

Thermal Conversion Technologies for Solid Wastes: A New Way to Produce Sustainable Energy

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1. Introduction

The solid waste generation is an important environmental problem, because it grows at a rate that exceeds the ability of natural environment assimilation and the treatment capacity available. Nowadays we need to reduce the consumption of raw materials and to increase the rate of recovery and reuse of waste materials.

An essential component in many integrated solid waste management systems is thermal conversion. This kind of technology allow to obtained volume reduction and energy recovery. The energy produce by solid waste treatment contribute for the use of less fossil fuels and can help meet renewable energy targets, as a consequence of global warning problem, and contribute significantly to achieving Kyoto Protocol objectives.

As it is knowledge of the scientific community, the integrated solid waste treatment follows a hierarchic management strategy, which is sequential and obeys to some steps, in decreasing order of waste best destination (Puna, 2002).

In the nineties the waste management hierarchy usually was composed by: source reduction, recycling, waste combustion and landfilling. Nowadays waste management hierarchy is more complete because the use of chemical and biological treatments (aerobic and anaerobic). The development of a proper waste management system depends on the availability data on the characteristics of the waste stream, performance specifications for alternative technologies and cost information. (Tchobanoglous *et al.*, 1993). The United Kingston and United State of America often disregard waste incineration on future waste management systems, but other countries like Switzerland, Japan and Denmark incinerate more than 65% of municipal solid waste (Damgaard *et al.*, 2007). There are advantages and disadvantages with all treatment options.

As mentioned before, the wastes have to be submitted to one or more waste solid treatment methods and technologies. These treatment methods actually available and suitable to treat those solid wastes are classified attempting to their dangerousness (no dangerous and dangerous wastes) (Puna, 2002).

2. Fundamentals of thermal processing

Thermal processing of solid waste can be defined as the conversion of wastes into gaseous, liquid and solid production, with or without energy valorisation (Tchobanoglous *et al.*, 1993).

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<p><u>No dangerous wastes:</u> Physical and Chemical treatments Biological treatments:</p> <ul style="list-style-type: none"> • Aerobic Digestion; • Anaerobic Digestion. <p>Thermal treatments with energetic valorisation:</p> <ul style="list-style-type: none"> • Incineration. 	<p><u>Dangerous wastes:</u> Physical and Chemical treatments Biological treatments Thermal methods with energetic valorisation:</p> <ul style="list-style-type: none"> • Incineration; • Co-incineration in cement furnaces; • Pyrolysis by plasma with vitrification.
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The mains objectives in the thermal treatment process of solid waste are the follows (Oliveira, 2005):

- Destruction of the organic components of wastes, specially the dangerous ones;
- Reducing their volume;
- Obtain solid and/or gaseous inert products;
- Achieve a significant energetic valorisation.

On the contrary of biologic, physical and chemical technologies, the destruction of dangerous contaminators by heat is much less dependent of the waste specificity. While the chemical and biological processes needs, for each kind of waste, particular operating conditions (contact time, atmosphere regulation where the reaction occurs, suitable reactants, etc.), in thermal treatment methods, its sufficient guarantee that certain temperatures are achieved in a minimum gap time, in order to consider that all initial organic molecules will be destroyed (Higgins, 1989).

For the heavy metals, the situation is more complex, because these substances, when they enter in the solid wastes, they will out in a natural way on the liquid and gaseous effluents, with the considerable risk that some of them can be volatilize during process and causing severe environmental impacts.

The thermal methods are a final solution for most of dangerous and no dangerous solid wastes, when isn't possible treat them by biological, physical and chemical techniques. However, the thermal methods are an important component in many solid waste integrated systems.

The more important thermal methods that have been used for the recovery of usable conversion products are: combustion, gasification and pyrolysis (Table 1) (Peavy *et al.*, 1985; Tchobanoglous *et al.*, 1993).

Process	Conversion product	Pre-processing
Combustion (Incineration)	Energy in the form of steam or electricity	None in mass-fired incinerator
Gasification	Low-energy gas	Separation of the organic fraction, particle size reduction, preparation of fuel cubes or other RDF
Pyrolysis	Medium-energy gas, liquid fuel, solid fuel	Separation of the organic fraction, particle size reduction, preparation of fuel cubes or other RDF

Table 1. Thermal process for the solid waste treatment (adopted of Peavy *et al.*, 1985).

The first one is an exothermic process, which means, its release spontaneously, significant energy to the process become autonomous and, also, to export energy in heat, or, most important, in electric energy. On the contrary, the gasification and pyrolysis processes are endothermic, which means, it's necessary to supply thermal energy to perform the pyrolysis reactions.

In order to judge the efficiency levels of thermal treatment techniques, normally, its employ some treatment parameters, described as follows (Russo, 2005).

DRE-Destruction and Removal Efficiency: Represents a measure of destruction and removal efficiency for a specific or a whole of specific dangerous substances, present in the solid wastes:

$$DRE = \frac{m_e - m_s}{m_e} \times 100\% \quad (1)$$

where:

m_e - contaminant mass at the incinerator inlet;

m_s - contaminant mass in the combustion gases at the incinerator outlet.

A value of 99.99% in the DRE meaning that, in maximum, only 0,0001. m_s can persist in the process combustion and flows through the combustion gases, after treatment. By another hand, a higher value of DRE doesn't meaning necessarily the elimination of a specific dangerous compound. On the contrary, it means that exists in very small concentrations on the combustion gases.

Burning index: In a waste containing several organic substances, its necessary settle which are the main dangerous organic compounds, the POHC (principal organic hazardous compound). To establish a DRE of 99.99%, its extremely important identify in each complex matrice waste, which is its POHC. With the efficient destruction of that compound, it's easy to achieve the optimal conditions to assure the elimination of the others chemical products, also dangerous. A suitable criteria for POHC determination is the burning index (I), defined as follows:

$$I = C + \left(\frac{a}{H}\right) \quad (2)$$

where:

C - concentration of each organic chemical substance in the waste;

a - constant with the value of 100 kcal/g;

H - combustion specific heat (kcal/g).

A higher value of index I for a specific compound indicates a great difficulty in their elimination, through incineration. So, bigger concentrations or small combustion specific heats are indicators of significant difficulties in the dangerous compounds elimination. These whole of criteria allows to estimate if will occur problems in the destruction of POHC.

DE -Destruction Efficiency: This parameter is more representative of elimination and removal efficiency process and, it's quantified by the following equation:

$$DE = \frac{m_e - m_s}{m_e} \times 100\% \quad (3)$$

where:

m_e – contaminant mass at incinerator inlet;

m_s – sum of all products masses formed in the combustion gases (ashes, combustion gases, slag's and products that remains in the washing systems and filters), produced by that contaminant.

An important aspect related with these parameters it's the possibility to know, in advance, which are the minimum temperatures and compositions atmospheres to achieve a minimum DE of 99.99% or 99.9999% in the presence of dioxins and furan's, identified as POHC.

3. Combustion treatment technologies for solid wastes

3.1 Incineration

The incineration consists in mass combustion technique of solid wastes, which are admitted to an incineration furnace. Inside the furnace occur the combustion of organic wastes including the dangerous ones with air excess to promote mixing and turbulence, in order to ensure a safety and completely burn of those substances. As co-products of this process, occurs the formation of ashes and solid slag's. The first ones are completely inertized in cement matrices for succeeding compactation in landfills and, the second ones, are valorised, separating the metals from the inerts. The metals are recycled to the recycling industry and the inerts are normally used on civil construction, such as road flooring, landfills covering, etc. (Puna, 2005). There are two incineration processes, regarded with energetic valorisation. As a great advantage of this process, it's possible to produce large quantity of electric energy, and therefore, it makes profitable this process, becoming autonomous and supplier of electricity.

It is important refer the control of main process variables of furnace incinerator, like, temperature, waste time residence on furnace, qualitative and quantitative analysis of solid wastes in admittance. Besides, the incineration and co-incineration processes are very restrictive in the admittance of several dangerous solid wastes, due to the legal limit values of gases that are produced in the incineration furnace and emitted to the atmosphere, which they are severally rigid, like, Dioxins, Furans, PCB's and Heavy Metals (Brunner, 1994).

Basically, the incineration furnace is a combustion chamber where, the solid wastes chemical elements (carbon, hydrogen and, if exists also in the wastes, sulphur) are burned to produced combustion gases, especially CO, CO₂, H₂O, NO_x and, if it is the case, SO₂. With fewer proportions, it's produced, also, acid gases like HCl and HF and, last but not least, heavy metals and macromolecules with high stability and higher molecular weight (Dioxins, Furan's and PCB's) (Freeman, 1988). The main elementary reactions of solid wastes in the combustion process at the incinerator are the follow ones:



The dedicated incineration works like an appropriate industrial infra-structure, which uses, to operate the incineration furnace, a secondary fuel, like natural gas, propane or fuel oil to improve and maintain the combustion of solid wastes. However, the main source of fuel is the solid wastes due to its higher specific heat. It's estimated that, the solid wastes can substitute the use of secondary fuel until a percentage of utilisation about 40-50% (Formosinho *et. al.*, 2000).

The rate of organic molecules destruction depends of the high temperature inside in the furnace and the time residence of gases combustion in the incinerator. Normally, a temperature higher than 900 °C and, a time residence between 2 and 5 seconds, with an

excess of air (oxygen) higher than 6% is sufficient to ensure the destruction of all organic molecules.

The figure 1 shows a *flow-sheet* of municipal solid waste dedicated incineration process. Valorsul is an integrated urban solid waste system, which include a incinerator, in order to burn urban solid wastes. This incinerator is located in Loures, near Lisbon, Portugal and, it operates since 1994 (Puna, 2002).

In the incineration of dangerous solid wastes with more than 1% of halogen organic compounds in their composition, expressed in chlorine, the temperature in the incinerator has to achieve 1100°C and the residence time of combustion gases must be, at minimum, 2 seconds (Brunner, 1994; European Legislation, 1994). The main final products in the incineration process are, the combustion gases. The appearance of CO in the combustion gases results from the inefficient burning of solid wastes with, most probably, a less air excess. To ensure the reduction of CO, it's important to increase the air flow and, consequently, the excess of oxygen. With the combustion gases, flows particles, specially, those with a diameter smaller than 10 µm (Russo, 2005). As remaining solid wastes, the incineration process produces ashes and slags, which will be characterized more ahead.

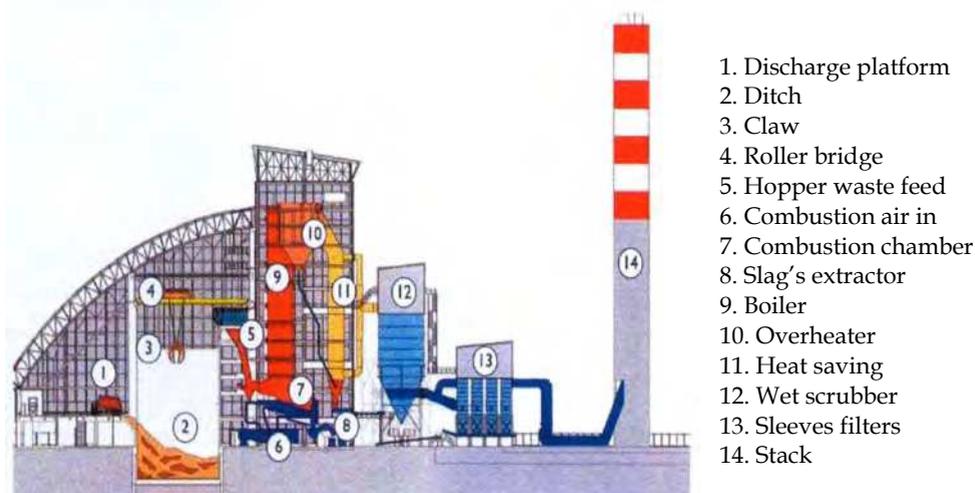


Fig. 1. Diagram of Valorsul's municipal solid waste dedicated incinerator (Levy & Cabeças, 2006).

Down the incineration chambers, the gases combustion have to be submitted to physical and chemical treatments, in order to ensure contents below to their respective legal limits. The main concerns are to achieve very low limits regarded with CO and volatile organic compounds (VOC's), which are proceeding from incomplete combustion with low air excess), NO_x (produced due to high temperatures in the furnace interior), acid gases (HF, HCl e SO₂), produced due to the presence of halogen (F, Cl) and Sulphur atoms in the solid wastes composition, heavy metals (Cu, Cr, Cd, Be, Mn, Hg and As), Dioxins/Furan's/PCB's, and particles.

Today, the European Directive on waste incineration (76/2000/EC), overcome to the Portuguese legislation, by the DL n.º 85/2005) considers a limit value for Cr together with

other eight heavy metals (Sb + As + Pb + Cr + Co + Cu + Mn + Ni + V) equal of 0.5 mg/Nm³ without taking into account the different toxicity of total Cr compared to Cr^{VI} (Cocarta, *et al.*, 2007).

Table 2 shows monitorization data related with treated gases combustion in the stack outlet of Valorsul's incinerator (CTRSU - S. João da Talha, Loures, Portugal), as well, the Portuguese legislation (Port. 286/93 and DL 85/2005), which establishes legal limits for each pollutant released to the atmosphere.

An incinerator powerplant must be gifted also, with sophisticated systems for treating the combustion gases; a turbine to convert thermal energy proceeded from super heated steam water into mechanical energy and, also, an alternator to convert this mechanical energy into electric energy. This last equipment is extremely important to profit the heat release from the combustion (exothermic process) to produce super heated steam water for subsequent production of electricity.

Atmospheric pollutant	Port. 286/93	CTRSU	DL 85/2005
HF (mg/Nm ³)	2,0	1 / 0,8	1
HCl (mg/Nm ³)	50	20 / 20	10
SO ₂ (mg/Nm ³)	300	50 / 50	50
Particles (mg/Nm ³)	30	20 / 10	10
NO _x (mg/Nm ³)	n.a.	250	200
CO (mg/Nm ³)	100	50 / 50	50
COV (mg/Nm ³)	20	10 / 10	10
Dioxins/Furan's (ng/Nm ³)	n.a.	0,1/ 0,05	0,1

Table 2. Monitorization of atmospheric pollutants at stack outlet, in the Valorsul's incinerator (CTRSU), as well, their respective legal limits.

The co-products resulted from waste solid combustion in incineration chambers are easy to compact and to store, due to their reduced volume and, they are classified as ashes and slags. Both are considered as remaining solid wastes. The ashes are submitted to an inertization process before their deposition in controlled landfill, while the slags are submitted to a valorisation process, which consists in separate the metals from the inerts. The metals can be conducted to the recycling industry and, the inerts can be used as covering of landfills, flooring roads, etc. The typical composition of slag's are 40% of SiO₂, 10% to 20% of Al₂O₃ and Fe₂O₃, 15% of H₂O and oxides, phosphates and sulphates, with a content below to 6%. By another hand, the ashes typical composition is 15% of sulphates, 13% of chlorides, 7-8% of SiO₂, 4-7% of Al and other alkaline and heavy metals with a proportion not higher than 5% (Puna, 2005).

There is still the production of volatile ashes, proceeding from the treatment of combustion gases in the depuration process. These ashes have to be also, submitted to an inertization procedure, before their deposition in landfill. Table 3 shows the main processes data of Valorsul's dedicated incinerator of urban solid wastes.

Furnace temperature	900 °C - 1200 °C
Wastes nominal calorific power	7600 - 7900 kJ/kg
Waste reception	662 000 ton./year
Solid slag's production	200 kg/ton. waste
Ashes production	30 kg/ton. waste
Electric energy production	587 kWh/ton. waste for 150.000 habitants
Water steam	Over-heated ($T > 300^{\circ}\text{C}$)
Turbine strength	Condensation, 50 MW

Table 3. Processes data of Valorsul's dedicated incineration (S. João da Talha, Loures, Portugal).

In summary, it's possible to express the main processes characteristics which define the dedicated incineration of solid wastes:

- The temperature in the inside of furnaces has to be controlled between 900°C and 1200°C;
- The combustion gases must have a short time residence in the chamber incineration, at high temperature, to avoid the considerable production of Dioxins/Furan's/PCB's. This can be achieved with 2-5 seconds for a temperature of 900°C and with an oxygen excess higher than 6% (Brunner, 1994);
- The admittance of solid wastes in the incineration chambers will only be possible with chlorine contents below 1% (w/w), to minimize and avoid, once again, the production of Dioxins/Furan's, which occurs in the combustion process, at high temperatures (below 900°C) and with high contents of Chlorine (Puna, 2002);
- A incineration powerplant has to be a installation to treat the combustion gases and, has to treat also, the co-products of incineration process (ashes, slag's and volatile ashes resulted from combustion gases treatment process);



Fig. 3. Inside of an incineration chamber in Valorsul's incinerator (S. João da Talha, Loures, Portugal).

- The dedicated incineration will only be an energetic valorisation process if the energy spontaneously released in the combustion chambers could be profited to produce superheated steam water. The high enthalpy of steam water at high temperature has a significant economic value and, it can be used to produce electric energy, in order to supply electricity, not only for the own incineration powerplant, but, more important, supply to the national electric network;
- The main incomes of an incineration unit are the admittance of solid wastes and, the supply of electricity to the electric network. Besides that, it's possible to avoid costs related with the purchase of electric energy coming from the operator's supplier electricity.

It's possible to see in figure 4, a typical diagram of industrial solid waste dedicated incinerator with energetic valorisation. The figure 3 shows the inside of an incineration chamber.

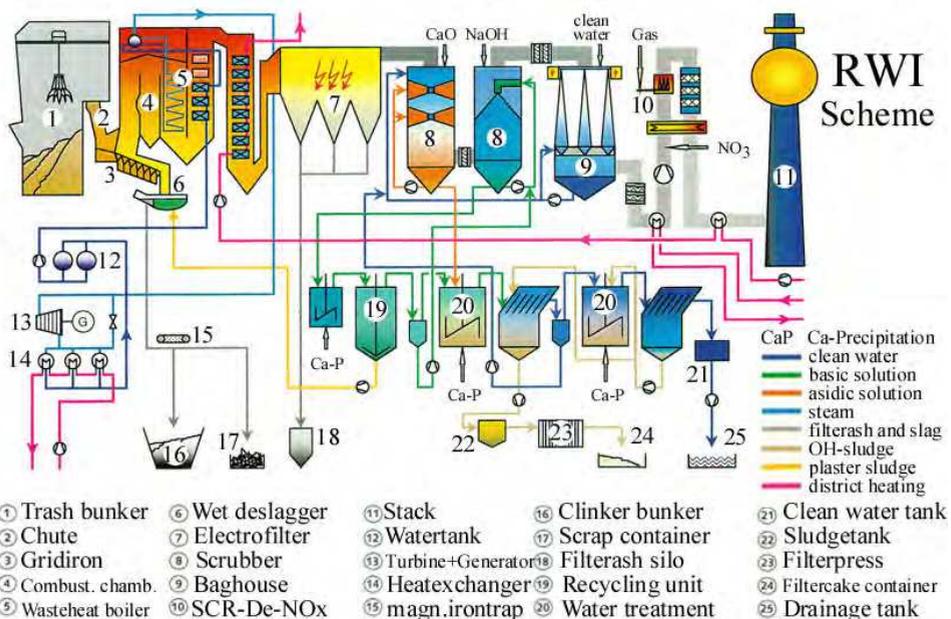


Fig. 4. Typical diagram of an industrial solid waste dedicated incineration process with energetic valorisation

(<http://www.sbg.ac.at/ipk/avstudio/pierofun/waste/residual/step-1.jpg>).

3.2 Co-incineration

Co-incineration of solid wastes is, also, a mass combustion process, which occurs, mostly, in cement furnaces, simultaneously with the clinker production. The difference results that this is a "dry" process, because there isn't, in any part of the process, the flowing of water/steam water as industrial utility (Puna, 2002). By another hand, the co-products (dangerous ashes, slag's and several heavy metals) are all incorporated in the hardness cement crystalline structure, becoming inerts. Regard the figure 5, which shows a typical scheme of a co-incineration furnace of dangerous solid wastes.

The co-incineration is a thermal destruction technique applied to several industrial solid wastes and, these wastes are valorised as raw-materials and/or fuels. Several industrial process which works at high temperatures, can be used for waste elimination, taking advantage of their calorific power. The elimination of industrial wastes with a calorific power minimum of 5000 kJ/kg in an industrial process can be considered as a technique with energetic valorisation (Oliveira, 2005). This method of thermal destruction of solid wastes has several benefits, even as an environmental perspective, but also, and more important, as an energetic perspective, because enables to substitute fossil fuels, like fuel oil, natural gas, etc., by dangerous wastes. These wastes are valorised in two forms: can be used as raw materials and, as fuel supplier to burning furnaces (Puna, 2002). However, the substitution of fossil fuels by dangerous wastes cannot increase the atmospheric pollutants emissions, resulting from combustion processes, in comparison with the normal use of conventional fuels. (Pio *et. al.*, 2003).

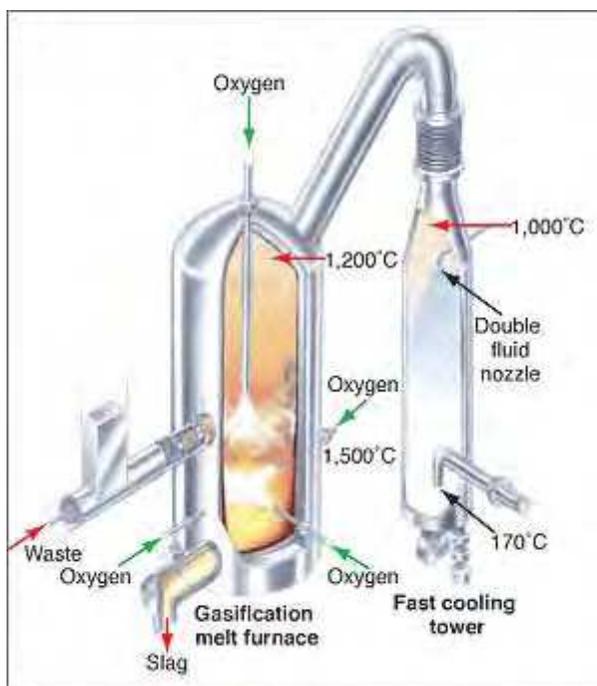


Fig. 5. Typical diagram of a co-incineration process of dangerous solid wastes (http://www.sumitomo.gr.jp/english/discoveries/special/images/100_07.jpg).

The co-incineration can be conducted in different industrial processes, like, for instance, in cement furnaces, or in industrial boilers. Nevertheless, the co-incineration in cement furnaces is considered the most efficient process of co-incineration, especially to dangerous solid wastes (Formosinho *et. al.*, 2000). The combustion of wastes in cement furnaces occurs at the same time with the production of clíiquer (cement product intermediate). The main characteristics in the co-incineration process of solid wastes in cement furnaces are the follow ones (Scoreco, 1997):

- Thermal valorisation method, alternative to dedicated incineration, only applied to burning wastes with higher calorific power, like, used oils and fatty slush's of industrial wastewaters treatment units;
- It's necessary a previous treatment for wastes before entering in the cement furnace, through physical and chemical process (impregnation, melting, centrifugation, fluidization);
- The industrial solid wastes are burned as fuel, with oxygen from air, in a mass combustion process, with temperatures between 1400°C-1500°C;
- The combustion gases achieve maximum temperatures near from 2000°C in the main burner and stay at temperatures higher than 1200°C in the second burner, with time residences between 4-8 seconds;
- The wastes admitted to co-incineration in cement furnaces cannot be contain chlorine contents higher than 1% (w/w), due to the significant production of dioxins/furan's, when the combustion gases are cooled faster at the outlet of clínquer furnace;
- These operating conditions are crucial to reduce and avoid the production of those macromolecules with higher molecular weight. It's important to remind that, dioxins/furan's molecules are produced, in a combustion process, with temperatures between 250-900°C and, with significant contents of Chlorine in the solid wastes. Besides that, the chlorine is harmful to the consolidation of cement structure, raising several weakness;
- It's necessary also, like in the dedicated incineration, the treatment of combustion gases, before they go out to the atmosphere, with temperatures between 150-200°C. To achieve this purpose, the process of cooling the combustion gases has to be very fast and, in a temperature gradient between (1000-1200)°C until (150-200)°C;
- The temperatures profile and the time residences are higher than any other combustion process, like dedicated incineration;
- Basically, a cement furnace is a place with optimal conditions to burn and eliminate any organic waste with capacity to be submitted for incineration;
- It's extremely important the control of operating parameters, like, temperature, oxygen content and time residence of combustion gases, to ensure an efficient and safety burning of solid wastes, mainly, the dangerous ones;
- The thermal energy to feed the furnace is obtain by a variety of auxiliary fuels, but with large preference to coal and/or pet-cock, with very low contents of sulphur, to avoid the production of SO₂;
- The burning dangerous industrial wastes with high calorific power can replace the coal, as fuel to supply the co-incineration furnace, until 40%, with, mainly, used oils, solvents and organic slush's.

Figure 6 shows some pictures of a cement furnace.

It is also important refer that, the combustion gases, before they go out to the atmosphere, are previously treated by physical and chemical appropriated process, like in dedicated incineration, in order to maintain the air quality and, therefore, assure that the gaseous emissions could be above their legal emission limit values, defined in the European and Portuguese legislation. Heavy metals, Dioxins, Furans and PCB's are treated by adsorption with activated carbon, while the acid gases (HCl, HF and SO₂) are treated by chemical reaction with lime milk (Ca(OH)₂) (Russo, 2005).



Fig. 6. Picture of inside (left) and outside (right) of a co-incineration unit in cement furnace used to burn dangerous industrial solid wastes (Puna, 2002).

The NO_x gases are treated by injection, without catalyst, of ammonia aqueous solution, producing N_2 , while the almost particles are filtered with sleeves filters of higher efficiency or, with electro filters. The wastes generated by these processes are called flying ashes and they are covered in safety and appropriate landfills, after an inertization process.

This group of combustion gases treatment is performed at clinker furnace exit and, they are the same methods, with the same technologies used in dedicated incineration, described in table 4. Table 5 identifies the emission limit values of several gaseous pollutants to the atmosphere, according with current Portuguese legislation (DL n.º 85/2005), overcome by EU legal framework.

Gaseous Pollutant	Gas Combustion Treatment Process
NO_x	Selective removal with injection of ammonia aqueous solution, producing N_2 .
HCl, HF, SO_2	Injection of $(\text{Ca}(\text{OH})_2)$, in the gases purifying, through a "scrubber" process (gases washing).
Dioxins/Furan's/PCB's	Injection of activated carbon in the gases purifying, to adsorb these substances; efficient control of furnace temperature and time residence of gases combustion, with very fast cooling.
Heavy metals (As, Cd, Be, Pb, Hg, Zn, Cu, Cr)	Injection of activated carbon in the gases purifying, to adsorb these substances.
Particles/dusts	Use of sleeves filters of higher efficiency or, with electro filters.
CO/VOC's	Ensure a complete burning, supplying air in considerable excess.

Table 4. Techniques and technologies used in the combustion gases treatment (Adapted from Pio *et. al.*, 2003 and Formosinho *et. al.*, 2000).

It's interesting to perform a comparison between dedicated incineration and co-incineration thermal methods for solid wastes. Stronger and weaker aspects can be confronted in table 6. Table 7 identifies the number of industrial units in Europe, where is possible to burn dangerous industrial wastes, by co-incineration in cement furnaces.

Pollutant	Unit	Limit-Value	Pollutant	Unit	Limit-Value
Particles	mg/Nm ³	10	CO	mg/Nm ³	50
SO ₂	mg/Nm ³	50	VOC's	mg/Nm ³	10
HCl	mg/Nm ³	10	Dioxins/Furan's	ng/Nm ³	0,1
HF	mg/Nm ³	1	Pb + Cr + Cu + Mn	mg/Nm ³	5
NO _x	mg/Nm ³	200	Cd + Hg	mg/Nm ³	0,2

Table 5. Limit values of gaseous pollutants emissions at incinerator stack exit (DL 85/2005).

Dedicated Incineration	Co-Incineration
Less efficiency of organic molecules destruction (1100°C/2-5 s).	Higher efficiency of organic molecules destruction (1450°C/4-8 s).
Can accept more contaminated wastes, like, organometallics and organochlorides.	Can't burn any dangerous industrial solid wastes with contents of chlorine higher than 1% (w/w).
It produces new remaining wastes, like ashes, slag's and washing effluents, which have to be treated also.	The ashes, slags, heavy metals and other pollutants can be fixed in the final matrix of cement, without lixiviation.
Higher energetic and economic yields, due to the electricity production and supplying.	Higher energetic yield, due to the substitution of fossil fuels, by solid wastes.
Doesn't need of any previous treatment for solid wastes, instead of co-incineration.	More restrictive related to the presence of some heavy metals in the solid wastes. Its need a previous treatment to admit the solid wastes.

Table 6. Comparison between dedicated incineration and co-incineration in cement furnaces (Adapted from Formosinho *et. al.*, 2000).

4. Pyrolysis and gasification of solid wastes

In the pyrolysis technologies, the most efficient is the PPV process, which means Pyrolysis by Plasma with Vitrification. Pyrolysis is a technology dedicated of waste destruction, which works at high temperatures, more than the typical temperatures in incineration chambers, with low oxygen, in order to avoid the combustion phenomena (Camacho, 2005). To guarantee the absence of oxygen, the wastes are decomposed in an inert gaseous atmosphere, through the utilisation of Nitrogen (N₂) (Puna, 2002). The process of pyrolysis

can be defined, generally, as the chemical decomposition of organic matter by heat, in the absence of air, unlike the incineration methods. The pyrolysis processes is endothermic, on the contrary of dedicated incineration or co-incineration, because it's need to supply heat to the pyrolysis reactor in order to occur the pyrolysis reactions. If any gas is heated at higher temperatures, there are significant changes in their properties. In the range of temperatures between 2000°C and 3000°C, the gas molecules decompose in ionized atoms by losing electrons. This ionized gas is called plasma (Lapa & Oliveira, 2002).

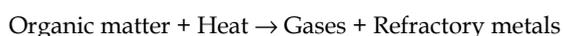
Country	Total units (B)	Units that perform co-incineration of dangerous wastes (A)	A/B (%)
Germany	46	16	35
Austria	9	7	78
Belgium	5	5	100
Denmark	1	0	0
Spain	39	6	15
Finland	3	0	0
France	47	19	40
Greece	8	0	0
Irland	4	0	0
Italy	62	5	8
Luxembourg	1	1	100
Netherlands	1	1	100
Portugal	6	0	0
U. Kingdom	15	2	13
Sweden	3	3	100
Switzerland	11	7	64
Total	261	72	28

Table 7. Industrial units in Europe where is possible perform co-incineration of dangerous solid wastes, in cement furnaces (Adapted from Formosinho *et. al.*, 2000).

Normally, the wastes are injected directly in the plasma, producing pyrolysis gas (essentially H₂, CO, N₂, CO₂, CH₄), and this gas can be burned in a combustion process, by incineration, in order to make profitable the entire process and to valorise it as a gas fuel, since CO and CH₄ are organic gases with high calorific power. Nevertheless, it's necessary a higher and significant annual flow admittance solid wastes to maintain the optimum operating conditions of PPV reactor and, also, to profit the all PPV system, since the production of plasma is a great consumer of thermal energy (Camacho, 2005).

The co-products of this process, specially ashes and heavy metals, are encapsulated in a vitrified matrix, to avoid the production of leachates. This vitrified matrix transform the PPV co-products in inert remaining wastes, without any chance of occur lixiviation. This is a great advantage in an environment and public health perspectives. This vitrified matrix is called "obsidiana" and, results from the cooling of glass file-dust, which is introduced in the pyrolysis reactor, on the temperature range of 2000°C-3000°C (Oliveira, 2000). The glass at these temperatures is liquid and, in the cooling step, is submitted to a solidification process, covering the remaining wastes, heavy metals and other dangerous gaseous/solid substances produced in the pyrolysis reactor. These vitrified ashes have large applicability in the road flooring, landfills covering and, as additive to the cement in civil construction.

In this process, the application range of dangerous solid wastes is almost total and much more all-inclusive that the admittance wastes in incineration methods. In all thermal processes, this is the one that is considered, in an environmental point of view, the most sustainable, although the higher energetic and economic costs (Puna, 2002). The general equation of a pyrolysis process can be traduced in the following way:



The plasma is a special form of gaseous material, capable to conduct electricity and, it's knower as the "fourth state of matter" (solid, liquid, gas and plasma). In the state of plasma, the gas can achieve temperatures extremely high, which can change from 5 000 to 50 000 °C, depending of its production conditions (Oliveira, 2000). In figure 7, it's possible to see a plasma jet.



Fig. 7. Plasma jet (<http://paginas.fe.up.pt/~jotace/gtresiduos/plasmapirolise.htm>).

This plasma is generated by the formation of an electric arch, through the cross of electric current between the cathode and the anode. Between them, a gas is injected and ionized. This ionized gas is, subsequently injected over the solid wastes. The plasma jet is produced and controlled in a torch capable to convert electric energy in heat, at higher temperature through the gas flow. In the torch, any gas rapidly reaches the plasma state. Figure 8 shows, in detail, the plasma jet production.

Basically, there are two kinds of solid waste treatment by plasma: the direct heating system and heating system with gasification chamber.

Direct heating system:

Through the plasma torch, occurs the production of an electric field of radiant energy with higher intensity, capable to dissociate the existing intra molecular bindings of solid, liquid and gaseous wastes, dangerous or inerts, organics or inorganics. So, when the wastes are submitted to the plasma jet, they loose their original chemical composition to convert in more simple compounds. Figure 9 shows a direct heated system diagram used in PPV system to treat municipal and hazardous solid wastes.

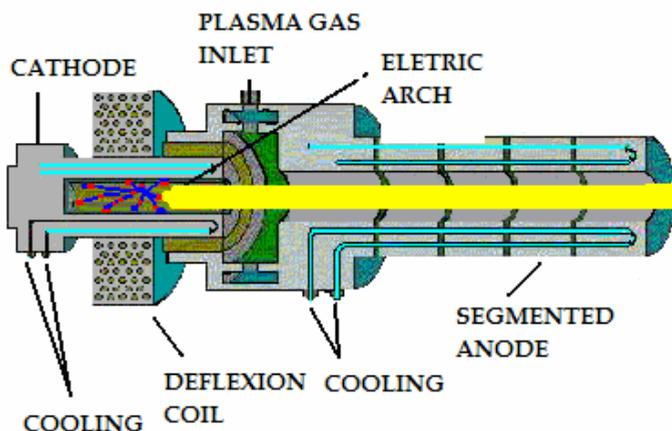


Fig. 8. Scheme of the plasma torch inside, showing the creation process of plasma jet (Adapted from <http://paginas.fe.up.pt/~jotace/gtresiduos/plasmapirolise.htm>).

Heating system with gasification chamber:

This system consists in two different stages of treatment. The solid wastes are injected in a first conventional gasification chamber, in order to gasify the organic compounds in a gas partially oxidized and, also, to melt the inorganic compounds. In this chamber, it's produced a gas and a liquid, which they are, subsequently decomposed in a second chamber, with a PPV reactor.

After the dissociation of all molecules, the matter is recovered in the following forms (Puna, 2002):

- **Plasma synthesized gas**, which is conducted to a combustion chamber, in order to valorise its calorific power and, to reuse the release heated, supplying into the PPV reactor;
- **Inorganic materials and vitrified silicates**, which will swim on the surface of liquid phase. These inorganic compounds, in the case of directed heating technology, were submitted to temperatures substantially higher than in the gasification chamber method.
- **Obsidiana**, which is a solid structure of higher hardness and, generally, with black colour, similar to a mineral of volcanic source. This solid contains the PPV ashes, the heavy metals and other dangerous inorganic atoms, all vitrified, without any chance of occur lixiviation. Figure 10 shows the typical aspect of Obsidiana.

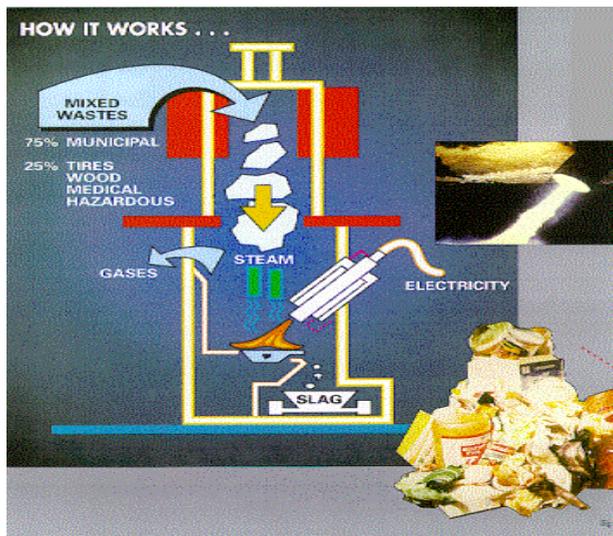


Fig. 9. Example of plasma utilisation directly over the solid wastes in the direct heating system (<http://paginas.fe.up.pt/~jotace/gtresiduos/plasmapirolise.htm>).



Fig. 10. Vitrified contaminants aspect after PPV reaction (<http://paginas.fe.up.pt/~jotace/gtresiduos/plasmapirolise.htm>).

Like other treatment techniques of industrial waste treatment, the use of pyrolysis with plasma presents advantages and disadvantages or inconvenients, as follows:

Advantages:

- PPV is a process more environmental friendly and safety, with “zero” pollutants emission or, with magnitudes lowers than those established in the environmental legal Framework related with air quality;
- Higher temperatures causes rapid and complete pyrolysis of organic wastes, melting and vitrifying certain inorganic compounds, in a high hardness structure, without lixiviation, called obsidiana;

- The plasma synthesized gas, with high calorific power, can be used in other process or, it can be submitted to combustion in order to valorise it;
- In PPV reactor, there isn't combustion of solid wastes, so, it doesn't occur the production of toxic compounds, like dioxins, furan's and PCB's;
- The gas volume obtained is substantially less than the gas volume achieved in other treatment process, like incineration, so, it's easier to be treated. The reduction rate volume from waste to gas, can be higher than 99%;
- The high temperature of PPV reactor to the molecules dissociation is produced from electricity, which is a clean energetic source;
- Enables the co-generation of energy, with production of electricity, steam and/or cold (freeze water/air conditioning).

Disadvantages:

- PPV it's a dedicated technology, requiring a high investment, due to the fact that, it can only be profitable when coupled with a thermoelectric powerplant, to supply the sufficient electricity for plasma production. It's also necessary, a significant higher and stable flow of solid wastes, which compromises any waste reduction/reutilisation/recycling policy strategy in medium/long time;
- The PPV system can't dispense a sophisticated washing gases system, as in any incineration process, especially for the retention of VOC's and acid gases, after the combustion of plasma synthesized gas;
- For different waste treatment, in particular, those containing organic matter in significant amounts, the pyrolysis techniques can't achieve great industrial development. The wastes are decomposed by pyrolysis but, after that, they are eliminated by combustion, through the incineration of plasma gas;
- The production of dioxins/furan's/PCB's in the incineration chamber, after PPV reactor, are strongly dependent of thermal recovery technologies used down the stream. It's not clearly that it can assure a significant advantage over more advanced incineration Technologies or over gasification simple techniques.

Synthesizing, the main process characteristics of PPV, are:

- It's necessary a thermal source with high enthalpy and reduced mass, which is the plasma (boiled gas at high temperatures);
- The pyrolysis temperature, the applied heating rate and the waste composition will determine the gas pyrolysis composition;
- The plasma corresponds to the fourth state of matter, the ionized gas, under temperatures between 2000°C and 3000°C and, it's produced by an electric discharge between the cathode and the anode, where flows an inert gas, which is injected over the wastes;
- Any organic compound, including wastes, is convertible in gas pyrolysis and in a mixture of refractile glass with PPV ashes and heavy metals, under a hardness solid structure without any material percolation;
- In this process, there isn't a final liquid phase and the higher temperatures leads to the elimination of macromolecules traditionally produced in the combustion process (dioxins, furan's, PCB's);
- The plasma is controlled under a torch, converting electric energy into heat, through the supplying of a higher amount of electricity, proceeding from a own powerplant electricity production;

- In this process, occurs the following elementary reactions in the PPV reactor, with the important auxiliary of heat generated by the plasma:



The average volumetric composition of plasma gas is, normally, 41% of H₂, 30% of CO, 17% of N₂, 8% of CO₂, 3% of CH₄ and, O₂, C₂H₂, C₂H₄ with contents lowers than 0,5%. The calorific recovery in PPV process around 10.51 MJ/Nm³ and the energetic yield is near from 612 kWh/ton of treated waste (Oliveira, 2000). Table 8 performs a comparison of the main characteristics between PPV and incineration processes. Table 9 presents the several PPV units located all over the world, especially applied in elimination toxic wastes, hazardous and radioactives.

Incineration	PPV
Combustion of wastes with air excess.	Thermal decomposition of wastes with absence of air, in an inert atmosphere, at closed reactor, with substantially higher temperatures.
System treatment conditioned to some kind of solid wastes, due to atmospheric emissions released.	System treatment applied to any kind of solid wastes.
Air volume very high.	Air volume 20 to 50 times below at incineration.
Production of ashes and slag's, which have to be treated.	Ashes and heavy metals are vitrified in a hardness solid structure, without lixiviation.
Production of several dangerous organic compounds with high stability, like dioxins, furan's and PCB's.	Destruction of organic compounds almost complete, leading to the release of pyrolysis gas, with H ₂ , N ₂ , CO, CO ₂ , H ₂ O, CH ₄ and other hydrocarbons in track amounts.
In the dedicated incineration, the gases can be valorised in the production of electric energy.	The pyrolysis gas can be valorised in energy production or used in the steam production, convertible in electric energy. However, due to the gap temperatures used, the energy production can represent 20%-80% plus than the energetic consumption.

Table 8. Comparative board with the main differences between PPV and incineration processes (dedicated and co-incineration in cement furnaces) (Puna, 2002).

Treatment of different wastes	
Love Canal, Niagara Falls (EUA)	Toxic slushes elimination
BNL/EPA/COE (EUA, GB)	Descontamination of special materials
IHI (Japan)	Incinerator slag's elimination
Westinghouse/PSI (EUA)	Treatment of contaminated landfills
US Naval Surface Warfare Center (EUA)	Treatment of special wastes
New York City Harbour	Toxic slushes elimination
Elimination of toxic wastes	
DOE/USN (EUA)	Elimination of special toxic wastes
DOE (EUA)	
Bordéus city council (France)	
Kawasaki Steel Company - TEPCO (Japan)	
Ebara - Infilco (Japan) - 1993 e 1994	
Wastes of lower radioactivity	
Westinghouse Hanford (EUA)	Inertization
Sandia National Laboratory (EUA)	
DOE (OTD), Ukiah (EUA)	
British Nuclear Fuels (GB)	
DOE/Argon National Laboratory (EUA)	
Urban solid wastes and similar	
Valencia (Spain) (start up at 2002/12/10)	500 ton./day of urban wastes + tanning wastes (with Chromium recovery)
Vicenza (Italy) (start up at 2002/12/10)	500 ton./day of urban wastes + Venice channels slush's
Kuala Lumpur I (Malaysia) (start up at 2003/07/04)	360 ton./day of urban wastes + hazardous wastes

Table 9. List of industrial units with PPV waste treatment (Oliveira, 2000).

5. Environmental and health impacts control systems

In any waste solid treatment technology, there are several environmental impacts associated to the function of those units. Those impacts must be identified and, if possible, quantified, in order to know, with more precision, what are the consequences and benefits for the environmental and public health, related with the labour of those treatments. It gives, also, information to optimise all operating conditions of those systems and, to ensure the accomplishment of legal framework, especially those who are related with air quality, ecotoxicological risks for human health, quality and discharge of wastewaters, noise, remaining solid wastes, etc (Adapted from Partidário & Jesus, 1994).

The final purpose of any environmental impacts characterization is supply a sustainable development to all communities in the neighbourhoods. After all, they are the bigger beneficiaries with the implementation of any waste solid treatment systems. Particularly, for thermal methods of solid wastes, the following aspects have to be considered, in order to ensure an efficient and safety function of those units, through a continuous monitorization and control processes (Adapted from Vanclay & Bronstein, 1995 and from Wathern, 2000):

- Production of wastewaters;
- Air quality (1);
- Noise from the electromechanic equipments used;
- Deep smells resultants, essentially, from the discharge and storage of solid wastes;
- Production of remaining wastes from combustion and pyrolysis processes, respectively, ashes and slag's, and, vitrified ashes, which they have, all of them, submitted to a suitable destination for valorisation and/or treatment;
- Water quality and silts in the hydric resources involving the treatment units, as well, the respective ecosystems (2);
- Public health monitorization and analysis;
- Possibility of occur serious industrial accidents.

Notes: (1) - By law, it's obligatory to perform a continuous monitorization of gases combustion at the way out of any incinerator chimney. It must be performed also, a continuous monitorization of air quality in the neighbourhood zones, especially, in the housing ones. The parameters to be analysed are, according with respective legislation, the follow ones: SO₂, NO_x, CO, O₃, particles, HF, HCl, heavy metals, VOC's, dioxins and furan's. (2) - Should be made a monitorization of superficial and underground hydric resources, with a schedule and a programme well constructed. The parameters to be analysed are the follow ones, according also, with the respective legislation: pH, temperature, salinity, conductivity, CQO, CBO, PCB's, PAH's, heavy metals, dioxins and furans.

However, the most important environmental parameters to be analysed is the atmospheric pollutants emissions, even in incineration or in pyrolysis processes. Table 10 shows the generic composition of gaseous pollutants emissions of PPV process and makes a comparison with the outlet gases of incineration processes. The PPV process presents less quantities of dangerous substances in their vitrified ashes, like some heavy metals (Hg, As, Pb, Zn, Cu), Nitrites, Phenol and Fluorides, unlike the incineration bottom ashes, which imply that, the PPV process is more environmental friendly. These ashes don't offer significant problems in terms of ecotoxicological risks. Additionally, it is possible to say that the provisional risks of vitrified residue material are nor significant (Oliveira, 2000).

Pollutants emissions	PPV (11% O ₂)	Incineration
PCDD (ng/Nm ³)	N.D.	19 - 298
PCDF (ng/Nm ³)	3 - 10	44 - 306
PCB's (ng/Nm ³)	N.D.	2 - 7
Cd (mg/Nm ³)	0,004 - 0,03	0,6 - 0,9
Cr (mg/Nm ³)	0,02 - 0,08	0,03 - 0,1
Pb (mg/Nm ³)	0,2 - 0,6	8,4 - 15
Hg (mg/Nm ³)	N.D.	0,5 - 0,9
HCl (mg/Nm ³)	0,1 - 0,6	
HF (mg/Nm ³)	0,07 - 0,7	
NO _x (ppm)	158 - 305	169 - 246
SO ₂ (ppm)	66 - 69	128 - 225
Particles (mg/Nm ³)	2,4 - 9,9	167 - 247

Table 10. Pollutants emissions from PPV and incineration processes (Oliveira, 2000).

The most dangerous pollutants for the environment and public health are the heavy metals and the dioxins/furans/PCB. Theoretically, there are 75 possible isomerous for all groups of dioxins, but only 7 develop serious toxic effects. In the same way, there are 135 possible isomerous for furans, but only 10 develop potential toxic effects. Related to PCB's, there are 209 possible isomerous, but only 11 with toxic properties (Odum, 2001).

6. The profit of energy recovered in Portuguese incineration units for solid wastes: A brief case-study.

The authors performed an economic study to achieve what were the best waste treatment methods with energetic valorisation, capable to produce large quantities of electric energy. The summary results of this study are presented here, in this book. In fact, it was possible to conclude that, attending to the description of the several techniques for waste solid treatment (dedicated incineration, anaerobic digestion and energy production in landfills), these treatment methods/technologies contributes with significant amounts of electric energy (Puna & Baptista, 2008). Table 11 shows the annual treatment capacity of solid waste for each method and, also, the respective amount of energy produced, express in MWh/year. These amounts are sufficient, by one hand, to become autonomous these waste treatment infrastructures and, by another hand, enables to export significant quantities of electricity to the National Electric Network.

Urban solid waste treatment methods	Ton./year	MWh/year
INCINERATION ^(a)	662000	388594
ANAEROBIC DIGESTION ^(b)	40000	12000
BIOGAS PRODUCTION IN LANDFILLS ^(c)	146000	14880
(a) - Valorsul's urban solid waste incinerator in Loures, Lisbon, Portugal (b) - Valorsul's organic valorisation plant in Amadora, Lisbon, Portugal (c) - Amarsul's landfill in Seixal, Setúbal, Portugal		

Table 11. Annual solid wastes treatment capacities and respective energy amounts produced.

This study was made, through the analysis of two waste solid treatment integrated management systems, Valorsul's, which operates in the Metropolitan Area of Lisbon, Portugal and, Amarsul's, operating in the south border of Lisbon. Both systems consist in an expressive case-study (Puna & Baptista, 2008). The first integrated system includes a dedicated incinerator and an anaerobic digestion unit. The second integrated system operates with a controlled landfill, taking advantage of the high calorific power of biogas, produced by the decomposition of the settled organic solid wastes.

Through the knowledge of these processes, it was possible to determine the nominal electric energy production for each of these treatment methods. For instance, it was important to know what is the ratio between each ton of waste treated by incineration and a kWh of

electric energy produced. In this example, 1 ton of urban solid waste treated by incineration, normally leads to 587 kWh of electric energy produced (Valorsul). These results are presented in table 12.

It's obviously that, not all the electric energy produced is exported, because some percentage is necessary to cover the energetic necessities of those waste solid treatment infrastructures. This is a great advantage because it gives them an energetic independence from the exterior. The distribution of the percentages of electric energy produced for each waste solid treatment method mentioned above depends of the respective efficiency (Puna & Baptista, 2008) and, their values are described in table 13. With this data, it's possible to estimate the annual production of electric energy exported to the National Electric Network and their respective profits or revenues, for each solid waste treatment method, attending that the kWh price to sell is 0,07€.

Treatment method	kWh/ton.waste	Efficiency (%)
INCINERATION	587	---
ANAEROBIC DIGESTION	300	30
BIOGAS PRODUCTION IN LANDFILLS	102	40

Table 12. Nominal production of electric energy.

Solid waste treatment method	Efficiency (%)	% of electric energy for own consumption	% of electric energy for exportation
INCINERATION	---	15 - 20	80 - 85
ANAEROBIC DIGESTION	30	30 - 35	65 - 70
BIOGAS PRODUCTION IN LANDFILLS	40	5 - 10	90 - 95

Table 13. Distribution of nominal production electric energy.

This price is called "green rate" because the energy produced is obtained from waste treatment, which corresponds to an energy production from renewable sources. The results obtained are presented in figures 11 and 12 (Puna & Baptista, 2008).

7. Conclusions

Now, it's important to stipulate some final conclusions, which results of all it was written here, in this chapter, highlighting the following ones:

- The incineration has a important rule in the integrated solid wastes management systems;
- If a specific solid waste could not be submitted to any other treatment process, like, biological, physical and chemical methods, then, the thermal techniques are the most suitable treatment solutions, according to the methods and technologies actually available;

Electric energy exportation (MWh/Year)

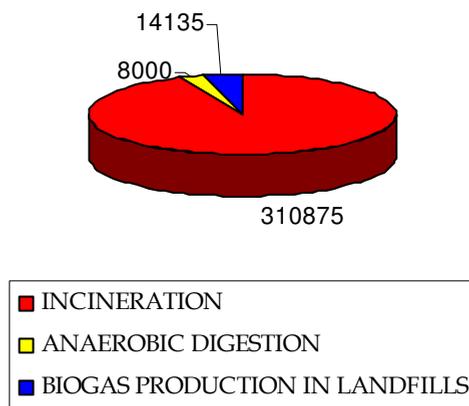


Fig. 11. Electric energy exportation.

Incomes from electric energy exportation (10⁶ €)

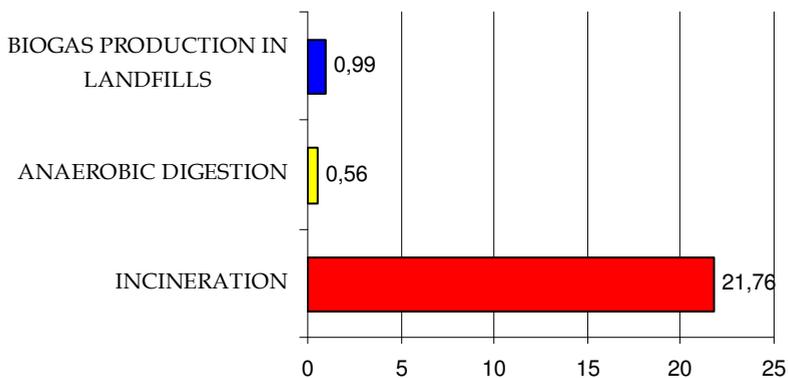


Fig. 12. Revenues proceeding from electric energy exportation.

- The controlled settling in landfills is, definitely, the last step of any integrated solid waste management system and, it's only be applied for wastes that cannot be treated by any other solution;
- In the selection of one or more solid waste treatment techniques and, looking for factors like, economic reality of the country, quantity of waste production and collected, advantages and disadvantages of each kind of treatment method, etc., the technique most recommendable for the treatment of dangerous solid wastes in Portugal, and, generally, in the 27's EU is the co-incineration in cement furnaces, because this option implies less investment costs when compared with the pyrolysis by plasma with vitrification (PPV). Although, it's sufficient adapt them to the gaseous emissions treatment;
- In the co-incineration on cement furnaces, the burn process is particularly controlled, since emits less pollutants atmosphere emissions than the dedicated incineration;
- The co-incineration brings also economic advantages through fuel savings, regarding that 60% of cement cost production are applied to the energy consume;
- However, there is a bigger restriction in the waste admittance on the cement furnaces than in the dedicated incinerators, because, in that ones, occurs, simultaneously, the clínquer fabrication process, which could be severe affected through the furnace inlet of undesirable materials;
- One big advantage of any solid waste management integrated system consists in the valorisation of co-products, such as, the ashes and slag's from the incineration process;
- It's in the incineration that the electricity production is substantially bigger, followed by the biogas energetic valorisation in landfills and, finally, followed by the anaerobic digestion. This fact is extremely important in order to implementate an energetic valorisation in a dedicated incinerator;
- The system PPV is a treatment method that can be applied to any kind of solid waste, including the dangerous ones that could not be incinerated;
- None technology is 100% clean, but the PPV system is, far away, the treatment method which less negative environmental impacts creates, which is a very important advantage under a environmental and social perspectives.

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Waste Management

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Solid Waste Management is one of the essential obligatory functions of the Urban Local Bodies/Municipal Corporation. This service is falling too short of the desired level of efficiency and satisfaction resulting in problems of health, sanitation and environmental degradation. Due to lack of serious efforts by town/city authorities, garbage and its management has become a tenacious problem. Moreover, unsafe disposal of garbage and wastewater, coupled with poor hygiene, is creating opportunities for transmission of diseases. Solutions to problems of waste management are available. However, a general lack of awareness of the impact of unattended waste on people's health and lives, and the widespread perception that the solutions are not affordable have made communities and local authorities apathetic towards the problems. The aim of this Book is to bring together experiences reported from different geographical regions and local contexts. It consolidates the experiences of the experts from different geographical locations viz., Japan, Portugal, Columbia, Greece, India, Brazil, Chile, Australia and others.

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