

ESCUELA TÉCNICA SUPERIOR DE INGENIEROS
INDUSTRIALES Y DE TELECOMUNICACIÓN

UNIVERSIDAD DE CANTABRIA



Trabajo Fin de Grado

**ANÁLISIS DEL CICLO DE VIDA DE
ALTERNATIVAS PARA EL TRATAMIENTO
DE CENIZAS VOLANTES DE LA
INCINERACIÓN DE RESIDUOS
MUNICIPALES**

**(Life cycle assessment of alternative
processes to treat fly ash from waste
incineration)**

Para acceder al Título de

Graduada en Ingeniería Química

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1. INTRODUCTION

1.1. CHALLENGES OF MUNICIPAL SOLID WASTE

Waste generation is one of the most complex environmental challenges faced by modern societies. Prevention and proper management are essential to avoid its negative impacts on ecosystems, biodiversity and human health.

From all waste flows, municipal solid waste (MSW) constitutes about 10 % of the total amount (EUROSTAT, 2016). Currently, around 1.3 billion tonnes of MSW are generated by world cities every year (Hoornweg et al., 2012), around 20 % is produced by European Union (EU – 27) (EUROSTAT, 2016).

Figure 1 shows the evolution from 1995 to 2015 of the generation and treatment of MSW in the EU – 27. In this sense, improving waste management is crucial to make Europe more resource efficient (Hoornweg et al., 2012).

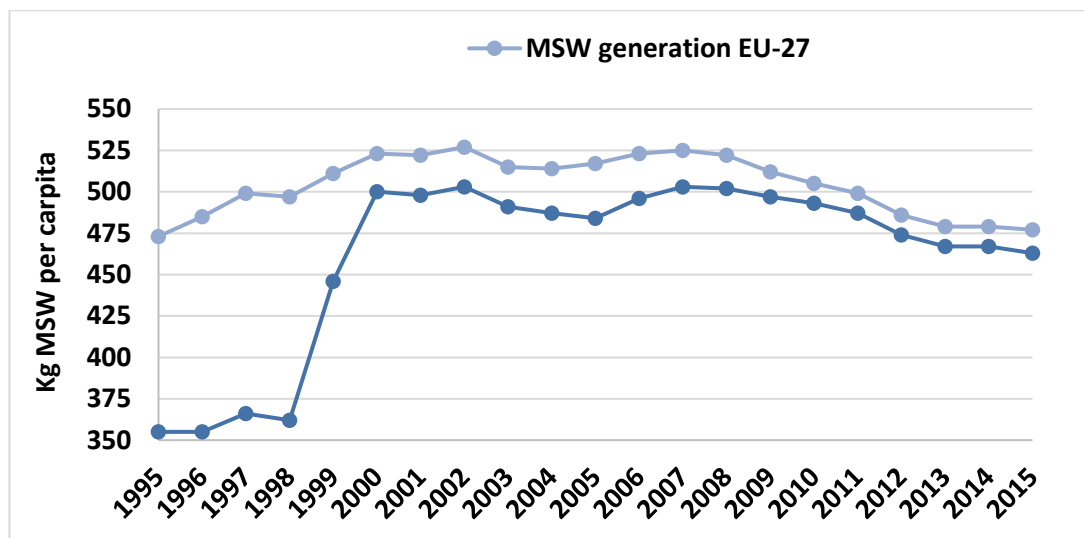


Figure 1. Evolution of MSW generation and total waste treatment in EU – 27 (EUROSTAT, 2016).

As reflected in Figure 1, the generation of MSW in EU – 27 has experienced periods of growth and decreases. These variations show different stages of consumption and economic health throughout this period. From 1995 to 2002, the amount of MSW generated per capita increased, which was mainly motivated by the increasing consumption pattern of our society. After a short

period in which the growth stopped, this trend changed in 2005, and there was a new increase from 2005 to 2007. This increase was followed by a new declination from 2008 to 2015. In 2015, MSW generation was 477 kg of MSW person⁻¹, this represents an increase of 0.85 % compared with 1995 (EUROSTAT, 2016). The MSW treated suffered great growth in 2000 and then has been fluctuating in relation to MSW produced. In the last 15 years, more than 95 percent of MSW generated has been treated (EUROSTAT, 2016). Regarding the MSW treatment methods, Figure 2 shows the amounts of municipal waste treated (kg per capita) in EU – 27 for the period 1995 to 2015. There are four main treatments: landfill, incineration, recycling and composting.

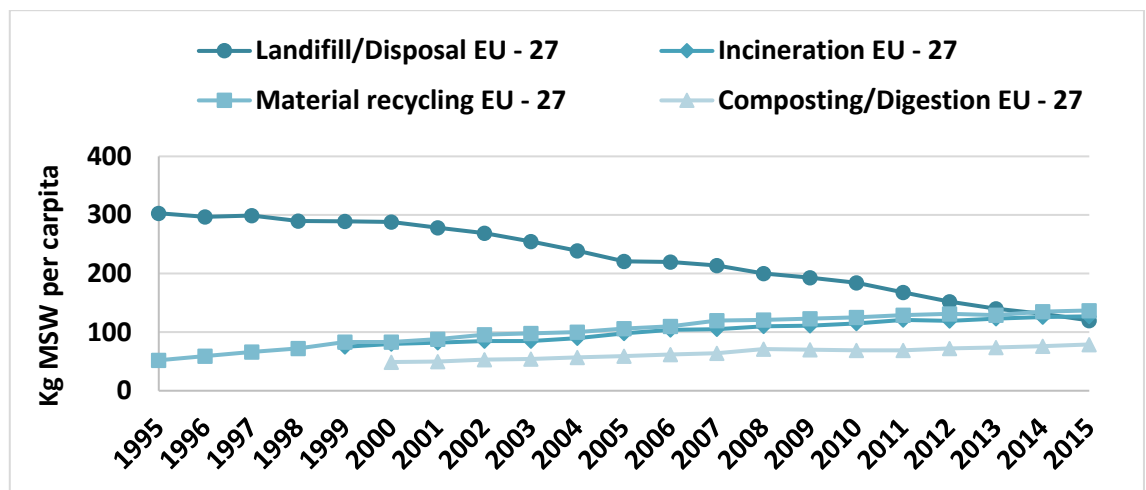


Figure 2. Evolution of waste management treatments in EU – 27 (EUROSTAT, 2016).

Despite the increase in waste generation, the amount of landfilled MSW has dropped from 63.8 % in 1995 to 25.3 % in 2015 (EUROSTAT, 2016). This reduction can be associated with the growth of legal restrictions, such as Directive 94/62/EC (EUROPE, 1994) and Directive 1999/31/EC (EUROPE, 1999), which have led to the development of different waste treatments. The recovery of organic matter by material recycling is the treatment method that has increased the most. Incineration has also grown and it equals recycling rates. On the other hand, composting is being implemented since 2000 but it is not as common as the other recycling technologies. Recycling and composting together accounted for 45 % in 2015 (EUROSTAT, 2016).

Figure 3 depicts the importance of the different treatment methods in Spain in 2014. In spite of the fact that the European trend to use landfills has been gradually replaced by incineration and, even more so by recycling and composting, 60 % of MSW in Spain ends up in landfills. Although waste incineration has increased, it has not been up to the degree of recycling and composting.

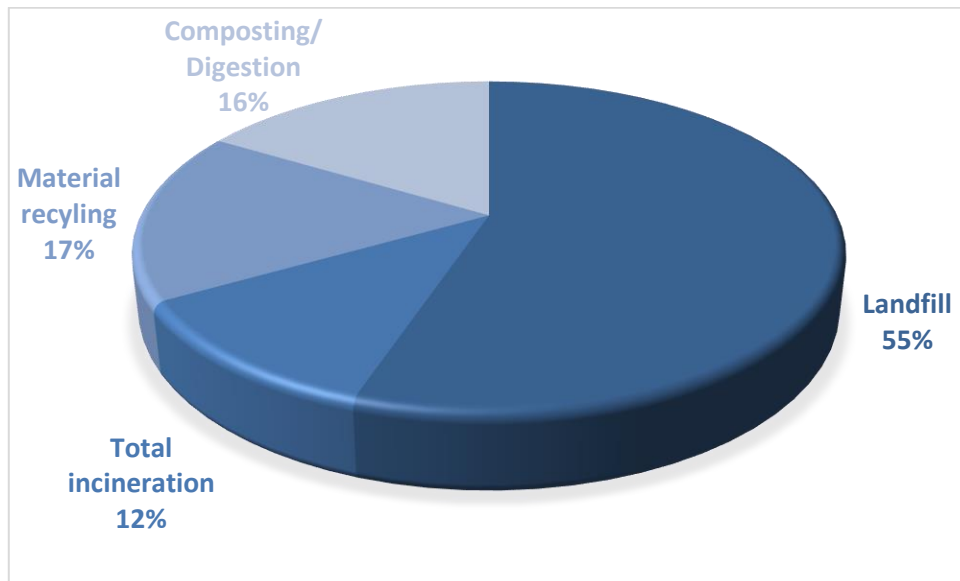


Figure 3. Final MSW destination in Spain (EUROSTAT, 2016).

1.2. INCINERATION

Incineration appeared in the late 19th century as a revolutionary way of waste elimination due to mass, volume, and hazard reduction (Margallo, 2014). Waste incineration is the oxidation of the combustible materials contained in waste. MSW is generally a highly heterogeneous material, consisting essentially of organic substances, minerals, metals and water. During incineration, flue gases that contain the majority of the available fuel energy as heat are generated (BREF, 2011).

Incineration is a thermal process which operates with excess air (primary and secondary air) to ensure that complete waste burnout is achieved. Incineration is used as a treatment for a very wide range of wastes like MSW, hazardous wastes, sewage sludge or clinical wastes.

The main advantages of using incineration as a waste management method are i) the reduction of waste volume (between 80 – 95 %) (Rand et al., 2000), with the consequent reduction in the need for land and landfill ii) the electricity and heat generated can be used in the nearby buildings (Fu et al., 2015) and the ash produced can be used by the construction industry (Margallo et al., 2015) iii) incineration eliminates the problem of the leachate produced in landfills.

On the other hand, there are some disadvantages. Incineration facilities are expensive to build, operate, and maintain. Moreover, smoke and ash emitted by the chimneys of incinerators include acid gases, nitrogen oxides, heavy metals, particulates, and toxic pollutants such as dioxins and furans (Rand et al., 2000).

The incineration process is divided into three main parts: incineration, energy recovery and air pollution treatment. The basic linear structure of a waste incineration plant, which can be seen in Figure 4, may include the following operations (BREF, 2011):

- ✓ Incoming waste reception
- ✓ Storage of waste and raw materials
- ✓ Pretreatment of waste
- ✓ Loading of waste into the process
- ✓ Thermal treatment of the waste
- ✓ Energy recovery and conversion
- ✓ Flue-gas cleaning
- ✓ Flue-gas cleaning residue management
- ✓ Flue-gas discharge
- ✓ Emissions monitoring and control
- ✓ Waste water control and treatment
- ✓ Ash management and treatment

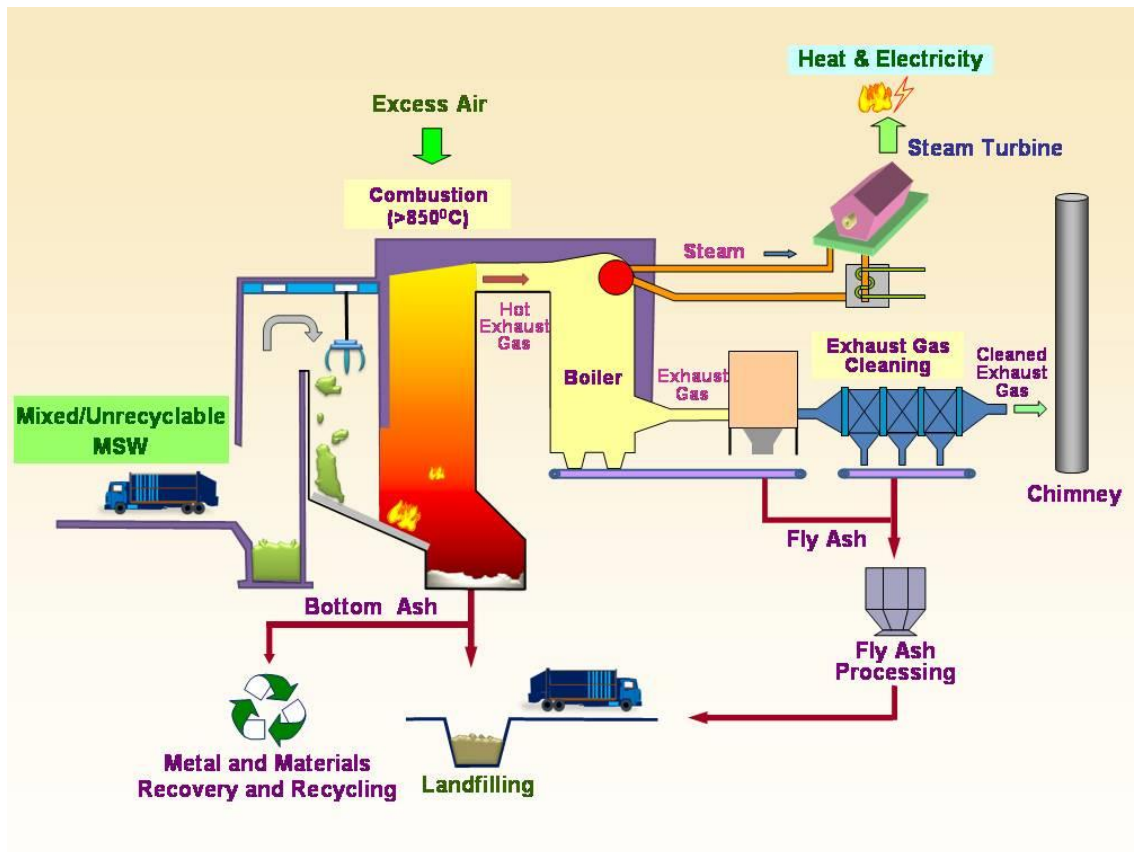


Figure 4. Flowsheet of a waste incineration plant (EPD, 2015).

The thermal treatment technologies applied to the waste are:

- ✓ Grate
- ✓ Rotary kiln
- ✓ Fluidised bed
- ✓ Pyrolysis
- ✓ Gasification

Gasification and pyrolysis are rarely applied to the treatment of MSW (Margallo, 2014). The main ones are moving grate, fixed grate, rotary kiln and fluidised bed.

MOVING GRATE

The waste is slowly propelled through the combustion chamber (furnace) by mechanically actuated grate. Waste continuously enters one end of the furnace and ash is continuously discharged at the other. Process conditions are

controlled to ensure complete combustion of the feed. At the end of the grate the hot ash is quenched to rapidly cool the remaining non-combustibles (DEFRA, 2013).

FIXED GRATE

These are typically a series of three steps with the waste being moved by a series of rams. The first step is a drying stage and the initial combustion phase, the second is where the remaining combustion takes place and the third grate is for the final carbon burn-out (DEFRA, 2013).

ROTARY KILN

Rotary kilns can be a complete rotational vessel or a partial rotational type. Incineration in a rotary kiln is normally a two-stage process consisting of a kiln and a separate secondary combustion chamber. The kiln is the primary combustion chamber. The rotation moves the waste through the kiln with a tumbling action which exposes the waste to heat and oxygen (DEFRA, 2013).

FLUIDISED BED

The use of this technique involves pre-sorting of MSW to remove heavy and inert objects, such as metals, prior to processing in the furnace. The waste is then mechanically processed to reduce the particle size. The combustion is normally a single stage process and consists of a lined chamber with a granular bubbling bed of an inert material such as coarse sand/silica or similar bed medium.

The bed is 'fluidised' by air (which may be diluted with recycled flue gas) being blown vertically through the material at a high flow rate (DEFRA, 2013). Wastes are mobilised by the action of this fluidised bed of particles.

1.3. TREATMENT OF THE WASTE GENERATED IN INCINERATION PROCESSES

The composition of MSW depends on countries, their economic development, lifestyle and recycling processes. Thus, the characterization of waste incineration varies with the feed. Solid and liquid residual materials as well as gaseous effluents are obtained as a result of incineration.

The typical residues of MSW incineration are the following (Sabbas et al., 2003):

- **Bottom ash (BA)** is the combination of non-combustible material with partially burnt organic matter.
- **Boiler and economizer ash** is composed of fine particles which are obtained from the energy recovery boiler.
- **Fly ash (FA)** is the solid residue that still accompanies the flue gases after the heat recovery systems.
- **Air pollution control (APC)** residues comprise waste from systems used to treat acid gases or micro-organic contaminants before being emitted into the atmosphere.

1.3.1. Bottom ash treatment

BA is the main residual material obtained in the combustion chamber and consists of the non-combustible components and partially burnt organic matter of the waste feed. BA usually represents around 20 – 30 % of the original waste feed by weight, and only about 10 % by volume (DEFRA, 2013).

BA has high contents in heavy metals (mainly Cd, Pb, Zn), organohalogen compounds (mainly dioxins and furans) and soluble salts (mainly chlorides).

The reuse or final disposal of BA in landfills is restricted by the potential release of contaminants into the environment. In order to extract the valuable metals, BA is treated. The ferrous and non-ferrous metals recovery

rate depends on waste composition and technology used (CEWEP, 2016). The available BA treatment methods include physical separation technologies such as sieves and magnets to extract ferrous metals from the ash. BA is then sorted in portions based on their size (CEWEP, 2016). Finally, eddy current separators are used to obtain various non-ferrous metals (Allegrini et al., 2014). This technique recovers non-ferrous metals such as aluminium according to their reaction to changing magnetic fields.

Stable BA possesses qualities to be later used. Road or construction sectors are of significant interest with respect to utilization of residues from BA treatments and adsorbent for dyes (Birgisdottir et al., 2007). For example, BA is used to replace sand and clay in concrete production (Ferreira et al., 2003).

1.3.2. Conventional fly ash treatment

FA is fine particles composed of heavy metals that might leach under certain conditions (Ferreira et al., 2003). Moreover, FA contains a high concentration of chlorides (Margallo et al., 2015).

In order to reduce the environmental impact, different kinds of treatments are used by developed countries. They can be classified as:

- ✓ Separation processes
- ✓ Solidification/Stabilisation
- ✓ Thermal treatments

Depending on the objectives of the treatment (to ensure landfilling in non-hazardous landfills or to improve the chances of further valorisation), the steps taken are different.

Separation processes aim at removing the highly polluting species from the residue, reducing the problems arising from its deposition. This can be

applied as a stage of preparation of the ashes for inclusion in other products.

– Washing

This treatment reduces chlorides, soluble salts, alkalis (oxides, hydroxides and carbonates of alkali metals) and heavy metals in FA or BA by using a liquid solution, generally water or acid (Margallo et al., 2015).

– Leaching

This process aims at extracting heavy metals from ashes by means of an extraction solution. Leaching of heavy metals depends on the type of extraction solvent and the L/S ratio (liquid/solid ratio) (Margallo et al., 2015). Moreover, studies show the influence of pH on leaching (Dijkstra et al., 2006). An increase in the pH of the leachate will reduce the leachability of heavy metals as insoluble hydroxides are created (Youcai et al., 2002).

– Electrochemical processes

Their main objective is to remove heavy metals and further recover them. They involve reduction/oxidation reactions of the metals on the surface of the cathode and anode, induced by a potential difference between the electrodes. The residues to be treated are characterised by the presence of specific substances called reducing agents and placed inside the electrolytic cell (Ferreira et al., 2005).

Stabilisation / Solidification is the most commonly used treatment. The process in which hazardous components of solid waste are immobilised in a solid matrix. That is, they are physically absorbed, encapsulated or a change in the physicochemical form of the pollutant components occurs.

The main mechanisms are precipitation, adsorption, macroencapsulation, microencapsulation and/or detoxification (Margallo et al., 2015).

- Solidification

It is a chemical treatment process that aims at immobilizing the waste within a solid cementitious matrix (Pollard et al., 1991).

- Chemical stabilisation

This process transforms the heavy metals in FA into naturally stabilised chemical forms, such as sulphides (Youcai et al., 2002). Different chemical agents are used like oxidizers, reducers, adsorbents or precipitation reagents.

On the other hand, the objective of the **thermal treatments** of FA is to reduce their volume, creating a more homogeneous, denser product, more resistant to leaching and more stable (Margallo et al., 2015). They are the only treatments able to eliminate dioxins (Aguiar del Toro et al., 2009).

- Vitrification

Vitrification of heavy metals in the FA at a high temperature is not cost-effective for a small-scale incinerator (Youcai et al., 2002).

FA is melted with the proper amount of glass-forming additives, inert glasses are produced and dioxins are completely destroyed. Moreover, heavy metals are also stabilised through their incorporation into the glass matrix (Jun Park et al., 2002).

- Sintering

It produces glasses and glass-ceramics from FA. Sintering involves heating the residues to a point where particles joints take place and chemical phases in the residues reorganise (Zacco et al., 2014).

There are some applications to give new uses to FA. These are classified as construction materials, geotechnical applications, “agriculture” (soil amendment) and others (Ferreira et al., 2003).

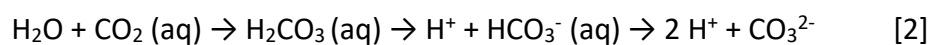
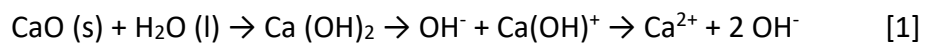
1.3.3. Fly ash carbonation

Accelerated carbonation improves the chemical properties of alkaline waste and allows it to be used for new industrial purposes, so it is an alternative to conventional FA treatments.

Heavy metals cannot be removed, but they can be separated and/or stabilised within other matrices. The main effect of carbonation is the encapsulation of certain mobile metals under alkaline conditions, which facilitates their reuse or deposition in non-special landfills (Grandia et al., 2011).

Carbonation involves the dissolution of CO₂ in water at initially alkaline conditions. This causes a decrease in the pH of the leachate and calcite to precipitate until the material is in equilibrium with CO₂, because of the change in the solubility of the metals (Rendek et al., 2006). Carbonation does not affect the mobility of chlorides.

The carbonation mechanism is often described as at least a two-step process including a prior CO₂ absorption in water, followed by the carbonation reaction in aqueous medium (Rendek et al., 2006). The main reactions are:



The formation of calcite (CaCO₃) induces an increase in the sample mass. On the other hand, water is required for the carbonation reaction to proceed, but too much water hinders the diffusion of CO₂ into the pores of the solid. The water in the pores hydrates and dissolves the CO₂ and the Ca²⁺ ions from the solid phase so that they can react to form calcium carbonate (Wang et al., 2010).

In conclusion, the carbonation reaction depends on three factors: dissolution of CO₂ in the liquid phase, mobilization of Ca from the mineral surface, and precipitation of the carbonated solids (Mayoral et al., 2013).

There are two types of carbonation reactions: direct routes in which the mineral is carbonated in one step or indirect routes in which the reactive components are first extracted from the mineral matrix and then carbonated in a separate step.

Direct carbonation of a mineral can be conducted by two routes: as a direct dry gas-solid reaction or in an aqueous solution. The aqueous route is the most suitable option for mineral carbonation. Process parameters can be optimised and acceptable kinetics can be achieved (Tamilselvi et al., 2016).

1.4. APPLICATION OF LIFE CYCLE ASSESSMENT

The life cycle assessment (LCA) of products, activities and industrial processes makes up an important tool for assessing their environmental impacts.

The main advantage of using LCA is that it provides an overview of the effects of a particular product, activity or process in order to determine the optimal strategies regarding their configuration (Curran, 2016).

LCA quantifies the environmental impacts throughout the life cycle of a product from the extraction of raw materials, to final disposal (cradle-to-grave) (AENOR, 2006a).

The International Organization for Standardization (ISO) provides an international reference with respect to principles, framework, and terminology for reporting LCA studies. Using the UNE – EN ISO 14044 (AENOR, 2006b), life cycle assessment is performed in four phases (Figure 5):

1. Goal and scope definition. This stage defines the subject of study, the functional unit and the system boundaries.

2. Life cycle inventory (LCI) analysis. The inventory includes the compilation and quantification of mass and energy inputs and outputs.
3. Life cycle impact assessment. The goal of this step is to understand and evaluate the potential environmental impacts from the LCI results. For each impact category, a life cycle impact category indicator is selected and the category indicator result (indicator result) is calculated.
4. Interpretation of results. Conclusions, recommendations and decisions can be made.

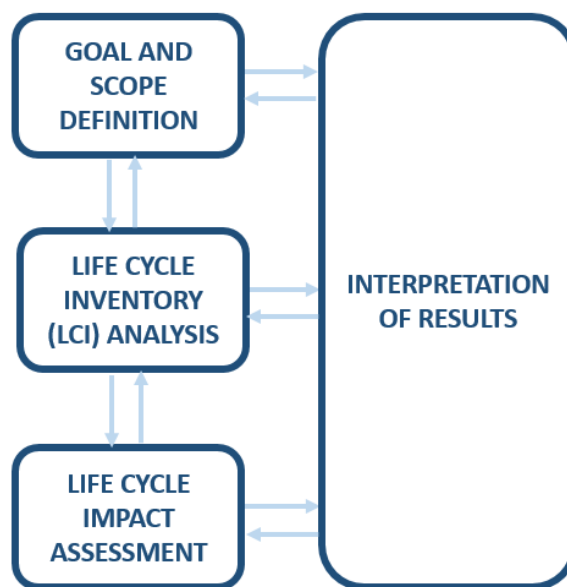


Figure 5. Steps of life cycle assessment (LCA).

In the last years, LCA has been increasingly used in MSW management to identify optimal strategies.

There is a wide variety of studies about incineration and the treatment of the waste it generates. A significant increase in the publications related to this field has occurred since 2009 (Laurent et al., 2014a). Most LCAs of solid waste management systems are developed in Europe, largely driven by Italy (Blengini et al., 2008; Cherubini et al., 2008), Spain (Muñoz et al., 2004; Rodríguez et al., 2003), Sweden (Bernstad et al., 2011; Björklund et al., 2007) and Denmark (Andersen et al., 2012; Birgisdottir et al., 2007). The United States and China

have fewer published researches compared to their population size (Laurent et al., 2014b).

LCA is applied to compare the different types of MSW treatments: biological (composting, anaerobic digestion), thermal (incineration, pyrolysis, gasification), landfilling and recycling (Denison, 1996; Mendes et al., 204; Finnveden et al., 2000; Arena et al., 2003; Banar et al., 2009).

Moreover, LCA has been successfully applied to assess conventional and new processes that deal with the waste ash produced in incineration processes. Several routes have been analysed like magnetic separation (Allegrini et al., 2014), cement and concrete production (Huntzinger et al., 2009; Chen et al., 2010) or road construction (Geng et al., 2010).

1.5. OBJECTIVES

The principal goal of this study is to compare the environmental performance of two alternative FA treatment processes: stabilisation and carbonation. The following impact categories are compared: global warming potential (GWP), abiotic depletion, ecotoxicity and freshwater consumption. To accomplish the general aim of this project the following specific objectives were addressed:

- ✓ Development of the environmental sustainability assessment methodology: definition of the system boundaries, the functional unit and the allocation procedure.
- ✓ Collection of all the inputs – raw materials, water, energy – and outputs – products, emissions, residues – of these processes.
- ✓ Life cycle modelling of the FA carbonation and stabilisation process using the LCA software Gabi 6.
- ✓ Life cycle impact assessment of the treatments under study and results interpretation.

2. METHODOLOGY

2.1. GOAL AND SCOPE DEFINITION

The LCA methodology has been applied to develop a model to assess FA carbonation and stabilisation processes. The functional unit (FU) is the quantitative reference that relates the inputs and outputs of the process under study (AENOR, 2006a). The FU selected was 4,655 tons of FA generated in Cantabria during 2014 (GOBCANT, 2016). Commonly, the FU is related to products (the system's outputs) (Laurent et al., 2014b); however, the function of a waste management system is to provide a service instead of a product: to deal with the waste of a specific area (White et al., 1997). Therefore, the waste input from certain geographical area (in this case Cantabria), which will be constant, can be a suitable FU.

The system is composed of MSW incineration and FA treatment. MSW incineration is identical in both scenarios so the associated impacts are the same and can be neglected in a comparative analysis. Both analysed scenarios can be seen in Figure 6.

Scenario A: FA carbonation. The FA carbonation includes the combustion of natural gas and the carbonation process. The combustion of natural gas has two functions: to generate natural gas and to produce energy. It is necessary to take into account that the environmental burdens are associated with both functions. The environmental impacts related to the energy production should be subtracted in order to compare both scenarios. It is explained in more detail in the next section.

Scenario B: FA stabilisation. The FA stabilisation includes only the solidification process. It employs a mixture of water (23.08 %), cement (17.75 %), and ashes (59.17 %).

Both scenarios include the previous processes necessary for the extraction and refurbishment of raw materials.

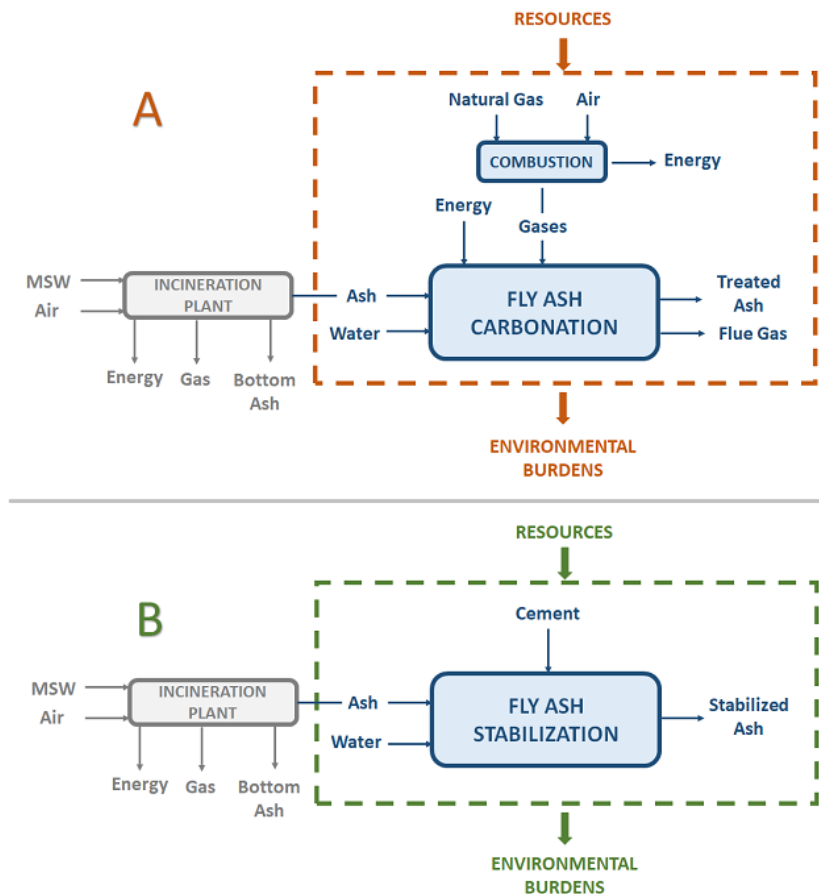


Figure 6. Flowsheet of A) FA carbonation and B) FA stabilisation.

2.1.1. Allocation procedure and methodological approach

Most industrial systems are multifunctional systems, that is, they comprise processes in which several interesting products and co-products or services are generated. According to the LCA methodology, allocating the environmental burdens of a system between its multiple functions should be avoided by i) dividing the unit process into two or more sub-processes (which cannot be applied to this case study) or ii) expanding the system to include the additional functions related to the co-products (AENOR, 2006b).

This last method, which was applied to the FA carbonation scenario, subtracts the environmental impacts of the secondary function of the system from the overall environmental impacts of the system (Thomassen et al., 2008). The combustion process of natural gas is considered a part of

the life cycle of the FA carbonation. Thus, the environmental impacts related to the generated electricity (the secondary function of the system) are subtracted from the system, as shown in Figure 7. This allows to compare the environmental impacts of FA carbonation and FA stabilisation.



Figure 7. Allocation procedure of the FA carbonation process between the system functions.

A strong connection exists between the selected LCA approach and the choice of how to treat co-products (Thomassen et al., 2008). There are two LCA approaches: attributional LCA (ALCA) and consequential LCA (CLCA). ALCA describes physical (pollution and resource) flows within a chosen system (Thomassen et al., 2008). ALCA assumes that the analysed system does not affect its environment (Bala Gala et al., 2015). CLCA calculates how physical flows within a system under study change in response to a change in the output, that is, CLCA assumes that this variation has effects on the background system (Thomassen et al., 2008; Bala Gala et al., 2015).

Since the combustion of natural gas can be coupled to a turbine that generates electricity, it is assumed that the generated electricity substitutes the same amount of electricity from the Spanish grid mix (average value). This way, the environmental burdens associated with the average Spanish generation of that electricity are avoided. This procedure falls within the description of an attributional approach.

If the source of the replaced electric energy and the details about the purchase were known exactly, the applied approach would be CLCA.

3. RESULTS AND DISCUSSION

3.1. LIFE CYCLE INVENTORY

In the LCI all the relevant inputs and outputs of the processes are collected. The data used for both process were calculated regarding the FU. The information about FA carbonation was based on UC (2015b). As for FA stabilisation, the data reported by Biellen et al., (2014) was used.

The LCI has been calculated for different pressures and excess of CO₂ in the flue gas with respect to the CO₂ that reacted in the experimental set-up described by UC (2015a).

$$F_{\text{CO}_2} = r V_L = K_L (C_e - C) V_L \quad [4]$$

$$C_e = K_H P Y_L \quad [5]$$

As a continuous stirred tank reactor is assumed, the reaction rate is calculated for the output conditions, so to calculate the CO₂ equilibrium concentration (according to Henry's Law (Eq. 5)). It is necessary to know the molar fraction of CO₂ in the gas phase at the output of the reactor. If the equilibrium concentration were equal to zero, the reaction rate would be zero too. So, an excess of CO₂ allows increasing the reaction rate in the perfect mixing reactor. Furthermore, in accordance with Henry's Law (Eq. 5), the total pressure will establish the equilibrium concentration, therefore the reactor volume will be known (Eq. 4). Because of this, the following scenarios were studied: 10 %, 55 % and 100 % excess of CO₂ in the flue gas at the outlet of the reactor, and pressures of 1, 5, 10, 15 and 20 bar, in order to determine the reactor dimensions that would be required for each scenario. The reactor dimensions (assuming equal height and diameter) are shown in Figure 8 for each scenario.

Figure 8 shows that for the 55 % and 100 % CO₂ excess, a similar diameter (and height) is obtained, while for the 10 % excess, the dimensions are noticeably

higher. The plot highlights that the higher pressure, the less reactor volume is necessary and, therefore, the required diameter (and height) is smaller. This gradient is particularly high for pressures below 5 bar. Thus, the LCA was performed for a pressure range between 1 and 5 bar, and a CO₂ excess of 55 and 100 %, in order to understand the trade-off between these variables.

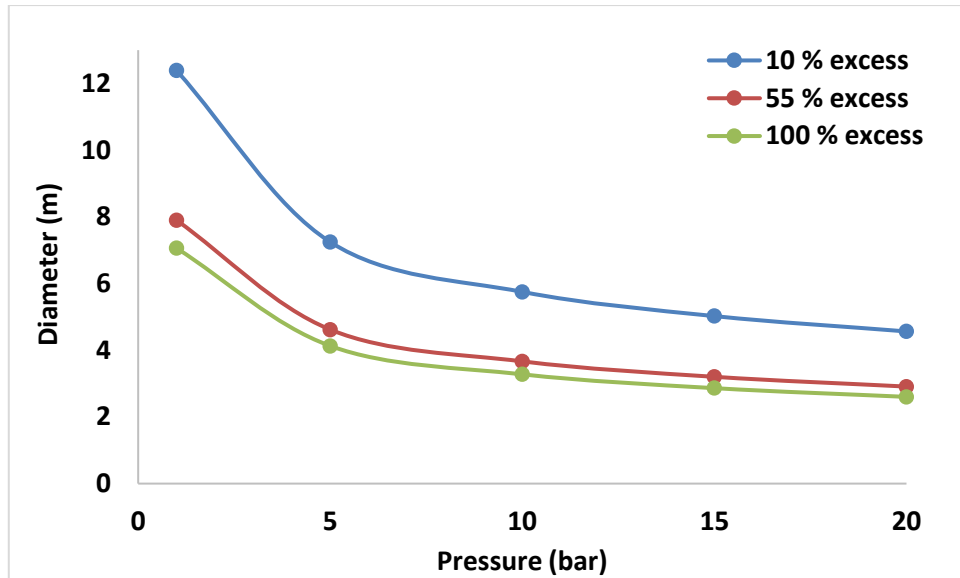


Figure 8. Variation of diameter of the reactor with pressure and composition of flue gas.

The inventory data of both processes are available in Table 1 and Table 2. Moreover, the calculations and details are provided in Annex 2.

Additionally, secondary data were taken from other databases such as PE International or IPCC (PE International, 2017; IPCC, 2006).

Table 1. Inputs and outputs of FA carbonation (5 bar / 55 % excess of CO₂ in the flue gas).

INPUTS	FLY ASH	4,655	ton / year	GOBCANT, 2016
	ENERGY			
	Compression	0.10515	kWh / kg flue gas	Calculations
	Stirring	1.306 · 10 ⁵	kWh / year	Calculations
	NATURAL GAS	1121.089	ton / year	Calculations
	WATER	27,930,000	L / year	Calculations
OUTPUTS	TREATED ASH	32,585	ton / year	Calculations
	FLUE GAS	20,452.964	ton / year	Calculations

Table 2. Inputs and outputs of FA stabilisation.

INPUTS	FLY ASH	4,655	ton / year	GOBCANT, 2016
	CEMENT	1,396.5	ton / year	Biellen et al., 2014
	WATER	1,815,450	L / year	Biellen et al., 2014
OUTPUTS	STABILISED ASH	7,866.95	ton / year	Biellen et al., 2014

3.2. LIFE CYCLE IMPACT ASSESSMENT

The life cycle impact assessment was conducted with the LCA software GaBi 6 (PE International, 2017). The environmental impact categories (Table 3) used for this study are described below. These impact categories have been chosen because i) climate change is a pressing issue nowadays, ii) abiotic depletion potential and total freshwater consumption allow putting into perspective the scarcity of raw materials and water in order to minimise resource consumption, and iii) ecotoxicity takes into account the detrimental consequences of the processes on the ecosystem, which are the reason FA cannot be directly landfilled.

- To analyse air emissions, the GWP impact category proposed by Intergovernmental Panel on Climate Change (IPCC) is studied. GWP is a relative measure which is related to greenhouse gases emitted in the atmosphere. It is calculated as the equivalent kg of CO₂ emitted.
- As for the consumption of natural resources, the abiotic depletion potential is used to describe the annual rate of depletion of the stock of minerals and fossil fuels relative to the final reserves. It is expressed as the equivalent kg of antimony consumed. Moreover, the total freshwater consumption represents the total water used by the processes.
- The ecotoxicity impact category provides information to quantify the effects of chemical emissions on fish, wildlife, plants, and other wild organisms. This factor is measured as Comparative Toxic Units (CTUe).

Table 3. Impact categories.

IMPACT CATEGORY	METHOD	UNIT
GWP	IPCC	kg CO ₂ – Equiv.
Abiotic Depletion Potential	CML2011	kg Sb – Equiv.
Total Freshwater Consumption	Swiss Ecotoxicity	kg water
Ecotoxicity	USEtox	CTUe

3.3. LIFE CYCLE INTERPRETATION

The environmental impact results were calculated following the ISO 14040 (AENOR, 2006a) procedure up to the characterisation step. Therefore, the results are not normalised.

Figure 9 shows the results of this LCA study of the FA carbonation for different pressures and the two studied scenarios: 55 % and 100 % excess of flue gas

(scenario I and II, respectively) for each selected impact category: i) GWP. Figure 9a shows the contribution of carbonation process to climate change. 100 % excess of flue gas displays the highest air impact due to the larger content of greenhouse gases (mainly CO₂) in this stream, ii) ABIOTIC DEPLETION (Figure 9b), iii) FRESHWATER CONSUMPTION (Figure 9c) and iv) ECOTOXICITY (Figure 9d): the comparison of scenarios displays an opposite situation to the above-mentioned impact category. Scenario II has a lower impact than scenario I in these environmental categories. In figure 9, each represented point reflects a different reactor volume. When the pressure increases, a higher equilibrium concentration is obtained and, therefore, the required reactor dimensions are smaller. Since the power of stirring depends on the agitator diameter (Annex 2), and this, in turn, is conditioned by the reactor diameter, which is raised to the fifth, as the flue gas pressure increases, less energy is required for agitation. The total energy of the process is equal to the sum of the energy required for compression and stirring, being the latter significantly higher than the former. As a consequence, the total energy consumption decreases as the pressure of the flue gas increases. Thus, the environmental impacts of the carbonation process decrease as the pressure increases.

Figure 10 illustrates the contribution, in terms of percentages, of the principal phases of the A) FA carbonation process (base case: 5 bar / 55 % excess of CO₂ in the flue gas) and B) FA stabilisation to each of the impact categories.

Regarding FA carbonation, Figure 10a indicates that, in general, the activities associated with energy generation contribute substantially to all the impact categories. Nevertheless, the consumption of water (process water: almost 70 %) is the main contributor to the environmental impact in the total freshwater consumption category.

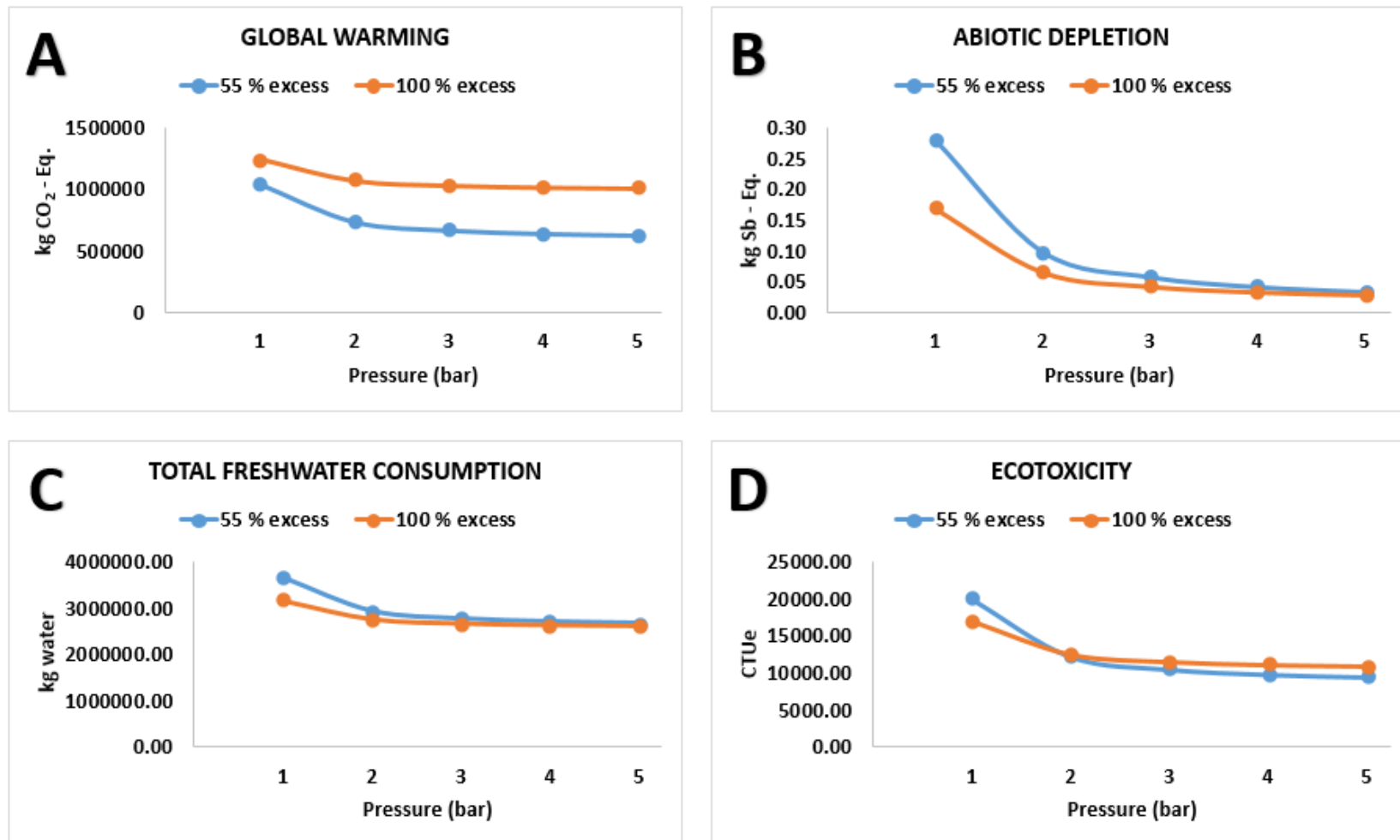


Figure 9. Results of all the impact categories A) GWP; B) abiotic depletion; C) total freshwater consumption; D) ecotoxicity for the carbonation process.

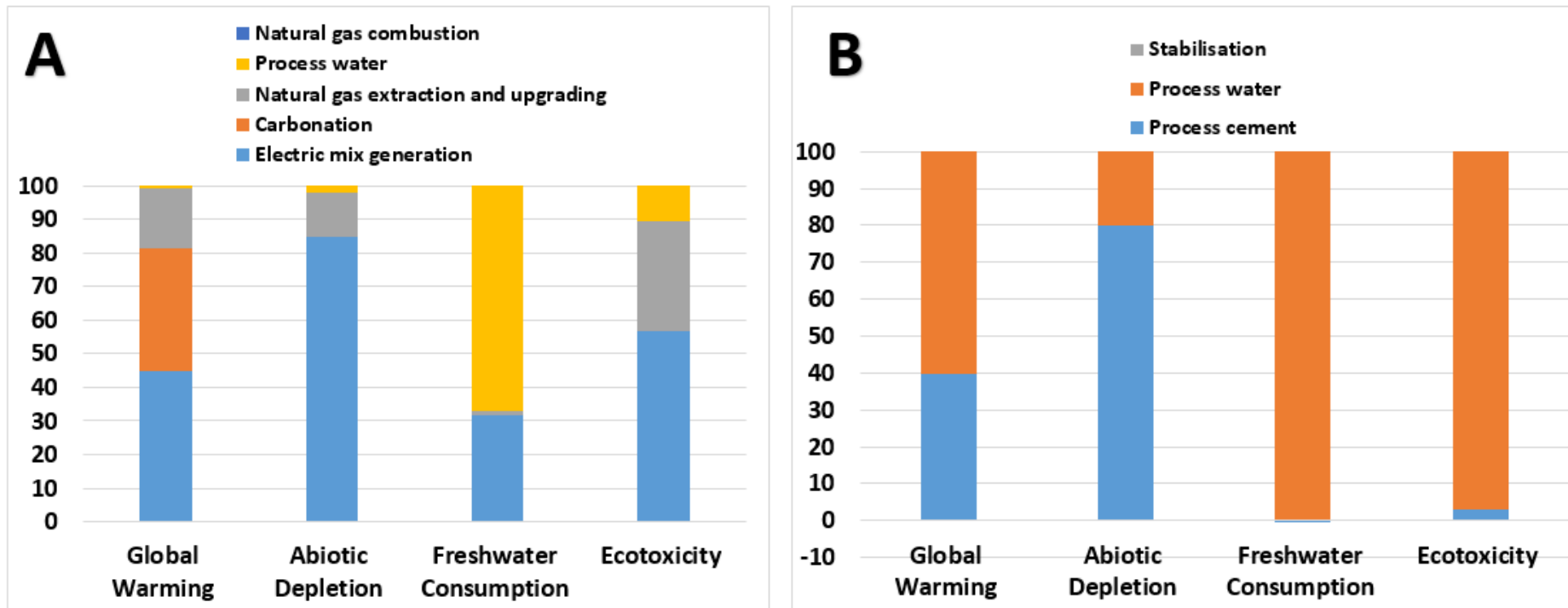


Figure 10. Analysis of the contribution the main stages of A) Carbonation (5 bar / 55 % excess of CO₂ in the flue gas) and B) Stabilisation to each of the impact categories.

The results show that not all the lifecycle stages contribute to all impact categories. That is, all steps contribute only in the GWP category. In particular, over 40 % of the GWP is due to the generation of electric energy. Similarly, this is also responsible for a large share of the abiotic depletion (over 80 %) and ecotoxicity (almost 60 %). Overall, the activity related to natural gas combustion makes the smallest contribution to GWP, it is even non-existent in the other categories. It is due to the fact that all the flue gas that is generated is used in the carbonation step and the related burden is considered in this step (not in the natural gas combustion).

Apart from that, as for Figure 10b, FA stabilisation has three stages (the stabilisation process, cement production and water treatment). What emerges from the results is that the main step of this process (“stabilisation”) does not participate in any of the impact categories, because it is assumed that the process is based solely on the mixing of the materials, and no energy is required. The lifecycle activity associated with the process water is dominant in terms of the contribution to the GWP (60 %) and the ecotoxicity (almost 98 %). The same can be stated about the total freshwater consumption, where negative consumption values were obtained in process cement (avoided burden), displaying only positive values for process water. The opposite case occurs in the abiotic depletion category. The process cement is responsible for nearly 80 % of the overall abiotic depletion indicator.

Figure 11 compares the results of this LCA study of the FA carbonation (base case) and FA stabilisation for each selected impact category. It can be clearly seen that the main way to treat FA (stabilisation) has higher impacts than the alternative technique (carbonation), due mainly to the reduction of lixiviation and CO₂ capture in the ash. Thus, the feasibility of this alternative, from an environmental point of view, is proven.

Apart from that, in Figure 12 two LCA approaches are depicted (attributitional LCA (ALCA) and consequential LCA (CLCA)) in order to assess the influence of the selected methodological approach. The main cause of the differences between

ALCA and CLCA is the fact that different systems are modelled. With the exception of GWP, the other impact categories are higher at CLCA than ALCA. It is due to the avoided burdens. As explained in section 2.1.1., in the ALCA, it is assumed that the generated electricity for the natural gas combustion replaces the same amount of electricity from the Spanish grid mix while, in the CLCA, the generated electricity from natural gas is avoided. In this case (CLCA), as the GWP of natural gas is higher and avoided, the GWP of the process will be lower.

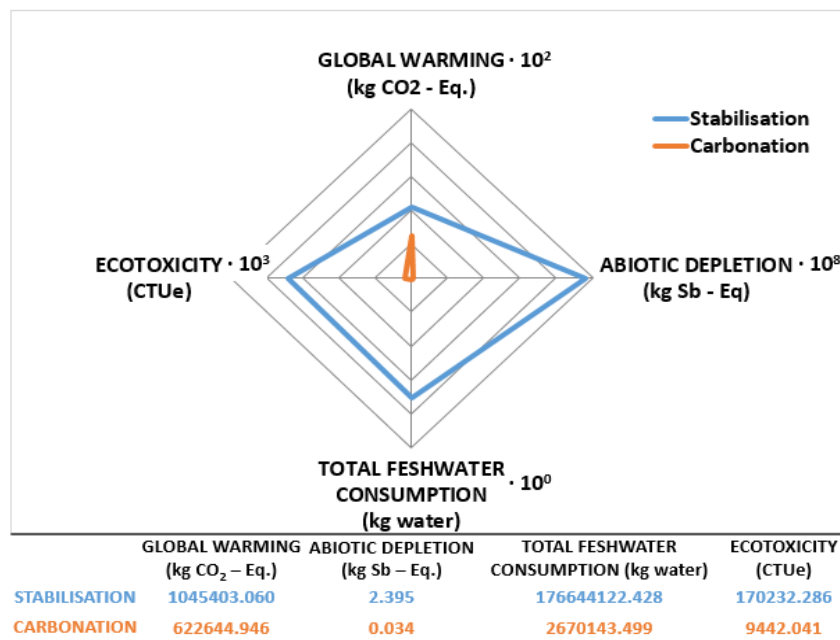


Figure 11. Comparison of environmental impacts between Scenario A: FA carbonation (5 bar / 55 % excess of CO₂ in the flue gas) and Scenario B: FA stabilisation.

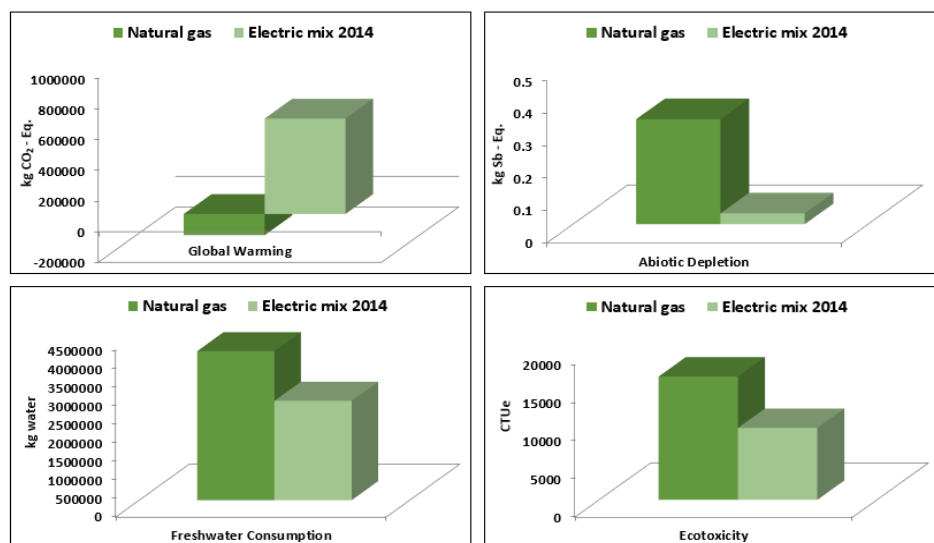


Figure 12. Comparison of environmental impacts between ALCA (Electric mix 2014) and CLCA (Natural gas) (5 bar / 55 % excess of CO₂ in the flue gas).

4. CONCLUSIONS

This final project deals with a quantitative environmental assessment of two treatments for the FA from MSW incineration (stabilisation and carbonation) in Cantabria (Spain). For this purpose, the LCA methodology was applied. The main goal of this report consists of an analysis of both the current stabilization treatment carried out by the majority of existing plants, and carbonation as an alternative process; however, FA carbonation (because of the natural gas combustion step) presents an additional function (energy production), which was solved by subtracting the extra process, generating avoided burdens. Also, the optimal operational conditions of carbonation (excess of CO₂ in the flue gas and pressure) have been studied.

The results of the analysis suggest that FA stabilisation is the least favourable treatment from an environmental point of view. The emergent technique of carbonation presents improvements in the chemical properties of FA and a new future use in the industry. Based on the obtained results, FA carbonation is presented as the best option from an environmental point of view because of the lower environmental impacts. This process allows reducing the riskiness of the waste and the discharge volume. Additionally, as for the avoided burdens, the FA carbonation process achieves to reduce the environmental impacts due to the fact that the generation of electricity from natural gas combustion can replace the required electricity in the process itself. Depending on the type of substituted electricity, the avoided burdens are different and, therefore, the impacts too.

Regarding the operational conditions, several pressures and CO₂ excesses were studied to evaluate the influence of them on the reactor dimensions. It can be concluded that on the one hand, the range of pressure between 3 and 4 bar, and on the other hand, 55 % excess of CO₂ in the flue gas provide an efficient result. As the results have revealed, for pressures higher than 3 bar, the environmental impacts decrease minimally, that is, there is not a significant difference among the choice of 3, 4 or 5 bar. So, this minimum pressure allows reducing the energy of compression. Furthermore, the choice of 55 % excess of CO₂ in the flue gas is due to the fact that

with this CO₂ excess and this range of pressures, less impacts are obtained in GWP and ecotoxicity while similar values are achieved in abiotic depletion and the total freshwater consumption. To sum up, this choice could not be the best option regarding the environmental impacts. Nevertheless, it allows achieving a balance between the environmental impacts, the total used energy and the adequate reactor volume.

This project aims at contributing to a future improvement of the present research with some ideas:

- Inclusion of economic evaluation metrics to provide the decision-making process in order to quantify another essential pillar of sustainable development.
- Taking into account the main responsible stages of the environmental impact, the resources extraction and preparation should be further studied in order to identify other more sustainable options (such as the source of electricity) or possible improvements (operating conditions, efficiency of the processes of water, natural gas extraction or electricity).
- It would be interesting to evaluate the drying process of the product from the reactor output (e.g., by plate and frame filter press) and the treatment of sewage. The current system could extend their system boundaries to include these new steps. If this scenario was studied, the current system (gate-to-gate) would become a gate-to-grave.
- As the landfill and the incineration plant are placed together in Cantabria, natural gas, which is used to generate CO₂, could be replaced with the combustion gases of the biogas generated at the landfill.
- The assessment of the life cycle environmental impacts of the FA carbonation reveals that the main variable contributing to the environmental burdens generated by the carbonation process is the energy consumption. As the main energetic consumption is due to stirring, and the energetic

consumption and agitator diameter follow an exponential relationship, putting several smaller reactors in parallel could be an alternative which should be studied in detail.

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ANNEX 1. REACTOR DIMENSIONS.

- Volume of water necessary to treat 1 ton of FA (UC, 2015b)

$$\frac{L}{S} \text{ Ratio} = 6 = \frac{\text{Water}}{0.1 \text{ kg}}$$

- Flow rate of CO₂

Table 4. Results of CO₂ captured for L/S = 6 (g CO₂ / 100 g FA) (UC, 2015b).

Sample	CO ₂ uptake (%)
SAMPLE 1	19.67
SAMPLE 2	14.92
SAMPLE 3	16.73
Average value = 17.107 %	

- Mass transfer coefficient

This coefficient was calculated from the experimental data of the UC (2015b).

Assuming a continuous stirred tank reactor:

$$F_{\text{CO}_2} = r V_L = K_L (C_e - C) V_L \quad [5]$$

$$C_e = K_H P Y_L \quad [6]$$

$$C_e = 0.03158 \text{ mol/L}$$

$$C = 0 (Y_L = 1)$$

$$F_{\text{CO}_2} = 7.198 \cdot 10^{-5} \frac{\text{mol}}{\text{s}}$$

$$K_L = \frac{F_{\text{CO}_2}}{C_e V_L} = 0.038 \text{ s}^{-1}$$

Table 5. Variation of dimensions of the reactor with pressure and composition of flue gas.

	Pressure (bar)	Reactor volume (m³)	Diameter = Height (m)
10 % EXCESS	1	1493.315	12.389
	5	298.663	7.245
	10	149.332	5.750
	15	99.554	5.023
	20	74.666	4.564
55 % EXCESS	1	387.030	7.899
	5	77.406	4.619
	10	38.703	3.666
	15	25.802	3.203
	20	19.352	2.910
100 % EXCESS	1	276.402	7.060
	5	55.280	4.129
	10	27.640	3.277
	15	18.427	2.863
	20	13.820	2.601

ANNEX 2. LIFE CYCLE INVENTORY.

· ENERGY OF STIRRING

$$\text{Re} = \frac{\rho D^2 N}{\mu} \quad [7]$$

$$\text{Re} = 1954305.002$$

$$\text{TURBULENT FLOW} \rightarrow P = b \rho N^3 D^5 \quad [8]$$

$$P = 18634.761 \text{ W}$$

$$\text{ENERGY} = 18.635 \text{ kW} \cdot 365 \text{ day} \cdot \frac{19.2 \text{ h}}{1 \text{ day}} = \mathbf{130592.401 \text{ kWh}}$$

Data

· $b \equiv$ Power number = 4

· Fluid properties. The fluid is a mixture of water and ash. It is assumed the same properties as water because the amount of ash can be neglected to calculate the Reynolds number.

- Density, $\rho = 1000 \text{ kg/m}^3$
- Viscosity, $\mu (T = 20 \text{ }^\circ\text{C}) = 0.001003 \text{ kg/m s}$

· $N \equiv$ Shaft speed = 45 rpm (UC, 2015b)

· $D \equiv$ Agitator diameter

Agitator diameter to vessel diameter ratio = 0.2 – 0.5 (McKetta, 1995).

The average value was used.

· **ENERGY OF COMPRESSION**

$$\text{Energy} = \sum_i \frac{Z_i \cdot R \cdot T}{M_i} \cdot \frac{\gamma_i}{\gamma_i - 1} \cdot \left[\left(\frac{p_2}{p_1} \right)^{\frac{\gamma_i - 1}{\gamma_i}} - 1 \right] \cdot \frac{1}{\eta_{is} \eta_m} \cdot X_i \quad [9]$$

E ≡ energy of compression

X_i ≡ molar fraction of component i

i ≡ CO₂, N₂, O₂, H₂O

Z_i ≡ compressibility factor of component

R ≡ universal gas constant (8.3145 J/(mole K))

T ≡ Temperature (473 K)

γ_i ≡ specific heat ratio of component

M_i ≡ molar mass of component (g/mole)

p₁ ≡ suction pressure (MPa)

p₂ ≡ discharge pressure (MPa)

η_{is} ≡ isentropic efficiency (80 %)

η_m ≡ mechanical efficiency (99 %)

Table 6. Variation of compression energy with pressure.

Discharge pressure (bar)	Energy (kWh / kg flue gas)
1	0.10500
2	0.10507
3	0.10509
4	0.10510
5	0.10515

ANNEX 3. ADDITIONAL PROCESSES.

· AMOUNT OF NATURAL GAS

From Eq. 4 and 5 (Henry's Law), CO₂, which is necessary to treat the FA, is known but it is necessary to calculate required natural gas to produce this amount of CO₂ since the next reaction.



Table 7. Composition of natural gas (Hammer et al., 2012).

Compound	Molar fraction
<u>Hydrocarbons</u>	
Methane	0.87
Ethane	0.08
Propane	0.055
n – Butane	0.01
Isobutane	0.005
n – Pentane	0.005
Isopentane	0.005
Hexane	0.005
Heptane	0.0005
<u>Nonhydrocarbons</u>	
Nitrogen	0.075
Carbon dioxide	0.15
Hydrogen sulphide	0.15
Helium	0.025

· EMISSION FACTORS FOR STATIONARY COMBUSTION IN THE ENERGY INDUSTRIES (kg of greenhouse gas per TJ on a Net Calorific Basis)

Table 8. Emission factors for combustion and net calorific basis of natural gas (EC –IPPC, 2006; PE International, 2017).

NATURAL GAS		
CO₂	CH₄	N₂O
56,100	1	0.1

NET CALORIFIC BASIS OF NATURAL GAS
44.9 MJ / kg