chimenos et al., 2000; Yao et al., 2010). Moreover it has been assessed that the biological degradation of the organic matter in the bottom ash enhance the Cu release, because the bearing substances are degraded by bacteria (Yao et al., 2010) and, once in solution, should be transferred to other minerals, ad Fe-oxides (Yao et al., 2010) and carbonates (Van Gerven et al., 2010). In our case the microbial activity in the bottom ash, incremented by the activity brought by the sludge, may have enhanced the degradation of the organic material to which Cu was bounded. In both cases the Cu leaching duplicate it's concentration in the leachate, but its concentrations in the CA eluates are 10 time lower respect to the one in the FA eluates. This may be due to the presence of bearing minerals, like Fe and Al oxides (Meima et al., 2002). Moreover Peng et al. (2011), after sewage sludge bioleaching, found that the Cu content in the solid matrix was largely decreased due to the bacteria degradation and bioleaching.

Chromium is present in the bottom ash as Cr(III) and Cr (VI). While Cr(VI) is soluble, Cr(III) is resistant to oxidation and is less common in bottom ash leachate. However, it is not possible to assess the predominance of one species on the other because of the non homogeneous combustion in the incineration chamber and the alternation of oxidizing conditions (Cornelis et al., 2008). Chromium presents a similar trend: a greater ash quantity and a high consumption of organic matter increment the leaching of this element. Moreover Cr is considered as a critical contaminant because, during accelerated carbonation, its mobilization is enhanced in greater proportion with respect to the natural weathering (Baclocchi et al., 2010; Van Gerven et al., 2005), especially in the finest grain-size (Baclocchi et al., 2010). This behavior can be linked to the competitiveness that exists between oxyanions in sorption or precipitation reactions in alkaline environment: because SO_4^{2-} and CO_3^{2-} that are present in higher quantities, this may cause the greater Cr leaching in the FA sample (Van Gerven et al., 2005; Cornelis et al., 2008).

Antimony is mainly present in the bottom ash in form of Sb(III) (antimonite) and Sb (V) (antimonate) (Cornelis et al., 2012), but the highest oxidation state is predominant (Cornelis et al., 2008). Tighe et al., (2005) attributed an important role to humic acid in retention of Sb in soils with high organic matter content. At high pH and Ca concentrations, Sb can also enter into complex such as $Ca[Sb(OH)_6]_2$, which can control its mobility (Johnson et al., 2005). In case of ash, it seems high pH and Ca concentrations may be affecting the Sb mobility.

Zn is found to be released from organic matter during bioleaching (Montserrat et al., 2006): the high quantities of organic matter present in the fresh ash (46 mg/l of TOC after 96 hours of respiration test), during aerobic degradation, may have released this element to which it was bounded. Moreover, the partial inhibition experienced by the microorganisms activity in the sample FA+3% (presenting a concentration of 89 mg/l of TOC after 96 hours of respiration test), can explain the low Zn concentration in the leachate for this sample. Finally, a higher content of Zn in the leachate was measured for the sample FA+5%, even if it was present with a lower amount respect to the FA sample. Moreover Zn was present in relevant quantities in the sewage sludge (35 µg/l), thus this fact may have contributed to the recorded concentrations in the samples leachate.

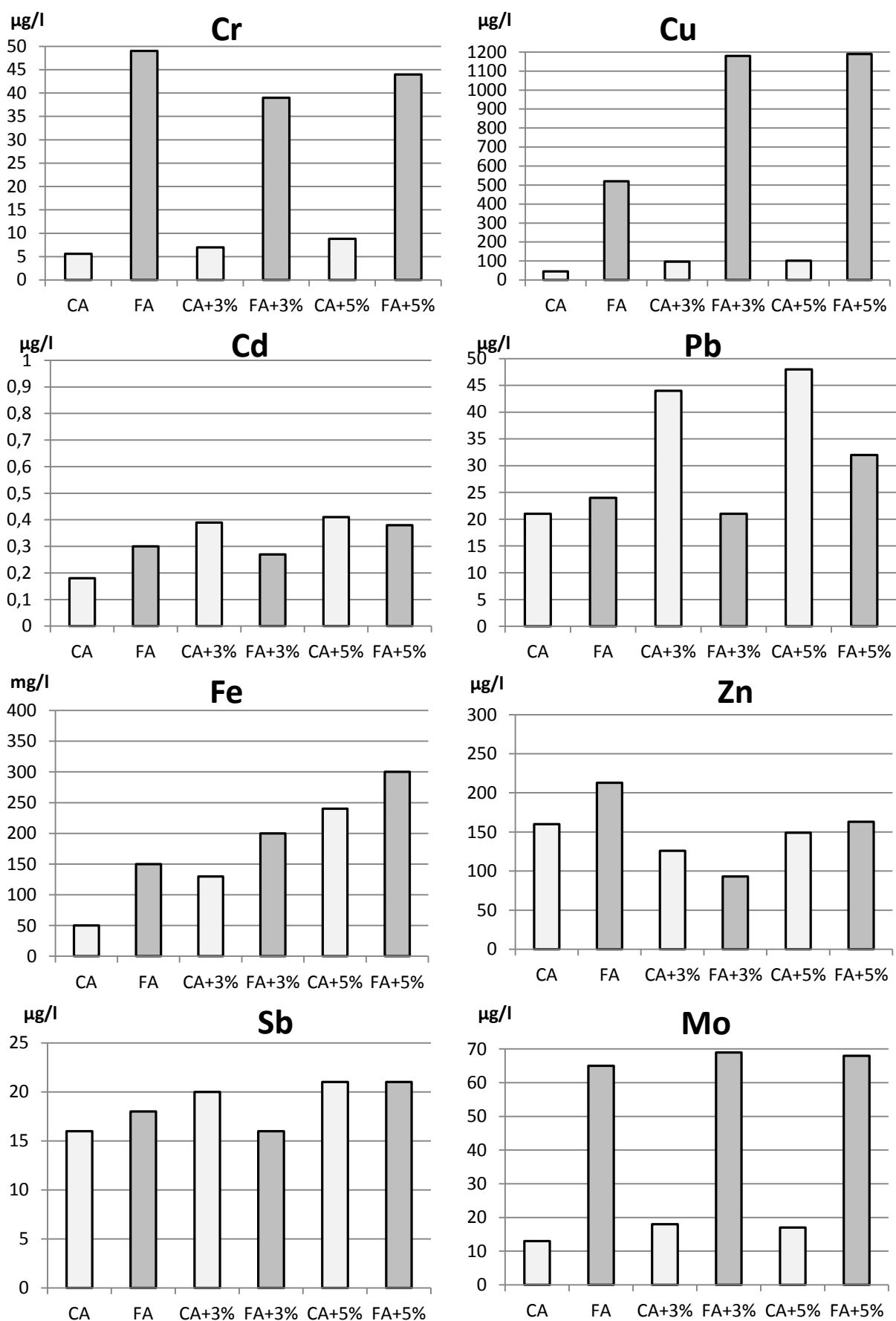


Figure 9.2: Cr, Cu, Cd, Pb, Fe, Zn, Sb and Mo leaching capacity after 4 days of respiration test

CONCLUSIONS

In this study the main objective was to assess the impacts that different typologies of external organic matter can generate on the municipal solid waste incineration bottom ashes. With this purpose several tests have been conducted in order to observe the reciprocal interaction between the ashes and the organic matter, to evaluate the capacity of the ashes to absorb the carbon dioxide generated by the bacteria both indigenous and external and to assess the elements leaching in order to classify from the environmental point of view the new material generated by the adding of external organic carbon to the bottom ashes.

The respiration tests highlighted that the carbonated ashes were in a medium weathering phase, characterized by a still high Ph (9.7) despite the ashes age (1.5), by an almost totally absence of degradable organic matter but still enriched in reactive elements. This phenomenon has been associated to the conservation methodologies: the not sealed plastic jar in which the ashes were stored, in fact, lead to an interaction of the first strata of the ashes with the atmospheric carbon dioxide, where the deeper strata were conserved almost unaltered.

While the oxygen consumption registered for the CA tests showed a linear increment as the quantities of sewage sludge were added in greater proportion, the FA samples demonstrated a different behavior. When no sludge was added to the fresh bottom ashes, in fact, it has been observed an initial adaptation period followed by an exponential growth. This behavior is typical of the fresh ashes in the first five months of ageing (Dougenest et al., 1999). The samples where low quantities of sludge were added, instead, showed a partial inhibition, that caused low oxygen consumption and thus a low CO₂ release. This fact has been linked to the presence of portlandite and to the release of heavy metals that negatively interacted with the bacteria activity. In particular this hypothesis is confirmed by the presence of stable Ca formations (low leaching of Ca in the fresh ash samples) and by the higher release of the majority of heavy metals as higher quantities of sludge were added.

The addition of crystalline cellulose to the ashes during the respiration tests showed a lower degradation capacity exerted by the bacteria. The reason of this inhibition, that was comparable for both the carbonated ashes and the fresh ashes, was correlated to the crystalline structure of the used material, that requires more time to be attacked, and to the presence of a calcium-rich environment, that improves the formation of those two saccharinic acids (Knill and Kennedy, 2003; Humphreys et al., 2010) and reduce the total degree of alkaline degradation because of the enhance of the stopping phase-reaction at the expense of the

peeling reactions. However, from the analysis of the carbon dioxide production, it has been possible to forecast a degradation rate similar to the one achieved by the adding of sewage sludge to the bottom ashes with a longer observation time.

The analysis on the carbonates production in the absorber liquid utilized during the respiration tests confirmed the hypothesis advanced by Rendek et al. (2006) that have highlighted the capacity of the bottom ashes to interact and absorb the carbon dioxide produced by the indigenous bacteria during the degradation of the organic compounds. While the results obtained for the fresh ashes were similar to the one reported by the Researches, the ones obtained with the carbonated ashes showed a greater absorption capacity. This fact was correlated to the used material: In Rendek et al. (2006) case, in fact, the “carbonated ash samples” were constituted by artificially carbonated ashes: this process stabilizes the Ca reactive elements but don't have effects on the organic matter degradation, thus the carbon dioxide produced by the microorganism activity couldn't interact with the stabilized ashes. In our case, as opposite, the used material was characterized by a low organic matter content but a high Ca reactive elements, thus the ashes still had the capacity to absorb the carbon dioxide produced. The absorption capacity of the ashes, both fresh and carbonated, increased with the increment of sludge added, and thus with the higher carbon dioxide production rate.

The heavy metals leaching, in general, experienced an increment for all the analyzed tests. In particular the behavior of several heavy metals was correlated to the degradation of the organic matter to which they were entrapped (this is the case, for example, of Zn and As) and to the formation of a reducing environment (for example for what concern Fe). Finally, the addition of water in the samples, that is required to improve the bacterial activity, had a negative effects on the dissolution of elements and thus on the release of heavy metals like Pb.

The improvement of carbon dioxide absorption by the bottom ashes didn't have any positive effects on the weathering of the ashes (the elements like Ca and Si were constant for the all tests independently to the quantities of sewage sludge added) and thus to the release of heavy metals. In order to better assess the impacts linked to the carbon dioxide absorption, further analysis should be conducted in the future on the ashes changes in weight and their mineralogical composition.

Moreover longer respiration tests should be repeated with the aim to evaluate the long-term behavior of the heavy metals leaching capacity.

Finally, due to the increment of metals emissions, is not possible to suggest the use of a material composed by bottom ashes mixed with external organic matter, and in particular sewage sludge.

APPENDIX 1

WASTE GENERATION AND MANAGEMENT IN EUROPE, ITALY AND SWEDEN

A1.1 Introduction

This chapter introduces the waste production and the most applied strategies for its management in Europe, Italy and Sweden.

The comparison of different policies applied for the waste management gives the possibility to assess which are the best choices for a sustainable and cost effective development.

A1.2 Waste generation in Europe

The total waste generation for the EU-27 Member States¹ in the year 2008 have been estimated in 261 million ton, showing a decrease from 2004 (268 million tonnes) and 2006 (273 million tonnes). Of this totality corresponding to the year 2008, the 3.7% (98 million tonnes) was classified as hazardous waste (Eurostat, 2012).

The following graph (Figure A1.1) represents the total waste generation in Europe (EU-27) for the main economical activities in relation to the year 2008. From this representation it is possible to see that the households category represents only the 8.5% of the total, but the attention reserved to this section is higher because of its various composition, variety of generators and because of the presence of different types of organic compounds that, degrading, produce greenhouse gases.

Figure A1.2 represents the MSW generated by country (EU-27) in the period 1995-2010, sorted by the major value of kg of waste generated per capita in the year 2010. From this representation it is possible to see that for 24 out of 27 Countries, since the 1995, it has been registered an increment of waste production; of those, only five of them are still registering an increment (Czech Republic, Slovakia, Greece, Portugal and Cyprus). Since 2006 an important decrease is reported for Latvia, Estonia, United Kingdom, Spain, Austria and Ireland.

¹ EU-27 member states: Belgium, Greece, Luxembourg, Denmark, Spain, Netherlands, Germany, France, Portugal, Ireland, Italy, United Kingdom, Austria, Finland, Sweden, Poland, Czech Republic, Cyprus, Latvia, Lithuania, Slovenia, Estonia, Slovakia, Hungary, Malta, Bulgaria, Romania.

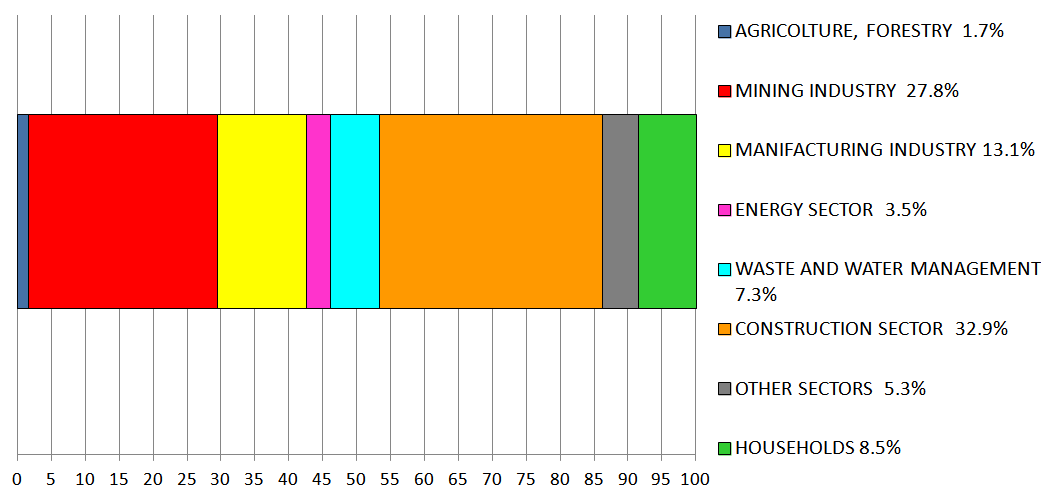


Figure A1.1: Total waste generation in the EU-27 subdivided by economic activity in 2008. (Eurostat, 2011²)

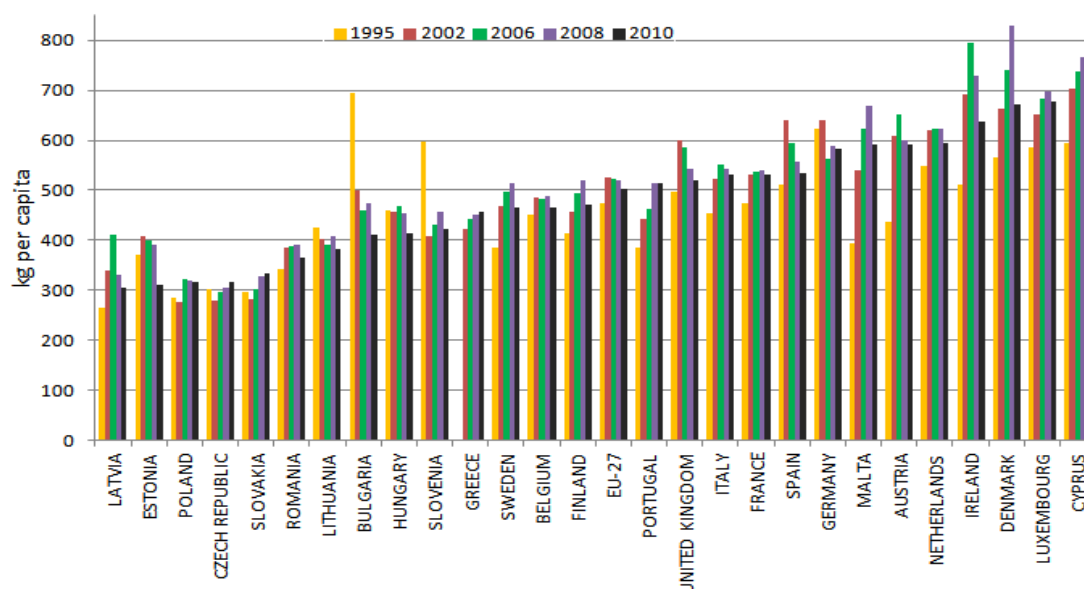


Figure A1.2: Municipal solid waste generated by country in 1995, 2002, 2006, 2008 and 2010 and sorted by 2010 level ($\frac{kg\ MSW}{capita*year}$). The 2010 values for Greece, Spain, France, Italy, Cyprus, Austria, Poland, Romania and United Kingdom are an estimation. Source: Eurostat, 2012³.

However in the last ten years, probably as a consequence of the implementation of the European Directives and of the economic downturn, seems that the municipal waste production is unchanged, stabilizing its value at 500÷520 kg per capita per year (Figure A1.3) (Blumenthal, 2011).

² Data Eurostat: http://epp.eurostat.ec.europa.eu/statistics_explained/index.php/Waste_statistics

³ Eurostat data: <http://appsso.eurostat.ec.europa.eu/nui/setupModifyTableLayout.do>

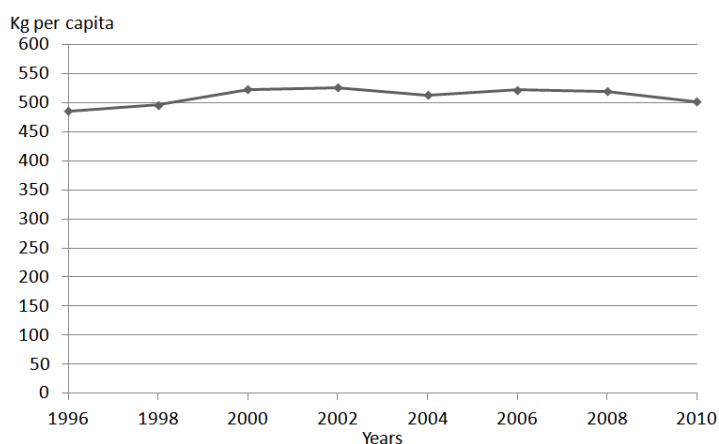


Figure A1.3: Municipal solid waste generated by the EU-27 in the period 1996-2010, expressed in kg per inhabitant (Eurostat, 2012¹).

A1.2.1 Municipal solid waste management in Europe

As it possible to see from the following figures (Figure A1.4 and A1.5), the activity of the European Union contributed to a significant decrease in the use of landfills as primary solution for the waste management, and improved the recycling and the incineration (especially with energy production).

The main directives that promote this trend are: the “Waste Directive”⁴, in which is introduced the waste hierarchy, a path that should be considered in every national legislation to implement a better protection of the environment (in the order: prevention, material recovery and recycling, energy recovery, final disposal). The directive 1999/31/EC on the landfill of waste⁵, in which it was recommended to classify the different kind of landfills (for hazardous waste, non-hazardous waste and inert waste) and to treat the material before disposal; decision 2003/33/EC⁶, that defines criteria for the acceptance of waste and bans the putrescible material from landfills. The directive 94/62/EC⁷ concerning the management of the packaging and packaging waste, that invited the member nations to implement the recycling and the incineration with energy recovery of the packaging waste.

From Figure A1.4 it is possible to see that, between 1995 and 2010, the final disposal into or onto land decreased by 34%.

⁴ Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives.

⁵ Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste.

⁶ 2003/33/EC: Council Decision of 19 December 2002 establishing criteria and procedures for acceptance of waste at landfills pursuant to Article 16 and Annex II to Directive 1999/31/EC.

⁷ European Parliament and Council Directive 94/62/EC of December 1994 on packaging and packaging waste.

On the other hand those actions against landfilling required the implementation of several types of waste pre-treatment and treatment. Is demonstrated, in fact, the increment of the use of different possibilities (Fig A1.5), like composting and digestion (for organic solid waste), incineration with and without energy recovery and recycling.

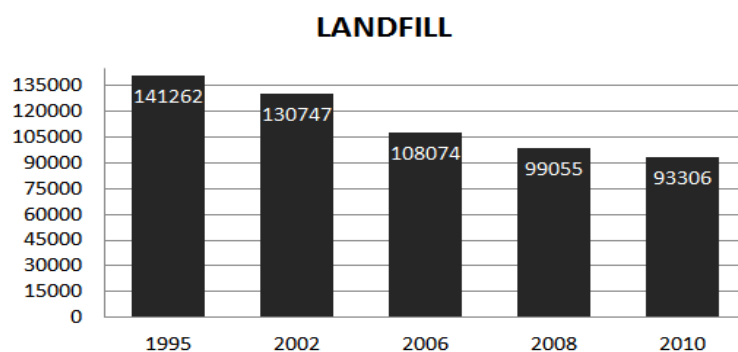


Figure A1.4: Landfilling trend for EU-27 in the years 1995, 2002, 2006, 2008 and 2010. Data are expressed in thousands of tonnes. (Eurostat, 2012⁸.)

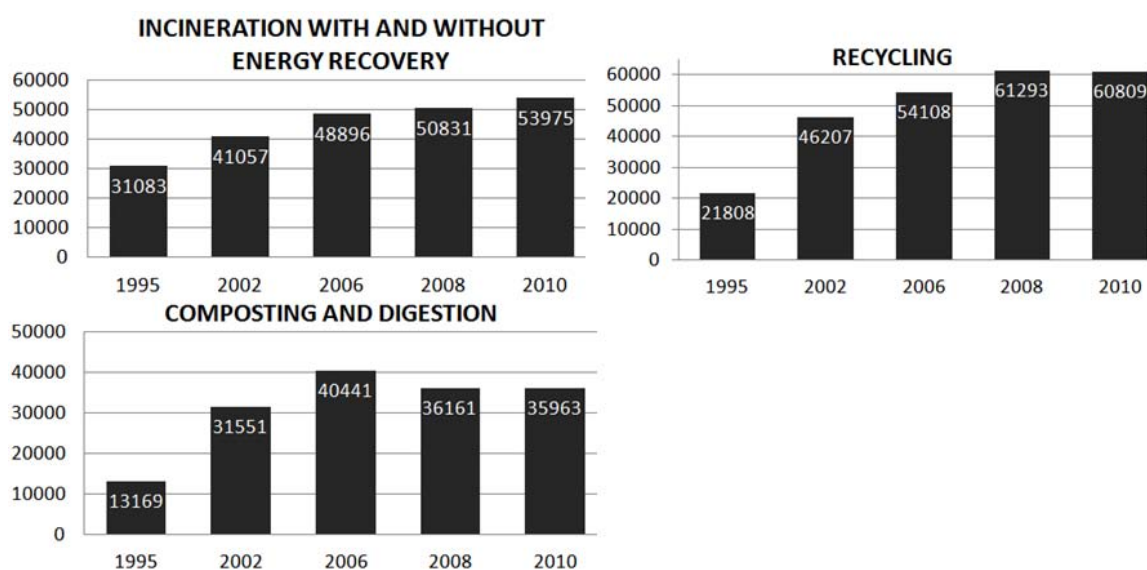


Figure A1.5: Incineration with and without energy recovery, recycling and composting and digestion trends for the years 1995 - 2010 for the EU-27. The data are expressed in thousands of tonnes. The criterion defined in the new Waste Directive to classify the incineration facilities in relation to their energy efficiency, were supposed to came into force by December 2010. Eurostat, 2012⁹.

⁸ Eurostat data: <http://appsso.eurostat.ec.europa.eu/nui/setupModifyTableLayout.do>.

⁹ Eurostat data: <http://appsso.eurostat.ec.europa.eu/nui/setupModifyTableLayout.do>.

From the above figure (Figure A1.5) it is possible to see that recycling and composting experienced the highest increment (respectively 64% and 63%) while incineration is growing with a lower rate (more 42% since 1995).

A1.2.2 Sewage sludge generation in Europe

Since the implementation of the Urban Waste-water Directive¹⁰, that suggests to the member states to provide all the agglomerates with collecting systems for urban waste water, it has been registered and implementation of sewage sludge production from 5.5 million ton of dry matter in 1992 to 9 million tonnes at the end of 2005. In order to face the problem of the disposal of this material, the European Union promotes the use of the high quality sludge in agriculture: the sludge, in fact is rich in nutrients (like phosphorous and nitrogen) that are useful for vegetation. In order to get an high quality sludge, is required to proceed a process of sanitation, by which the pathogens are eliminated, and chemical treatment in order to mobilize heavy metals (European Commission, 2012).

A1.3 Municipal solid waste generation and management in Italy

The data related to the waste generation, collection and treatments are collected by the Ministry of the environment and by several national agencies like ISPRA, APAT, ONR and others.

The Italian legislation, to what concern the management and the protection of the environment, is mainly guided by the Legislative Decree 152/2006 and the Legislative Decree 36/2003¹¹ and modifications: the first legislates, among the other aspects, about waste management, water and soil protection, air pollution, remediation of contaminated sites and environmental impact assessment; the second, instead, represents the transposition of the European directive 1999/31/CE concerning the landfills.

The Italian population (slowly increased from 58.8 million inhabitants in 1995 to 60.3 million inhabitants in 2010, Eurostat, 2012) is distributed in a total surface of 301338 km² (ISPRA, 2012), divided in 20 regions aggregated in three geographical areas: North, Centre and South.

¹⁰ Council Directive 91/271/EEC of 21 May 1991 concerning urban wastewater treatment.

¹¹ Decreto Legislativo 3 aprile 2006, n°152: "Norme in materia ambientale"; Decreto Legislativo 13 gennaio 2003, n°36: "Attuazione della direttiva 1999/31/CE relativa alle discariche di rifiuti".

In the period 2004 - 2008 the total waste production in this country in slightly increase from a value of 2403 kilograms per capita in 2004 to 2992 kilograms per capita in 2008, with a percentage +0.2% (Eurostat, 2012).

The municipal solid waste generation, instead, experienced an important increment since 1995 to 2010, even if it has been registered a low decrease in the year 2008 (Eurostat, 2012, ISPRA 2012), registering a production of 539 kg per capita (Figure A1.6). The northern regions are the ones who show a major production: this reality could be linked not only with a higher number of residents (27.7 millions of citizens against 11.9 million in the Centre and 20.9 in the South) but also to different economic situation and a greater improvement of the separate collection. The last one, in particular, give the possibility to better monitor the trend of the MSW generation (ISPRA, 2012).

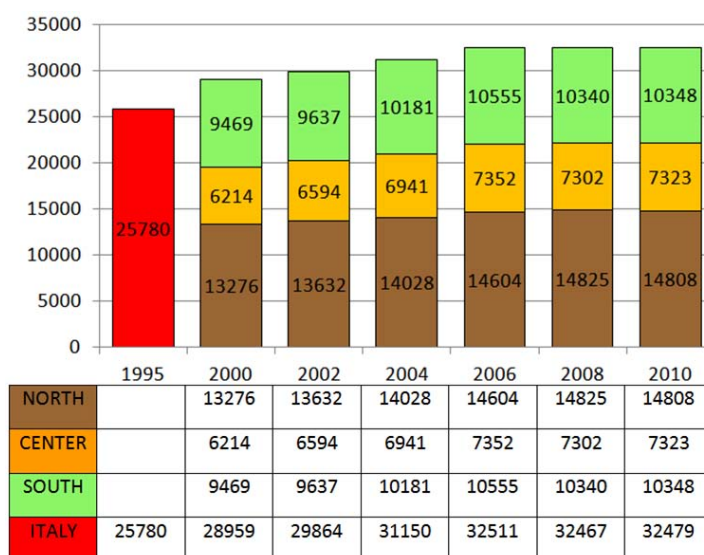


Figure A1.6: Municipal solid waste generation in Italy and in the macro-areas North, Center and South for the years 1995, 2000, 2002, 2004, 2006, 2008 and 2010. The values given for the voice “Italy” in the table are the sum of the values estimated for the macro-areas. The all data are expressed in thousands of ton. Eurostat, 2012 (for the year 1995), ISPRA, 2012 (for the other years).

For what concern the municipal solid waste management, the Italian cities, since the 90s, are required to implement the separate collection. Nevertheless the data shows that still the percentages of separate collection are low and greatly under what the national legislation have programmed (50% before the 31 December 2009 for the Dlgs. n°152/2006 and L. 27 December 2006, n°296). Moreover vast differences have been registered between the three Italian macro-areas: 49.1% of separate collection for the North, 27.1% for the Center and

21.2% for the South, moving the national average to a percentage of 35.46% evaluated in 2010 (ISPRA, 2012).

The incineration technology in Italy experienced an important increase in the last 10 year, shifting from the 2.2 million of tonnes burned in 2000 to the 5.2 million tonnes burned in 2010. The total number of incinerators in Italy is 50 and the majority of them are situated in the North (28 plants). Among the totality, 46 plants are equipped with energy recovery systems. Nevertheless, the final disposal in landfill still represents the most applied solution for the municipal solid waste management, covering the 46% of the total treatments, against the 16% of incineration, the 12% of composting/anaerobic stabilization and 19% of recycling (ISPRA, 2012).

The highest percentages of waste incinerated is MSW (3 million ton), against the 0.9 million ton of RDF. The most applied technique is the moving grate systems (41 plants) while the fluidized bed systems are present in nine plants. The bottom ash and fly ash produced in the Italian plants are almost 2 million ton for the year 2010.

A1.4 Municipal solid waste generation and management in Sweden

Sweden population increased from 8.8 million inhabitants in 1995 to 9.3 million inhabitants in 2010 (Eurostat, 2012) and is distributed in a territory of 450300 km² (European Commission, 2012).

The total waste production in 2010 was 113.6 million ton, showing an increment of + 30% respect to 2004, when the waste production was 87.7 million ton (Eurostat, 2012).

Sweden is implementing an active policy of waste minimization with the direct collaboration of the municipalities and the institutions, especially with the schools. The results sees a decrement of the households production from 480 kg per capita in 2009 to 463 kg per capita in 2010 (AVFALL Sverige, 2011). The municipal solid waste disposed in landfill was only the 1% among the other treatments, while 49.2% undergone to material recycling or biological treatments and the 48.7% have been incinerated in plant with energy recovery devices (AVFALL, 2011).

In Sweden there are 30 incineration plants that produce 14.4 GWh of energy

APPENDIX 2

MUNICIPAL SOLID WASTE INCINERATION

A2.1 Introduction

The waste incineration is a controlled process that develops for a required period of time needed to ensure the complete combustion of the material and is coupled with APC devices, to limit the environmental impacts that can derive from the direct flue gas emission in the atmosphere. This process can be exploited also for the energy recovery (Unipr, 2001).

This thermal treatment, moreover, offers the possibility to reduce fuel waste mass up to 70% and volume to 90% (Rougame et al., 2009) and to accomplish a complete sanitation. Nevertheless the secondary waste that derives from the waste combustion are several: 15÷25 % of the waste mass is transformed in bottom ash and fly ash (respectively 15÷25 % and 1÷3% of the initial waste mass, Unipr, 2001), wastewater from the quenching tanks and flue gas emissions. Moreover, around the incinerator installations, it may be increased the traffic intensity due to the tracks that carry the wastes, noise and odors.

The research around the incinerators furnaces, the APC systems, and a careful environmental planning, however, can guarantee an high level of control on the whole processes, that make this kind of treatment a good alternative to the landfilling for the waste that cannot be recycled. Despite this, the installation of a new plant often have to face with the reluctance of the local population, that sees this kind of treatment as a source of environmental degradation, especially for what concern the air quality (NIMBY-syndrome, Not In My Back Yard).

A2.1.1 History of waste incineration

The waste incineration practice started to develop in the 19th century in the United States and in some European Countries, with the aim to face the always growing problem of the waste management (Chandler et al., 1997). In particular in the United Kingdom was designed the first incinerator provided of energy recovery devices and the first MSW incinerator, while the moving grate and the rotary kiln furnace technologies can be referred to the years 1920 and 1930 (Christensen et al., 2010). The economic boom which had succeeded the Second World War had given rise to a fervent consumerism and as a consequence, higher quantities of waste

were produced. In consideration even with the fact that waste avoidance and recycling were not a concern. In the late 1970's and 1980's, moreover, the poor quality of the effluent gasses that flowed out from the incinerators (mostly of them were designed in the 1920's, when there was not much effort on the air pollution control systems engineering) raised alarms in population, especially on the emission of dioxins (Chandler et al., 1997). In those years, in fact, the first APC devices were installed (Christensen et al., 2010).

In relation to that, as reported by Olle Åslander (1987¹), Sweden has been one of the first countries that imposed a moratorium on the construction of incinerators in 1985/1986: in those years 1.5 Mton of waste were annually incinerated in 25 plants. Those waste-to-energy plants produced 3.5 TWh of heat per year, corresponding to 9% of the total energy produced in the all districts. Despite this, the government realized that the electrostatic precipitators or the baghouse filters were not enough to prevent high quantities of dioxins emissions. Therefore decided to suspend the incinerators construction until new devices were engineered. The moratorium was lifted in June 1986.

A2.2 Waste input characteristics

The composition of the waste flow and the expected future changes in waste management on an area should be taken in account for the design of a plant. Some plants, in fact, require only a little pretreatment of waste, while others can operate only with waste that have been subjected to mechanical- biological treatments (SRF, Solid Recovered Fuel) and have been subdivided in streams (RDF, Refuse-Derived Fuel)².

A2.2.1 Waste composition

The waste characterization, as said before, represents an important stage in the design of an incinerator. In order to understand which could be the required dimensions and devices of the plant, to evaluate the heating value of the wastes (mathematical models like Bento's³, that evaluate the heating value from the knowledge of the organic matter and moisture content, or the Modified Dulong model⁴, that evaluate the HV from the knowledge of the content of carbon, hydrogen, oxygen, sulfur and nitrogen) and to estimate the outputs of the process

¹ "The Swedish dioxine moratorium", from the symposium "Dioxin and resource recovery", New York, 1987.

² Database of Waste Management Technology - <http://www.epem.gr/waste-c-control/database/html/WtE-00.htm>

³ Bento's model: $HV = (44.75x OM) - (5.85xW) + 21.2$, Abu-Qudais and Abu-Qdais, 2000.

⁴ Modified Dulong model: $HV = (80.5xC) + (338.6xH) - (42.3xO) + (22.2xS) + (5.55xN)$, Tchobanoglous et al., 1993.

(mathematical models like “EASEWASTE”⁵, are able to evaluate the air emissions, bottom and fly ashes, sludge, gypsum and waste water released by the incineration and APC treatments), should be characterized the merceological composition and, consequently, should be analyzed the proximate and the ultimate structure of the material (Komilis et al., 2011; Nhuchhen et al., 2012). Those properties usually depend on the socio-economic conditions, population size, climate and environmental legislation of a country (Komilis et al. 2011; World Bank, 1999).

The municipal solid waste merceological categories are mainly composed by the following materials (Cossu, 2011):

- Cellulosic fraction (paper, cardboard, paper materials, textiles, leather, wood);
- Plastics (packaging, containers or plastic films of several typology of plastics, like PET, PP and others);
- Metals (aluminium containers, copper cables, iron or other sources);
- Glass and inherits (bottles, ceramics);
- Putrescible (food waste and garden waste);
- Hazardous fraction (batteries, pharmaceuticals);
- Composites (Tetrapak, nappies).

The following figure (Figure A2.1) shows the MSW composition for the European territory.

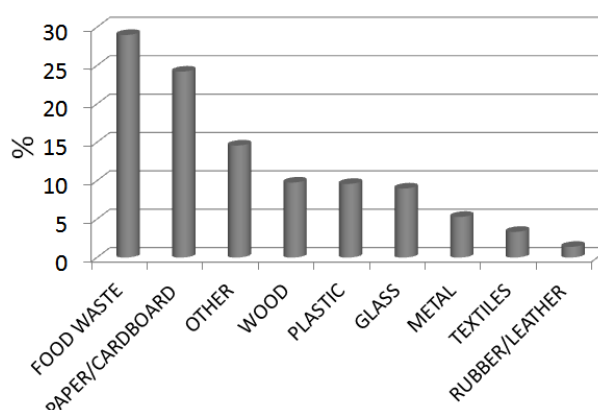


Figure A2.1: MSW composition data by percent for the European territory. (Pipatti et al., 2006. Average values between the data reported for Eastern Europe, Northern Europe, Southern Europe and Western Europe)

The proximate analysis, that is linked to the biomass components, should give the following parameters: moisture content (%), total solid (TS, %), volatile solids (% of TS), fixed solids

⁵ Kirkeby et al.: “Environmental assessment of solid waste system and technologies: EASEWASTE”, 2006.

(% of TS), organic carbon (%), COD ($\frac{mg\ oxygen}{mg\ SW}$), heating value ($\frac{J}{kg}$) (Kumar et al., 2008; Nhuchhen et al., 2012).

The ultimate analysis, instead, is applied to evaluate the chemical composition by weight percentages of the material, and several studies are developing to assess the HV also from this parameter (Nhuchhen et al., 2012; Yin 2011). In particular the ultimate analysis is used to identify the most combustible substances in the raw waste, that usually contains carbon, hydrogen, nitrogen, sulphur (organic sulphur, sulphide and sulphate), oxygen and chlorine (organic-insoluble and inorganic-soluble) (Table A2.1) (Liu et al., 1997).

Table A2.1: Ultimate elemental composition of some organic substrates frequently present in the raw waste. Komilis et al., 2012.

| <i>Element</i> | <i>Material and quantity (% DM)</i> |
|-----------------|--|
| <i>Carbon</i> | Newsprint (43.7), Tetrapack (43.1), Raw meat fat (62.6), meat (52.5), Branches (45.1), PS (93.5), LDPE (87.3), HDPE (82.4), PET (61.4) |
| <i>Nitrogen</i> | Cardboard (0.17), meat (11.3), Grass (1.75), PP (0.42), |
| <i>Hydrogen</i> | Tetrapack (6.8), kitchen paper (6.61), raw meat fat (9.41), meat(8.35), branches (7.06), HDPE, LDPE (15.2), PP (14.4) |
| <i>Sulphur</i> | Meat (0.79), vegetables (0.66) |
| <i>Oxygen</i> | Kitchen paper, toilet paper (47.7), office paper (44.0), fruit (47.3), cooked pasta(46.9), branches (40.1), PET (32.7), PVC (4.1) |

The inorganic (non combustible) waste categories are the major sources of ash content in MSW, but a secondary source is determined by inorganic components of combustible materials, like clay in glossy and high-grade papers, bones and shells in food waste, fiberglass in reinforced plastic (Liu et al., 1997).

In order to assess the feasibility of a waste for combustion, is possible to evaluate, as first indicative parameters, the combustible fraction, moisture content and ash content (Hulgard and Vehlow, 2010; World Bank, 1999). Once that the values of these parameters are obtained, then it is possible to understand, by plotting the values in the Tanner's diagram (Figure A2.2), if the waste have the right properties to be combusted without any auxiliary fuel, and in particular if $W\% < 50$, $A\% < 60$ and $C\% > 25$ (shaded area in the triangle).

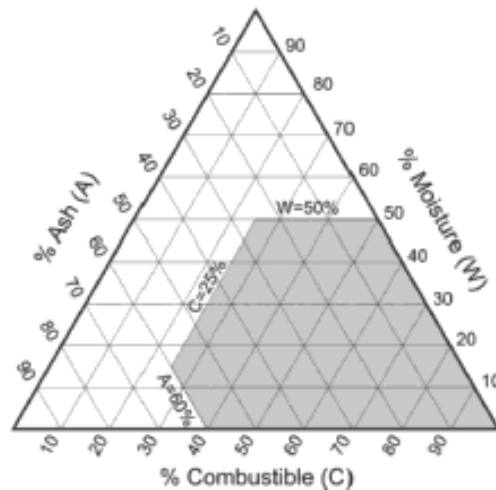


Figure A2.2: Tanner's diagram. Waste within the shaded area can be combusted without auxiliary fuel (Hulgard and Vehlom 2010⁶).

The HV of a waste is an important parameter for the design of an incineration plant, because the furnace requirements strictly depend on this property. In particular, HHV is used to evaluate the necessity to equip the furnace by a boiler in order to extract the heat released by the process. While the LHV, is considered to assess if the furnace should have some devices to dry the material before the ignition, and so to prevent as more as possible the heat losses (Hulgard and Vehlom, 2010; World Bank, 1999).

In the following table (Table A2.2) are listed the characteristics of moisture, total solids, ash content, combustible, higher and lower heating value for common merceological categories of municipal solid waste.

Table A2.2: Fraction basis (moisture, total solids, ash and combustible) of several fraction of waste from waste collection in Germany, and related heating values (higher and lower). Zentner, 2011.

| <i>Fraction</i> | <i>W%</i> | <i>TS%</i> | <i>A%</i> | <i>C%</i> | <i>HHV</i> $\frac{kJ}{kg}$ | <i>LHV</i> $\frac{kJ}{kg}$ |
|-------------------------------|-----------|------------|-----------|-----------|----------------------------|----------------------------|
| <i>Food and organic waste</i> | 66 | 34 | 13.3 | 20.7 | 17000 | 1912 |
| <i>Plastics</i> | 29 | 71 | 7.8 | 63.2 | 33000 | 20144 |
| <i>Textiles</i> | 33 | 67 | 4 | 63 | 20000 | 11789 |
| <i>Paper and cardboard</i> | 47 | 53 | 5.6 | 47.4 | 16000 | 6440 |
| <i>Glass</i> | 3 | 97 | 97 | 0 | 0 | -73 |
| <i>Inerts</i> | 10 | 90 | 90 | 0 | 0 | -245 |

⁶ "Incineration: Process and Technology" Hulgard T. and Vehlom J.; from the book "Solid waste technology and management", Christensen T. H., 2010.

A2.3 Incinerators characteristics and operating systems

The design of any plant should be linked, among other aspects, to the waste characteristics and amount (heating value, pollutants emissions potential, ash content, structural and mechanical requirements for the plant), to the possibility to recover energy from the process and from the location. In the EU the guiding Directive is the number 2000/76/EC, on the incineration of waste.

Generally, all the MSW incinerator facilities are equipped with the following process sections:

- waste receiving and storage area
- feed system for the incinerators
- furnace
- exhaust heat recovery system
- air pollution control devices
- stack
- ash handling system

A2.3.1 Waste receiving, storage area and feeding systems

This initial part of the incineration plan is used to control and register the incoming waste and, in relation to the kind of material, to reduce the size or sort the waste. After these first operations, the refuse is moved into a storage area where is also mixed in order to obtain a more homogeneous fuel for the furnace (World Bank, 1999). From the storage area, a crane collects the waste and moves it to a hopper, from which the furnace is fed.

A2.3.2 Furnace

The most important step of the process, combustion, occurs in the furnace. There are several kinds of burning devices, but the choice should be driven by the typology of waste that incinerator will treat: inhomogeneous and homogeneous waste, hazardous and with high moisture content (World Bank., 1999; Hulgard and Vehlom, 2010). In particular if the plant have been designed to receive inhomogeneous material, that have not been subjected to any treatment, usually the moving grate technology represent the best choice, because of its ability to treat large variations of size and heating value material (World Bank., 1999; Hulgard and Vehlom, 2010).

As for what concern the homogeneous waste (RDF), that have been widely subjected to mechanical treatments (for example sorting or shredding), it usually applies to the fluidized bed technology (Hulgard and Vehlom, 2010). The rotary kiln furnace, that follows the same ideal concept of the moving grate combustion process, can be used for both homogeneous and inhomogeneous waste, but seems to be not appropriate for the MSW (Unipr, 2001; Di Pietrantonio, 2004).

In the following pages will be given a deeper introduction on the moving grate, fluidized bed and rotary kiln incineration systems.

A2.3.2.1 Moving grate incineration

The moving grate incineration devices are the most common because they offers the possibility to burn an inhomogeneous waste like the MSW without any pre-treatment (Di Pietrantonio, 2004).

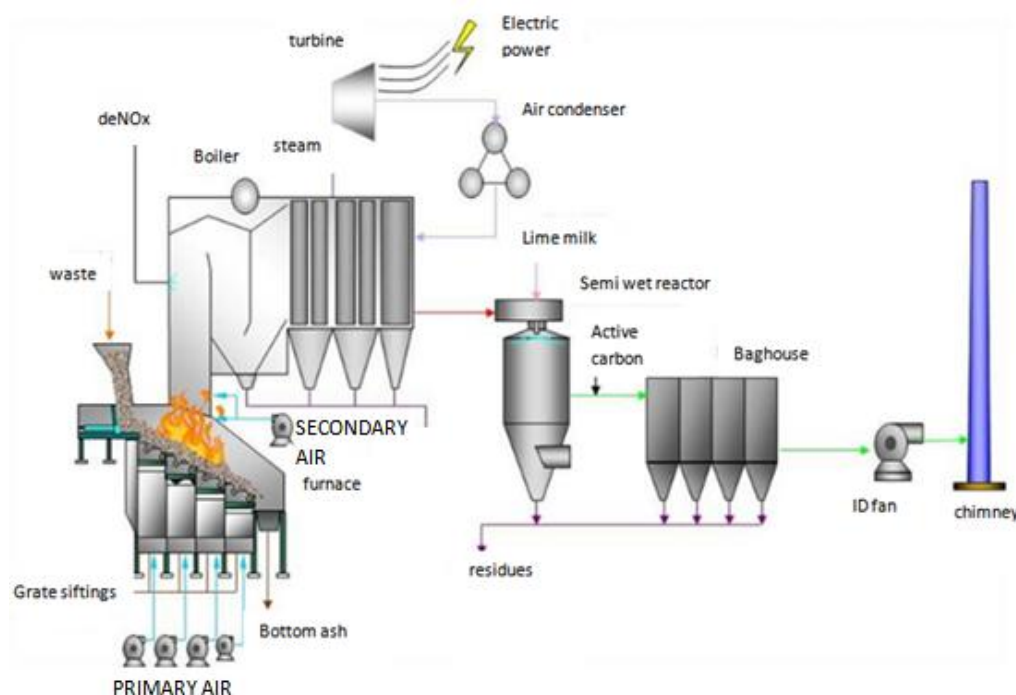


Figure A2.3: Example of MSW incinerator plant with moving grates, energy recovery system based on Rankine cycle and APC devices (Database of Waste Management Technologies⁷).

⁷ Database of Waste Management Technologies: <http://www.epem.gr/waste-c-control/database/html/WtE-01.htm>

As soon as the waste is introduced in the furnace is dried at a temperature of 100°C by the heat emitted from the furnace walls and from the primary air. Proceeding along the grate, the temperature arises until 500°C-600°C: in the range of temperatures between 250°C and 500°C the material is deprived of the volatile compounds (e.g. hydrocarbons) with no supplying of any oxidizing agent and, in the areas where oxygen is absent, can take place the pyrolysis (Di Pietrantonio, 2004; Chandler et al., 1997). The products of those passages are a partially oxidized gaseous phase (syngas), a liquid phase (tar) and a solid phase (char) (Di Pietrantonio 2004, Di Blasi 2008).

The layer of fuel material distributed in the moving grate is then subjected to combustion and gasification of the organic component, and transformed in an unburned phase and in a gas phase; the gasses are finally oxidized and the solid residues are unloaded in a quenching tank at the end of the furnace (Rogaume et al., 2009; Unipr, 2001⁸). The parameters that controls this stage are: temperature, residence time, turbulence and oxygen content. In particular the ignition temperature should be gained and maintained for the sufficient time to ensure the complete combustion of the waste (Chandler et al., 1997), that comes into contact with the primary air (with a stoichiometric content of oxygen sufficient for maintain activated the combustion process) blown from underneath the grates. The gasses that are released by this process should be stationed in the combustion chamber for 2 to 6 seconds kept in contact with the secondary air (air excess), before being proceeded through the APC treatments. The secondary air, blown from an upper section of the chamber, is needed to ensure the complete oxidation of the flue gas, to guarantee the turbulence of the gaseous particles and to control the temperature of the system (Di Pietrantonio, 2004; Unipr, 2001).

The walls of the furnace, refractory lined, can be cooled behind the lining by two systems: with air cooling or with water walls. This second system requires less excess of air in the furnace and so a lower volume of both furnace and APC devices (Hulgard and Vehlom 2010, World Bank, 1999).

A2.3.2.2 Fluidized bed incinerator

This kind of devices are used for the incineration of an homogeneous waste, like sewage sludge (after drying the material or after preheating of the combustion air) or RDF (Di Pietrantonio, 2004; Van Caneghem et al., 2012). Nevertheless more recent technologies can be applied also for MSW, even if a size reduction for the coarser fraction can be still required

⁸ Università Degli Studi di Parma: http://www.dsa.unipr.it/trezzo/uni_parma/capitoli/tecnologie/

and a pre-mixing of the material can be needed if the HV are widely different through the fuel waste (Van Caneghem et al., 2012).

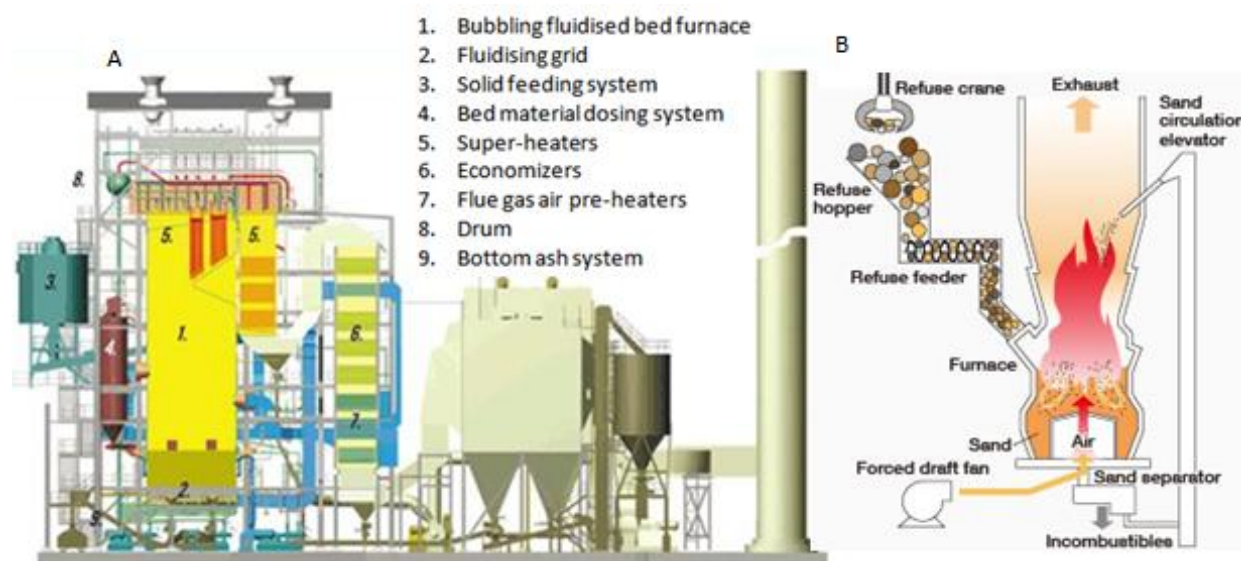


Figure A2.4: A: General representation of a bubbling fluidizer bed incineration plant, with energy recovery system and APC devices (Database of Waste management Technologies⁹); B: enlargement on the furnace with general operating system (Tokyo Environmental Public Service Corporation¹⁰)

The main section of this device, with a cylindrical shape and fed by a lateral input channel, is characterized by a bed of sand or sand-like material held in suspension by an ascending air stream, blown from the bottom of the furnace (Figure A2.4, B). (Van Caneghem et al., 2012; Unipr, 2001).

There are three kinds of fluidized bed incinerators: bubbling fluidized bed (BFBC), rotating fluidized bed (RFBC) and circulating fluidized bed (CFBC) (Van Caneghem et al., 2012). In the BFBC, characterized by a slower fluidization velocity (0.5 to 3 m/s), a more accurate prior size reduction of the waste is needed, to avoid segregation phenomena; the solid material that has been transported with the flue gas is separated in the cyclone and partially reintroduced in the system. The CFBC, instead, is characterized by a high gas velocity (3 to 9 m/s) that causes the transport of the solid material in cyclone: this material is totally separated and reintroduced in the furnace (Van Caneghem et al., 2012; Saxena et al., 1994). Van Caneghem et al. (2012) distinguish an ulterior typology of fluidized bed incinerator, the rotating fluidized

⁹ Database of Waste Management Technologies: <http://www.epem.gr/waste-c-control/database/html/WtE-02.htm>

¹⁰ Tokyo Environmental Public Service Corporation: <http://www.tokyokankyo.jp/tokyoprogram/en/recycling-technologies/incinerator-type>

bed (RFBC): this device requires less restrictions on the waste size, because they guarantee a better recirculation of the material by imposing a better circulation of the solid bed; the blown air is distributed in well aerated ascending stream and in a poorly aerated descending stream.

A further distinction can be done in relation to the pressure operation conditions: some beds, in fact, are designed to work at higher pressure (up to 10 atm), in order to reach higher energy recovery, even if the gasses should undergo to a pollutants breakdown before being addressed in the turbine (Di Pietrantonio, 2004; Unipr, 2001)

The furnace can be sectioned in 3 main areas: the primary air blowers and the wind-box at the bottom, to uniformly distribute the primary air flow through the furnace section; the solid bed, where the combustion is implemented (at the temperature of $850\div 900^{\circ}\text{C}$ for a residence time of $50\div 90$ minutes for the waste and more than 3 seconds for the flue gas, Unipr, 2001); and the freeboard zone, immediately upon the fluidized bed area, where the complete combustion of the flue gas takes place by the effect of the blown secondary air (Van Canegham et al., 2012; Saxena et al., 1994).

The major disadvantages of this technology are linked to the necessity to treat the waste before its combustion and to control the pollutants emission potential. In particular the lower operating temperature and the lower excess of air required ensure a minor release of NO_x and CO, but in the meantime have a negative effect on the chlorinated compounds, that, when transported in the flue gas, can cause the corrosion problems and can enhance the particle aggregation in the bed, decreasing its yield (Van Canegham et al., 2012.)

A2.3.2.3 Rotary kiln incinerator

The rotary kiln incinerator furnace is based on a steel cylinder, refractory lined, rotating around its own axes and with an average slope of $1\div 3\%$, that improves the movement of the material (Figure A2.5, B) (Lategano, 2009; Di Pietrantonio, 2004).

The most common dimension of the rotating cylinder are 1-5 m of diameter and 8-20 m of length, with a minimum flow of 2.4 t/day to a maximum of 480 t/day (Hulgard and Vehlom, 2010).

The fuel material is introduced upstream and forms a 10 cm thick layer. The combustion air is not directly mixed with the waste (like in the moving grate system) but is blown parallel to the cylinder axes co-current or counter-current. The counter-current option is applied to reach a better mixing between the material and the combustion air, but can cause some problems for the flue gas collection (Lategano, 2009)

Those devices are usually used for industrial waste, and in particular for hazardous waste, but can be applied also for liquids, sludges and MSW or RDF. Nevertheless the utilization of the rotary kiln for the urban waste combustion is not recommended because of the long time required to burn the fuel material (from 90 to 120 minutes), that makes this device inappropriate for the treatment of high quantities of waste, and for the difficulties for the combustion air to enter in contact with all the waste (Lategano, 2009; Di Pietrantonio, 2004)). In particular high air excess of air are required, and so the energy efficiency is lower respect to the other described incineration systems (80%) (Hulgard and Vehlom, 2010, World Bank, 1999).

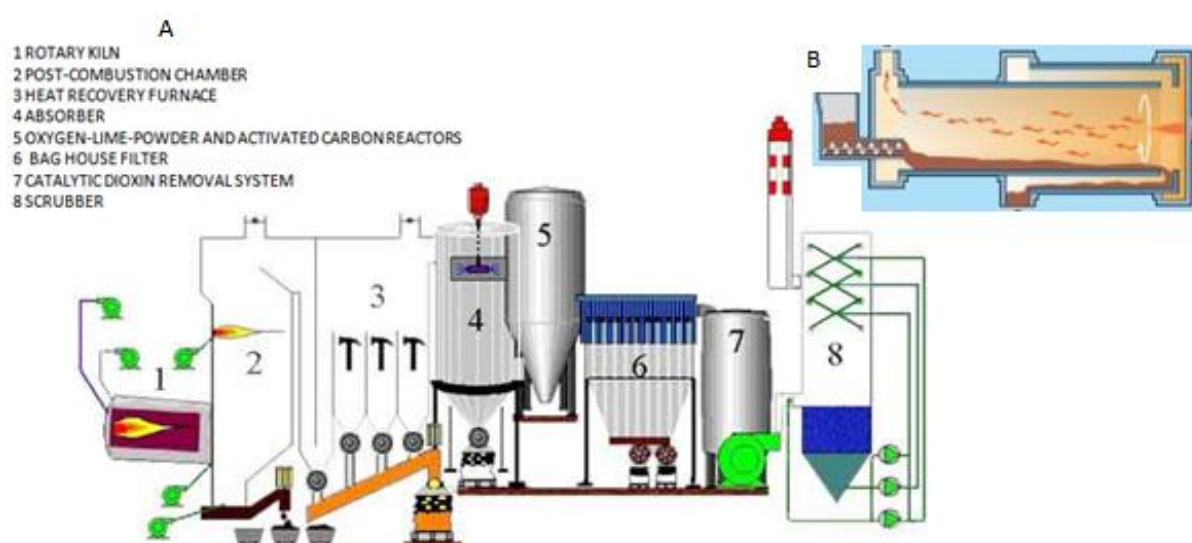


Figure A2.5 A: General rotary kiln incineration plant with APC devices (Veolia Environmental Services¹¹); B: Enlargement on a counter-current rotary kiln (Eisenmann¹²)

In order to reach a complete combustion, usually the rotary kiln is coupled to a post-combustion device downstream the furnace (Lategano, 2009; Hulgard and Vehlom, 2010) or to a moving grate upstream, used for ignition accomplishment (Hulgard and Vehlom, 2010).

A2.3.3 Energy recovery systems

The modalities to exploit the MSWI for energetic purposes are mainly two: with direct combustion and with indirect combustion.

¹¹ Veolia Environmental Services: <http://www.sarpi.hu/en/plant/technology/>

¹² Eisenmann: <http://www.eisenmann.com/en/products-and-services/environmental-technology/waste-disposal/rotary-kiln.html>

A2.3.3.1 Direct combustion

This modality is based on the heat that develops during the combustion of waste, and can be used for the production of heat, electricity or both (co-generation).

The electricity production is based on the Rankine cycle (Figure A2.6) and gives the possibility to recover the 35% of the all heat energy (Christensen et al., 2010). In this cycle a liquid, present in the boiler and usually water, is transformed in vapour phase by the high temperatures that develops in the furnace, and its temperature is increased in the superheater (immediately downstream the evaporator), to ensure higher thermal energy. The vapour is then sent to the turbine where, thanks to the acquired kinetic energy, is able to activate the rotor connected to the electricity generator by investing a series of blades. After this passage, the vapour enters in a condenser where is transformed in liquid phase. Finally the liquid is pumped in boiler and to overcome to a new cycle (Christensen et al., 2010; Unipr 2001).

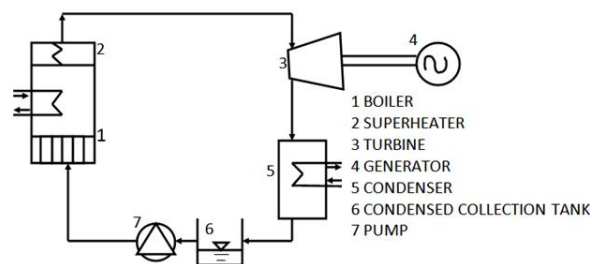


Figure A2.6: General Rankine Cycle with superheater, applied to the MSW incineration for the electric energy production.

The Rankine cycle can be coupled with other systems applied for the district heating: the back pressure and turbine extraction.

In the back pressure solution the vapour in the condenser is cooled at the same temperature of the district heating circulation fluid. (Christensen et al., 2010; Unipr, 2001). With this procedure, achieved by a back pressure turbine for combined electricity and district heating, is possible to save up to 65% of heating energy and 27% of electric energy (Christensen et al., 2010).

In the turbine extraction procedure, instead, the steam is spilled from the turbine at a pressure directly correlated to the needed heating temperature (Unipr., 2001).

A2.3.3.2 Indirect combustion

This procedure is based on the production of a combustible gas with an high heating value, that can be used in endothermic engines or in gas turbines. This combustible syngas is produce by the pyrolysis and gasification of the waste fuel (Unipr, 2001).

If the obtained gas is clean can be directly used in turbines for the production of electric energy; if the syngas in not complete cleaned can be use in boilers for the district heating (Christensen et al., 2010). The gas can, however, be depurated by cooling it to a temperature of 90°C in absence of oxygen, washing it with acid and basic solutions and finally conveying it through an active-carbon bed (“Thermoselect” process) (Unipr, 2001).

APPENDIX 3

GLOSSARY AND LIST OF ACRONYMS

Glossary

Ash content: part of the material that, during combustion, doesn't change its physical properties. Those residues can be collected with the bottom ash and the fly ash¹.

Combustible fraction: part of the material that, during combustion, changes its physical and chemical properties, developing gaseous products that can be oxidized by high exothermic reactions. Those materials are mainly composed of carbon, hydrogen, oxygen, sulfur and nitrogen¹.

Combustion: oxidation process in which the chemical energy is degraded as thermal energy, with the developing of flames¹.

Gasification: thermochemical transformation of a carbonaceous material in a combustible gas by the use of an oxidizing agent. The gas produced by this process usually contains: CO, CO₂, H₂, CH₄, H₂O, hydrocarbons and tar in vapor phase². The gasification temperature is around 1100°C³, but can reach higher values (2000°C) if applied for the production of combustible flue gas in the indirect energy recovery plants⁴.

Hazardous waste: materials composed or entered in contact with chemical elements characterized by hazardous properties for human health and environment. For example the constituents could be heavy metals, inorganic compounds, PCB, pharmaceutical or veterinary compounds; while properties that make them hazardous could be explosive, oxidizing with highly exothermic reactions, carcinogenic if inhaled or ingested, corrosive and toxic⁴.

Heating Value: quantity of thermal energy that is possible to obtain at the pressure of 1 atm, by the reaction with a quantity of combustible at the temperature of 25°C with a required quantity of oxidant, bringing the temperature of the products to the one of the reactants¹.

¹ Università degli Studi di Parma: http://www.dsa.unipr.it/trezzo/uni_parma/capitoli/tecnologie/

² Università degli Studi di Parma: http://www.dsa.unipr.it/trezzo/uni_parma/capitoli/tecnologie/

³ Di Pietrantonio, 2004.

⁴ Directive 2008/98/EC of the European Parliament and of the council of 19 November 2008 on waste and repealing certain directive

Higher Heating Value: quantity of thermal energy released by the system when the combustible is brought to its initial temperature and when the water vapor present in the combustion gasses is condensed, releasing its condensation heat⁵.

Ignition temperature: temperature that develops during the combustion process and that triggers the flames on the fuel materials. When this temperature (that depends on the heating value of the material, on the homogenization between the oxidizer and the combustible and on other aspects) is reached, the combustion can continue without any external thermal support^{4,5}. Usually ignition is reached at the temperature of 500°C for the MSWI⁶.

Lower Heating Value: quantity of thermal energy released by the system when the combustible is brought to its initial temperature and when the water vapor is lost with the flue gas without condensate. The LHV is equal to the HHV minus the steam condensation heating value².

Municipal solid waste: waste originating from households and from all the locations that produce a waste with similar qualities, like small businesses, office buildings, institutions (schools), from the public gardens maintenance, street sweepings or emptying streets litter bins. The collection of this refuse is organized by municipal authorities by door-to-door collection, traditional collection or voluntary deposits⁷.

Peeling: first reaction step of the cellulose degradation in which the end-wise glycosidic rings are eliminated with the successive formation of saccharinic acids. The products of this reaction are low-molecular weight acids⁷.

Pyrolysis: irreversible transformation of material (solid fuel decomposition and formation of low-molecular weight gases and char from the reaction of the volatile organic products) at high temperatures (350 – 800°C and higher) and in absence of oxygen. The products of this process are a liquid phase (tar), a gas phase (syngas) and a solid phase (char). The kinetic of the process has a great influence on the products: if the rate is slow (lower temperatures or larger dimension material) the char production (carbonaceous material) will be prevalent; if the kinetic is fast (higher temperatures) the syngas production will be prevalent. The syngas is mainly composed by CH₄, CO, CO₂⁸.

⁵ "Heating values of the combustibles", Galbiati Luca. From "Prontuario dell'ingegnere", Guadagni, 2010.

⁶ Chandler et al., 1997

⁷ Calvini, 2008

⁸ Di Blasi, 2008.

Treatment of waste: all physical, thermal, chemical or biological processes, including sorting, that change the characteristics of the waste in order to reduce its volume or hazardous nature, facilitate its handling or enhance recovery⁹.

List of Acronyms

| | |
|--------------|--|
| APAT | Agenzia per la Protezione dell'Ambiente e per i servizi Tecnici (Agency for Environmental Protection and Technical services) |
| APC | Air Pollution Control |
| C | Combustible |
| CA | Carbonated Ash |
| COD | Chemical Oxygen Demand |
| Dlgs | Legislative Decree |
| DM | Dry Matter |
| DOC | Dissolved Organic Carbon |
| EU-27 | European Union, 27 member countries |
| HDPE | High Density Polyethylene |
| HHV | Higher Heating Value |
| HV | Heating Value |
| ISPRA | Istituto Superiore per la Protezione e la Ricerca Ambientale (National Institute for Environmental Protection and Research). |
| LDPE | Low Density Polyethylene |
| LHV | Lower Heating Value |
| M | Molar |
| MSW | Municipal Solid Waste |
| MSWI | Municipal Solid Waste Incineration |
| NACE | Nomenclature of Economic Activities of the European Communities |
| OECD | Organization for Economic Co-operation and Development |
| ONR | Osservatorio Nazionale Rifiuti (National Waste Observatory) |
| PCB | Poly Chloro Biphenils |
| PET | Polyethylene Terephthalate |
| PP | Poly Propylene |
| PS | Polystyrene |

⁹ Directive 1999/31/EC, Article 2.

GLOSSARY AND LIST OF ACRONYMS

| | |
|-------------|---------------------------|
| PVC | Polyvinyl Chloride |
| RDF | Refuse-Derived Fuel |
| T/FC | Toxic/Flammable Corrosive |
| TOC | Total Organic Carbon |
| TS | Total Solids |
| W | Moisture |
| WM | Wet Matter |

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