UNIVERSITY OF PADUA

Second Cycle Degree in Environmental Engineering

ICEA Department

Master Thesis:

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CARBON MASS BALANCE IN THE FIRST PHASE OF SEMIAEROBIC-ANAEROBIC-AERATED (S.An.A.) LANDFILL MODEL

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Theory is when you know everything but nothing works.

Practice is when everything works but no one knows why.

In our lab, theory and practice are combined: Nothing works and no one knows why.

A.E.

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Part 1

Theoretical and technical overview

1. Introduction

Landfilling is the last phase of the integrated waste management, as it has the function of final disposal of residual fractions derived from previous treatments. Mind that a landfill has not to be seen as the final destination of a territory, but as an opportunity for a further use of an area.

Since it is impossible to think to have no waste going to landfills or, in other words, a landfill is always needed as final step of a waste management system, it is necessary to reduce, at least, the overall amount of residues destined to it and to stabilize them, to prevent further environment pollution.

The idea is to design a type of landfill that incorporating the positive aspects of past landfills (e.g. control of unsaturated background, containment and treatment of emissions, waste minimization and pretreatment) together with a coherent long-term strategy for the control of emissions and climate change issues.

In this scenario, Sustainable landfills play a fundamental role. This type of landfill is design in order to give to next generations an environment in the same conditions as it is characterized of nowadays (Cossu, 1995). Starting from this idea, a landfill can be defined as sustainable if it gives, at the end of the management stage (30 years fixed by the Europe regulation), emissions and impacts do not change in a considerable way quality of the surrounding air, water, groundwater (Hjelmar e Hansen, 2005; Stegmann et al.2003).

In order to obtain a sustainable landfill, the processes that occur naturally in the waste mass are controlled whit modern technology in order to optimize the processes, so that the landfill body will be stabilized as fast as possible (before 30 years i.e. time of a generation).

The aim of this treatment is to accelerate the utilization of natural processes, so that after a period of active control and active after-care we can safely release the landfill from post management because the landfill is completely stabilized. It's important to achieve the sustainable situation, and several approaches have been proposed to reach. In particular is based on the modification of the characteristic of the waste to be landfilled such us mechanical-biological pretreatment, or on the modification of the landfill construction and operation procedure such us aerobic, semi aerobic, leachate recirculation.

Starting from these considerations, Spinoff Srl, in collaboration with the University of Padua, has developed an innovative system of landfill: the S.AN.A. ® model, aimed at ensuring the environmental sustainability of landfills. This system involves the alternation of three distinct phases during the operation period and management of the landfill: Semi-aerobic phase, aimed at reducing the duration of the acetogenic phase, the anaerobic phase, which is maximized in the production of methane, Aerobics final phase, in which will accelerate the processes of stabilization

of waste to achieved the final quality of the deposit in equilibrium with the environment (the Final Storage quality concept).

The main objectives of this research are:

- Check the effects of pre-aeration on the subsequent anaerobic phase. The first phase of semi-aerobic want to achieve optimum values of pH, volatile acids, alkalinity and temperature that favor the establishment of the methanogenic phase . This can be done by different type of aeration on the waste just deposited until the above-mentioned parameters do not reach optimal range.

- Assess the conditions for the achieving of the Final Storage Quality (FSQ) in a Sustainable way (within 30 years, simulated) . Through of in situ aeration and flushing process, we want to accelerate the process of stabilization and leaching of the remaining potentially contaminating substances, taking advantage of the increased aerobics kinetics reaction. The lab-scale test wants to investigate the behavior in the long term of the main characteristic parameters of the leachate and demonstrate that it is possible to bring them under certain values only with adequate treatment technologies such as aeration and flushing

- Perform a mass balance for the most important elements such as Carbon, Nitrogen, Chlorides, Sulfates and heavy metals. Particular attention will be placed on carbon speciation (focus on non-reactive and slowly biodegradable substances) and nitrification and denitrification pathways.

The research study is currently in progress; the present paper refers to the result obtained respect to quality of emission as observed after 90 days for lab column.

In particular will be analyzed the first part of the S.An.A. model management. The goals are:

- first, to investigate the effect of pre-aeration on the subsequent anaerobic phase, in order to achieve an optimum values of pH, VFA, alkalinity and temperature that can enhance the methanogenic phase in simulated bioreactor landfill (SANA).

- refine the transition parameter between first and second phase, set a significant aeration period and investigate on which pre-aeration method is the most appropriate.

- analyzing mobility-stability of compounds by a mass balance approach. Focus on the first phase of the experiment, Carbon mass balance has been used to allow to understand how a specific elements has been distributed during the time among the principal emission form, such as leachate, biogas and residual waste.

The present work, is the result of an accurately bibliographic research and the experimental activity based on laboratory processes carried out in the LISA laboratory of the ICEA department of the Padua University from July 2014 until October 2014.

The test was performed on six refuse leaching columns and the emission were observed. Emission behavior, hydraulic properties, as well as behavior of waste under different operational conditions will be evaluated.

This thesis is subdivided into three different sections. The first part provide a theoretical and technical overview. In particular were introduced the environmental sustainability concept and discussed the importance of waste management. Summarizes the landfill scenarios with emphasis on the main management strategy to achieve successful and efficient waste stabilization, and reviews landfill legislation in Italy and Europe.

In the chapter 3 particular attention will focus on carbon and its speciation. It's important to understand what are the carbon flux that enter in a landfill and through which paths go away.

For this reason, mass balances are a useful tool for analyzing mobility-stability of compounds, and allow to understand how a specific elements has been distributed during the time among the principal emission form, such as leachate, biogas and residual waste. Carbon mass balance are presented.

The theoretical study of the proposed performance-based methodology has been described.

The second part is presented in the form of scientific article and focuses on the experimental activity. Here the test and its elaboration are explained and analyzed.

The third part is composed by annexes which report the experimental data and the calculation preformed during the experiment.

2. Waste management and environmental sustainability

2.1 Environmental sustainability

In the recent years, the environmental sustainability issue is becoming increasingly important not only at administrative level but also for the public opinion. Considering the disconcerting phenomena, such the limited resources, climate change, increasingly widespread pollution, population growth, depletion of nonrenewable energy sources, global warming and its increasing effects, have shed light on the many global environmental issues. Numerous have been the community and national legislative interventions in order to define the goal and strategies for the environmental rebalancing.

The general EU policy included in the Single European Act, the Maastricht and Amsterdam Treaty, are the general objectives of protecting and improving the quality of the environment.

Additionally, more detailed policy statements in relation to the environment are included in Environmental Action Programmes (EAP). These Action Programmes include EU policy development in relation to waste treatment and disposal. There have been six EAP since 1973.

The general approach and strategy in terms of waste in the EAP has been:

- To considering the waste as a remedial problem requiring control at Community level.
- The need for waste prevention, recycling, re-use and final disposal, via environmentally safe means.
- The need for action in regard to waste minimization at the production process through the use of clean technologies.
- Set out hierarchical structure of waste management as a long-term strategy for the EU.
- The integration of environmental decision-making and policy formulation into all major policy areas of the EU.

In particular, the main objectives of the Sixth Environment Action Programme were the introduction of 'sustainable development' concept and the interest of focuses on the sustainable management of natural resources and waste. The Programme identifies the reduction of waste as a specific objective and sets a target of reducing the quantity of waste going to final disposal by 20% by 2010 and by 50% by 2050(Williams, 2005). The actions required to achieve these targets include:

• the development of a strategy for the sustainable management of natural resources by laying down priorities and reducing consumption;

• the taxation of natural resource use;

• establishing a strategy for the recycling of waste;

• the improvement of existing waste management schemes;

• investment into waste prevention and integration of waste prevention into other EU policies and strategies.

The concept of 'sustainable development' has developed from the 1992 United Nations Rio Conference on Environment and Development, through to the Johannesburg World Summit on Sustainable Development (2002). The most widely recognized definitions is:

"Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs "(WCED, 1987)

The concept requires that society takes decisions with proper regard to their environmental impacts. The concept tries to strike a balance between two objectives, the continued economic development

and achievement of higher standards of living both for today's society and for future generations, but also to protect and enhance the environment.

The economic development of society clearly has an impact on the environment since natural resources are used and by-product pollution and waste are produced in many processes. However, sustainable development promotes development by encouraging environmentally friendly economic activity and by discouraging environmentally damaging activities. Such activities include energy efficiency measures, improved technology and techniques of management, better product design and marketing, environmentally friendly farming practices, making better use of land and buildings and improved transport efficiency and waste minimization (Sustainable Development 1994; This Common Inheritance 1996).

In the same year, Hermann Daly, one of the most important founders of ecological economics, brought back the sustainable development conception three general conditions, concerning the use of natural resources by the human. They are:

- The speed of the consumption of resources equals the speed of regeneration.
- The rate of production of the waste does not exceed the natural capacity of absorption by ecosystems in which waste is emitted.
- The stock of non-renewable resources must remain constant over time.

The treatment and disposal of waste is one of the central themes of sustainable development.

The approach of the European Union and its member states for the management of waste has developed via a series of Directives and Programmes into a strategy concerning the treatment of waste which has the key objectives of minimizing the amount of waste that is produced and to minimize any risk of pollution of the environment.

2.2 Waste management strategy and legislation aspect

Our society is growing wealthier, and as a consequence, the quantity of waste produced is increasing more and more. In this contest, it is clear that treating and disposing of all this materials, is a problem of major importance. The EU Environment Action Programs, identifies waste prevention and management as one of the priorities. The EU is aiming for a significant cut in the amount of waste generated, through new waste prevention initiatives such as a better use of resources and a sustainable development.

A modern waste management strategy is based on a strategy that actually follows the European waste management hierarchy, that can be summarized into the figure 1.1.
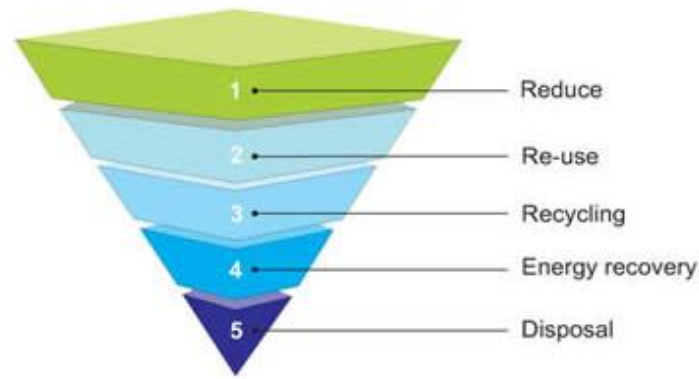
figure 1.1:Waste management hierarchy in Europe. The priority decrease from the top to the bottom.

All member states shall apply this priority order in their waste management strategies. The waste framework directive is the Directive 2008/98/CE, that sets the basic concepts and definitions related to waste management.

The directive lays down basic waste management principles that have to be applied by member states; it requires that waste be managed without endangering human health and harming the environment without causing risk to water, air, soil, plants or animals, without causing a nuisance through noise or odours.

Another directive of primary importance is the one concerning landfilling of waste, the Directive 1999/31/EC European directive for waste disposal by landfill (European Community, 1999).
The purpose of this directive is to set up prescriptions with the aim of prevent and reduce the negative consequences on environment on water, soil, atmosphere and human health, caused by the use of a landfill. It distinguish three different types of landfill, define standard procedure for the acceptance of waste, establishes a procedure for granting authorization to operate a landfill.
It requires that member states should operate a national strategy in order to proceed with the reduction of waste biodegradable in landfills. This gradual reduction of the quantities of biodegradable municipal waste to be placed in landfill shall be in accordance with an established schedule. Changes have been made by Directive 2003/33/CE, concerning new procedures for the acceptance of waste. In the Italian law, the Directive 2008/98/CE has been enforced by the D. Lgs 152/2006 (Italian environmental code)in the fourth part containing rules on waste management and remediation of contaminated sites (Articles 177-266) and then modified by the D.L.gs 205/ 2010 that is a remedial to the Italian environmental code.

The Directive1999/99/CE has been enforced by the D. Lgs 36/2003 in which are of particular relevance the construction criteria and management exposed in Annex1 and plans of operations, environmental restoration, post-operative management monitoring and financial control in Annex2.

To summarize, the reference regulation on solid waste are the following:

- Landfill Directive 1999/31/EC European directive for waste disposal by landfill (European Community, 1999).
- D. Lgs 36/2003 Italian decree for waste disposal by landfill (D. Lgs 36/2003).
- D. Lgs 152/2006 Italian environmental code (D. Lgs 152/2006).

2.3 Sustainable landfill

According to the different management options (figure 1.1), landfilling is always the bad solution, to be avoided or minimized; but landfill represent a fundamental step because it is impossible to think to have no waste going to landfills or, in other words, a landfill is always needed as final step of a waste management system.

Is possible to consider the landfill as a Continuous Stirred Tank Reactor (CSTR) (Cossu, 2004) in which liquid, solid and gaseous materials interact giving rise to liquid (leachate) and gas (biogas) emissions together with a solid phase (the landfilled waste) representing a source of potential residual emissions (figure 1.2). Gas and leachate emissions contain substances capable of contaminating the environment, in particular for a given input, the output is function of the inside reaction that occur in the reactor (chemical, physical, biological) (Cossu, 2010).

The emissions control occurs by means of barrier understood as instrument to reduce, attenuate or prevent the spread of uncontrolled emissions to the environment and consequent onset of environmental and health (Cossu, 2004).

In the recent decades it has developed a new concept of the landfill, the contained landfill, where the control of biogas and leachate emission occur by physical barriers (liners and drainage systems).

However, many researchers have found that the physical barriers lose their efficiency in approximately 10-30 years. When liners fail a variety of compounds whose concentration may be above the acceptable level (table values) spread into the environment. Table 1.1 shows a comparison of the approximate duration of the different types of barriers (Cossu, 2005).

Duration, years	10	30	>100
Geomembrane	X		
Clay liner	X	X	
Drainage	X		
Top cover	X	X	
Natural barrier	X	X	X

The major problem consists in the fact that the emissions potentials from landfills (biogas and leachate) can last for a very long time (centuries). Different landfill concepts have different long term behavior that is qualitatively represented in Figure 1.2.
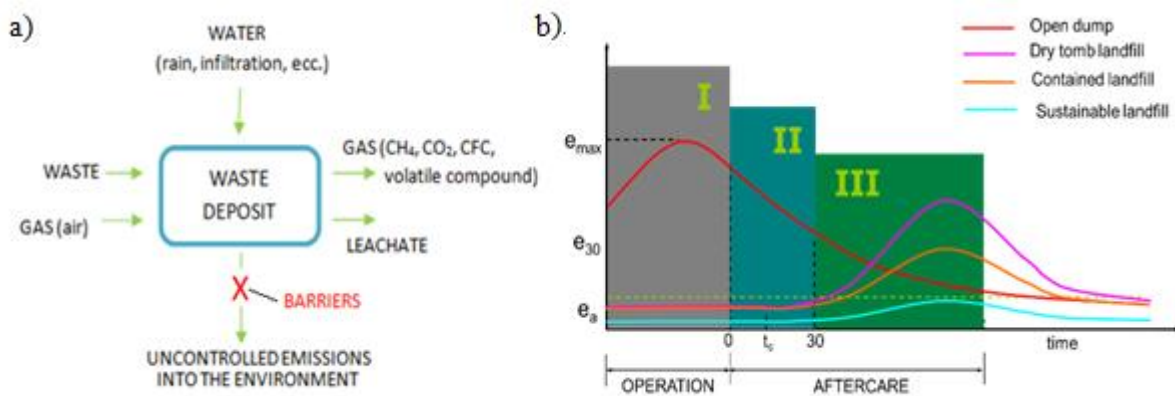
figure 1.2 :figure a) on the left, the landfill reactor. In the figures the input (water, waste, air and water) and output (biogas and leachate) flows are indicated. Figure b) on the right, the long term behavior of different landfill concepts: open dump, dry tomb, contained landfill, sustainable landfill. The acceptable level of emissions to the environment (EA) is indicated. (Cossu 2005)

Open Dumps

The oldest practice of waste disposal was open dumps. In open dumps, all types of waste are stacked on top of each other and they are in contact with the environment. Therefore, open dumps did not provide adequate environmental protection and have not been accepted as a good waste management method. The problems related to open dumps include the ground water and surface water contamination with leachate, uncontrolled production and release of greenhouse and toxic gases, and slow rate of waste degradation and stabilization (Pacey et al., 1999; Yuen, 2001). Open dumps presents very high emissions during the management phase, which, however, tend to decrease over time: the infiltration of air and the flushing effect, due to the entry of rainwater, allow a significant reduction in the pollution potential of the landfill.

Contained landfills and Dry tombs

Contained landfill are designed respecting the national law. They include a cover to reduce infiltration, an impermeable lower liner to block the movement of leachate into ground water and a leachate and biogas collection system.

In the case of a contained landfill, uncontrolled emissions remain below the acceptable emission value for all the time in which the physical barriers (liners and drainage of leachate) maintain their efficiency.

When the barriers lose in the short or medium term their efficiency (to a malfunction), in this case you can register uncontrolled emissions that may exceed the level of acceptability.

In the case of dry tomb, the long term emissions are even more substantial. This type of landfill, provides for a total sealing of the landfill body, so as to minimize not only the emission of biogas and leachate, but also any air or water infiltration of rainwater into the waste body. The necessary conditions for the degradation reactions, doesn't establish, the emission potential of the waste thus remains unaltered until the insulation systems do not begin to deteriorate, again allowing the ingress of water and air. So those types of landfill which tend to maintain low the production of leachate (contained landfill, dry tomb) are the ones that most can create environmental problems in post-management.

Sustainable landfills

Sustainable Landfill is a modern type of landfill currently being developed on the basis of past experience, on the findings of technical and scientific research and according to ongoing environmental challenges (Cossu, 2010).

This landfill are designed in order to take into account the positive aspects of past landfills such containment and treatment of emissions, waste minimization and pretreatment together with a coherent long-term strategy for the control of emissions and climate change issues (Cossu, 2010).

The aims of sustainable landfill is:

- achievement of final storage quality (FSQ) of the landfilled waste, i.e. a situation where active environmental protection measures at the landfill are no longer necessary and the leachate is acceptable in the surrounding environment,
- controlling the accumulation of mobilizable substances and uncontrolled emissions,
- closing the material cycle (Cossu,2009).

Starting from the first point a landfill can be defined as sustainable if it gives, at the end of the management stage (25-30 years), emissions and impacts that are sustainable for the natural

environment or better that do not change in a considerable way quality of the surrounding air, water, groundwater (Hjelmar and Hansen, 2005; Stegmann et al., 2003).

Current European landfills legislation (1999/31/CE) dictates that aftercare should continue for at least 30 years after closure of a landfill; during this period monitoring and maintenance are guarantee by waste fee. If the emissions doesn't achieve sustainable impact when aftercare will be interrupt and the site has been closed, the landfill will be a contaminated soil.

In order to achieve environmental sustainability in landfilling an important role is played not only by appropriate waste pretreatment but also by in situ treatment measures such as flushing, aeration or leachate recirculation.

2.3.3 Strategy to achieve final storage quality

In order to achieve landfill sustainability objective, it's necessary to work applying technologies and operative methods that allow to overcame the traditional landfill model.

There are numerous strategy. It's possible to act on the quantity (reduce the amount of waste to landfilling) and on the quality of the waste (reduce biodegradable organic matter content).

For this reason, waste pretreatment play an important role for reach sustainable situation.

It's possible to adopt a combination of mechanical and biological pretreatment (MBP), whit the aim to reduce the processes taking place in the landfill over a long period of time (decades) into several months. The emission potential of the waste will be reduce to a large extent during pretreatment so that, compared to un-pretreated waste, significantly reduced emission occurs (Stegmann, 2005). However, the use of pretreatment it's not sufficient to guarantee the final storage quality in a sustainable time-span, for this reason, it's possible to associated on MBP a in situ treatment, such us flushing, leachate recirculation, or in situ aeration. In the table 1.2 were described the most important characteristic and the main objective of the single branch of treatment.

Tabella1.2: Most important waste pre-treatment.

	Main objectives		
Mechanical biological pretreatmet	• Reduction of leachate and biogas emissions due to the stabilization of waste before disposal • Reduction of the volume occupied landfill due to the recovery of substance and recyclable materials from raw waste • Reduction of permeability and settlement of the waste mass, due to the increase in density • Reduction of odour • Reduction of clogging by biofilm • Lower cost of compaction	Mechanical pre treatment	• Modify the physical characteristic of the material (increase the specific surface area of the waste available to bacterial attack and increase the density of the waste) • Remove particular fraction from the material incoming flow • Obtain different fraction for subsequent treatment or use
		Biological pretreatment	• Stabilize the organic fraction contained in the residual waste • Giving a waste for which residual emission potential is drastically decrease (High stabilization) • Reduce the readily biodegradable organic fraction; acceleration of the subsequent anaerobic reactions (slight stabilization) • In case of anaerobic pre-treatment, we have the following advantages: recover the biogas produced, less space is need, less production of sludge, possibility of odour control, greater efficiency in the reduction of pathogens. On the contrary we have greater construction complexity, long treatment time,management of biogas emissions, increase sensitivity to toxic substances.
Thermal treatment	• Disposal of waste tal quale • Energy recovery		• Reduction in volume (90%) and in weight (70%) of the waste • Reducing the environmental impact of the landfill in relation to gaseous and pollutant load of the leachate • Sterilization of the waste from a biological point of view • It has the disadvantages of high operating costs and investment, secondary impact related to air emissions • Concentration of heavy metals in the ash
In situ treatment	• Substantial reduction in emission potentials of the waste • Rapid transformation and degradation of organic matter • These treatment are applied during normal landfilling activities-aftercare and designed before construction	In situ aeration	• Reduction in the duration of long term environmental impact due to the very fast aerobic kinetics • Fast transformation of biodegradable organic compound present in the leachate. The leachate has a inorganic and refractory products load that do not involve environmental hazards. • Once achieve stabilization, the production of methane is minimal . The uncontrolled emission of landfill gas to the atmosphere are eliminated. • Improves the stability of the site, which can also be reinstated whit the landscape.
		Leacahte recirculation	• Stimulate biological reaction • Supply the optimum moisture requirement • Reintroduced nutrients in the waste mass • Homogenizing the environmental allowing better contact between the microbes and substrate • Diluting the inhibitory compounds • In anaerobic landfill increase the production of biogas. Attention must pay during the acidogenic phase
		Flushing	• Reduce the polluting potential of waste by strong washout • The contaminants are converted into liquid phase (in traditional landfills, 90% is removed by biogas) • The addition of liquid is such as to ensure a uniform distribution of moisture and to reach a water content value equal to the field capacity of the waste • In anaerobic landfills, the potential biogas is reduced by the removal of compound via the leachate • Possible saturation condition of the waste

3. Carbon uptake in landfills and its speciation

The pollutants in a landfill can be thousands, form different families, with different effects. This abundance is due to the delivery to disposal of almost everything, potential hazardous objects too. Generally, the trace pollutants are not a problem because the mineral barriers will catch them and because they can be diluted in waste body. The real problem comes from the family of compounds present in great quantity. The idea is to make a mass balance considering the elemental species: carbon, nitrogen, chlorides, sulphur (sulphates), and heavy metals mainly. The balances that generally regard a landfill are mainly the carbon and the nitrogen ones, because biodegradable organic substance and ammonia are the main two problematic polluters in leachate and because anaerobic conditions generate biogas that must be managed. In these chapter particular attention will focus on carbon and its speciation. Before to implement a mass balance, it's important to understand what are the carbon flux that enter in a landfill and through which paths go away. Landfill can then be placed in a broader context, considering the role that it occupies in the global carbon cycle. Mass balances are a useful tool for analyzing mobility-stability of compounds, their chemical or biological reactions, the oxidative states and their influence in other compounds presence and allow to understand how a specific elements has been distributed during the time among the principal emission form, such as leachate, biogas and residual waste.

3.1 Carbon flux in a landfill

In the previous chapters has been discussion about the concepts of Final Storage Quality and sustainable landfill, underlining the importance to give to next generations an environment in the same conditions as it is characterized of nowadays (Cossu, 1995). In this context, the landfill is perceived primarily as a source of emissions, in particular due to migration of biogas and leachate: the achievement of the sustainability condition and Final Storage Quality provides the reduction of these emissions up to a level that can be considered environmentally acceptable. Particular attention, however, must be paid not only to quantify the release of various contaminants, but also the assessment of the capacity of the landfill to uptake them, in a manner and variables form. In particular, it is interesting to observe and study the fate of carbon, since it represents one of the main constituents of the biodegradable and not biodegradable organic matter present in the waste.

It is contained in proteins, carbohydrates and fats derived from animal waste, which are degraded by anaerobic processes; in cellulose, hemicellulose present in paper products and garden waste, which represent in the long-term almost 90 % of the methanigen potential in a landfill (Barlaz, 1998) and in the lignin, which is present in all the derivatives of the wood, recalcitrant to anaerobic

decomposition. Moreover, the carbon is contained in the composite products from plastic, biodegradable although in very long times (Bogner and Spokas, 1993).

The most common types of waste containing organic carbon and considered in the global carbon balance are: municipal solid waste, sludge derived by treatment plant, agricultural and animal waste, construction and demolition waste, industrial waste.

During operating phase of the landfill a part of the carbon is gasified and converted into biogas (CO_2, CH_4) and another is leached in the form of leachate composed mostly from soluble organic compounds (volatile fatty acids, humic acids, fulvic). Therefore, the organic carbon in landfill can be expressed by

$$Ctot = Cgas + Cliq + Csol$$

The carbon that is not released into the biogas or the leachate, is mainly due to the presence of plastic substances and lignin, and less due to cellulosic material. This portion of the solid fraction remains in the long period in a landfill and contribute to the formation in a long period of a geological deposit. This shows that the landfill may be have a value as a carbon sink (see sub chapter 3.3) and to participate in the potential reduction of CO_2. A detailed description of how the carbon is removed through biogas and leachate is provided in the sub chapter 4.2. Considering a short time span, the transformation of the readily biodegradable compound lead to the formation of non-reactive solid mass, which has the characteristic of humic substances. It may be present under different form such as humin (insoluble substances in acid and basic solution), humic acids (Substance soluble in solution whit pH>2), fulvic acids (soluble substance at any pH). Humic substances are generally characterized by a color between yellow and black and by high molecular weight and are refractory to degradation (Nimmagadda and McRae, 2007). Their structure is not well known, behave as anionic polyelectrolytes, being their charge due to the presence of phenolic and carboxylic groups. Contain both aromatic and aliphatic groups: the degree of aromatic condensation increases with age of the waste, indicating an increase in structural complexity. Generally, fulvic acids have a greater number of carboxyl groups and a lower degree of aromaticity with respect to humin (Aulin et al.,1997). Their importance in landfill is linked to their ability to create complex with heavy metals, influencing the mobility and retention during the stabilization processes. The final degree of decomposition of the waste and the speed with which it occurs is related to the environmental conditions in which degradation processes occur, especially on factors such as pH, moisture and temperature.

3.2 Carbon mass balance

To verified the achieving of geological repository condition, it's possible to use, from the one hand, a mass balance of the total carbon present in the landfill, on the other a speciation of carbon in the

residual waste. The mass balance allow to evaluate and quantify, how carbon is distributed over time among the main forms of emissions, leachate and biogas, and the residual waste.

Here Carbon mass balance is explained.

Generally, assuming the landfill as a CSTR, the balance equation may be resume as follow:

$$Accumulation = input - output + production - consumption$$

That is the mass conservation formula where: accumulation is what remains in landfill after the time dt, input is the waste income, output are the wanted or unwanted emission of leachate and biogas, production and consumption are the reaction happening inside waste body (Cossu et al., 2004).The global balance are represent by

$$\frac{dx}{dt}fix + \frac{dx}{dt}mob = \sum_i (Xsi * Qsi) - Xl * Qlc - Xl * Qlu - Xg * Qgc - Xg * Qgu - rV$$

The accumulation is in the left, the summary is the input considering all the different commodity-related source of the compound, the reaction term is the last one and all the subtractions are the emissions. Below are explained the single term:

$\frac{dx}{dt}fix$	Is the accumulation in fixed form, no more mobile, that does not cause problems anymore. This is the term is wanted to be increase
$\frac{dx}{dt}mob$	Is the accumulation in mobile form. This matter can still react or be emitted somehow
$\sum_i (Xsi * Qsi)$	Is the total waste input that is the sum of the quantity of the flux each merceologic category (t/y) multiply by the carbon content of each merceologic category (KgTOC/ t).
$Xl * Qlr$	Is the mass of carbon emitted in a controlled way by leaching: Qlr is the flux of leachate collected (m^3/y), Xl is the compound fraction in leachate (KgTOC/ Nm^3).
$Xl * Qlu$	Is the mass of carbon emitted in an uncontrolled way by leaching: Qlu is the flux of leachate that escape the collection and reach the environment outside the barriers (m^3/y), Xl is the compound fraction in leachate (KgTOC/ Nm^3).
$Xg * Qgc$	Is the mass of carbon emitted in a controlled way by gas: Qgc is the flux of biogascollected (Nm^3/y), Xg is the carbon fraction in biogas (KgC/ Nm^3).
$Xg * Qgu$	Is the mass of carbon emitted in an uncontrolled way by gas: Qgu is the flux of biogas that escape the gas collection systems (Nm^3/y), Xg is the carbon fraction in biogas (KgC/ Nm^3).
rV	Is the reaction term, composed by the volume of reactor plus the kinetic constant. According with the compound characteristics and with the reaction conditions the kinetic constant can change very much
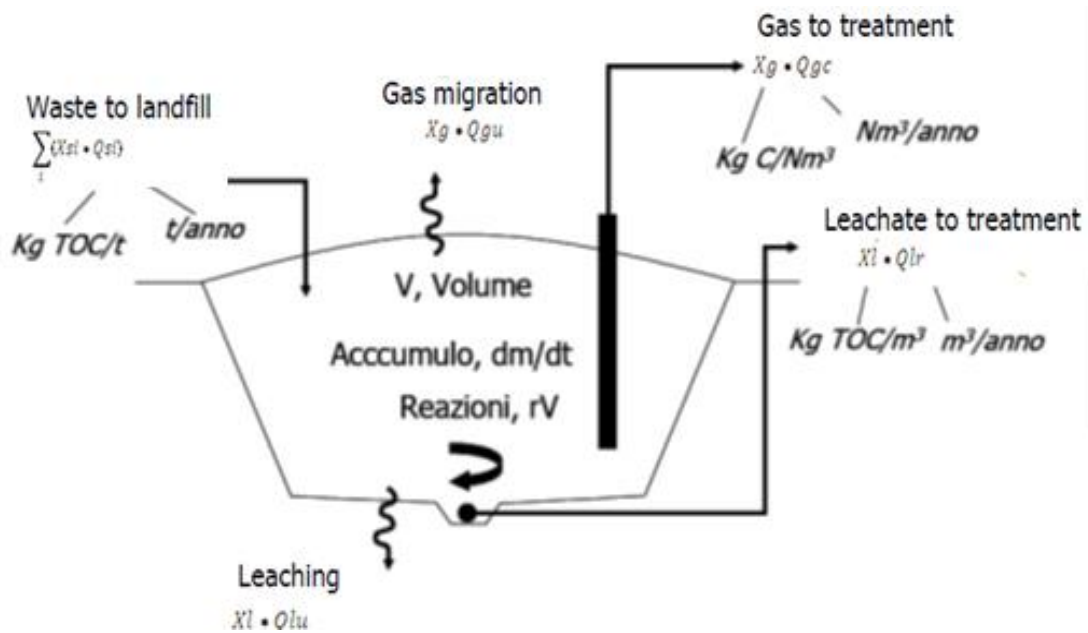
figure 1.3: Mass balance scheme and its related terms (Cossu 2004)

The landfill goal is to avoid environmental pollution, before the stabilization of the waste. For this purpose it is necessary to rewrite the main equation transferring to left the uncontrolled emission to be avoided and to right all other terms.

$$Xl * Qlu + Xg * Qgu = \sum_i (Xsi * Qsi) - Xl * Qlc - Xg * Qgc - \frac{dx}{dt} fix - \frac{dx}{dt} mob - rV$$

According with this mathematical equation, in order to avoid the uncontrolled pollution, in short and long term, it is necessary to avoid waste input (with minimization of waste, reuse, recycle), increase reactions (with increase kinetics, aerobic reactions, nutrient supply, recirculation of leachate), increase stable accumulation forms, increase leachate controlled emissions (allowing and facilitating water input in landfill) and increase gas controlled emissions (with a good collection pipes system).

In particular, the main objective is to achieve, in long-term period, an equilibrium condition, in which the mass of carbon is mainly present in a stable form, not further degradable or leachable, forming the basis for the geologic deposit.

Finally It's possible to use a speciation in order to evaluate in which form the carbon result in the residual waste and thus be able to distinguish the accumulation in stable form from that in the mobilizable form.

3.3 Landfill as Carbon sink

In any cycle of individual element (Carbon ,Nitrogen, ecc) we mobilize geological resources (ore, fossil fuel) to obtain a supply of energy and material, after sequential transformation. In order to

avoid dystrophic accumulation of element and their uncontrolled mobilization in the environment, a sink returning the element to a geological like deposit in which they are permanently immobilized (mineralized to rock or transformed into a stable form), is mandatory (Cossu and Piovesan, 2007). Whit regard the mobility of Carbon, in waste composition, two distinct fraction can be identified: non mobile, stable solid fraction (insoluble non degradable) Xs such as lignin, humic acid and plastic, and mobile solid fraction Ss (cellulose, hemicellulose, fat). The mobile fraction Ss, by means of leaching, biodegradation or other reactions, can be transferred from the solid to the liquid (Sl = leached fraction, such as VFA, carbohydrates, COD) or gas phase (Sg = gasified fraction, such as CO_2 and CH_4) or could be converted into a non-mobile stable form that contributes towards increasing the Xs fraction. (Cossu, 2012). To achieve the safest protection system possible, environmental engineers must work to minimize the mobile fraction Ss and to increase the non-mobile one.

This can be achieved by means of waste pretreatment before landfilling and/or by means of in-situ treatment during the operational phase of the landfill until an optimal waste quality, or by additional treatment during the aftercare phase until a FSQ is reached. This intervention will be capable of progressively transforming the mass of mobile elements and compounds into leached or gasified compounds and in a residual low or immobile fraction in equilibrium with the environment.

Subsequently geological processes will gradually establish rock quality conditions (Cossu, 2012).

In achieving the above goals, the landfill acts as a final sink, along-term geological deposit which closes the material loop. This aspect is particularly evident when referring to the role of carbon sink undertaken by a landfill in limiting the production of greenhouse gases. Numerous researchers maintain that this role maybe of a similar importance to that carried out by the major natural sinks such as marine sediments (Bogner, 2005).

To conclude, landfill, conceived as the long-term burial of waste, is an unavoidable virtuous system implicated in the control of the environmental mobility of elements. A modern landfill will be called upon to carry out the following fundamental roles: environmental sustainability and final geological sink (Cossu, 2012).
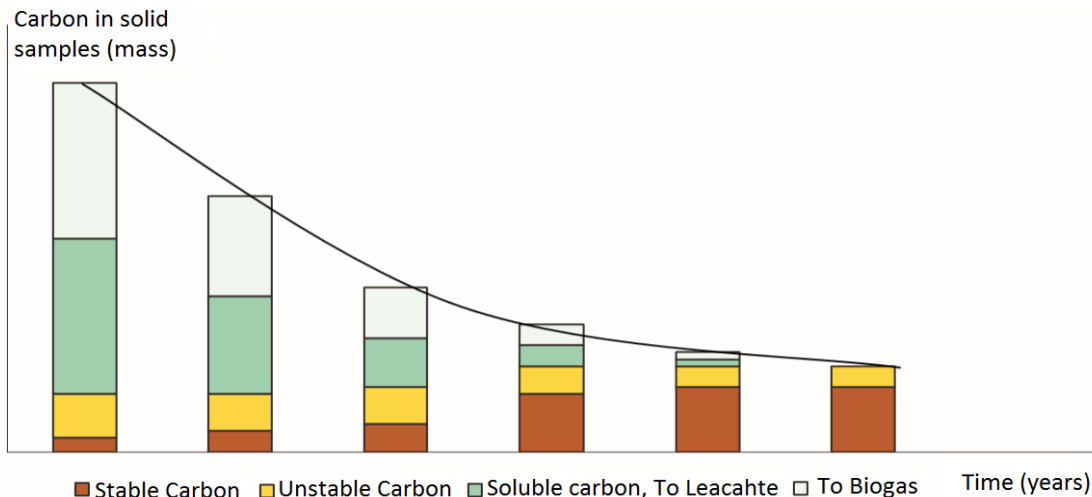
Figure 1.4: Speciation of carbon in a landfill. The carbon initially deliver in a landfill inside waste is mainly unstable degradable and/or soluble carbon that can generate leachate pollution, gas production and reactions. During years, the carbon will be partially extract and partially becomes a stable immobile form. At the end of this process it will be all stable compound that create no problems anymore (Carbon sink). The velocity of this process depends mainly on the site conditions and on the landfill management apply.

4. Processes and impact of traditional sanitary landfill

As seen in the previous chapter, landfill should be considered as a physic-chemical reactor where the input are represented by rain water, waste or infiltration, and the output by leachate and biogas. The quality and the quantity of the output depends by the biochemical reaction that occur inside the landfill body and the characteristic of the input. It's important to understood this mechanism if we wont to minimize the potential environmental impact.

The chemical, physic, physico-chemical and microbiological processes related to the organic substance are the major responsible to the formation of biogas and leachate in MSW landfill. The biodegradability of organic fraction depends also on the physical and chemical properties as well as environmental factors such as temperature, moisture and pH.

The mechanism which regulate the biogas formation and the mass transfer from wastes to leaching water, from which leachate originates, can be divide into three categories:
- Hydrolysis of solid waste and biological degradation;
- Solubilization of soluble salts contained in the water;
- Dragging of particulate matter.

Among the processes described above, the most important are the hydrolysis and the aerobic and anaerobic degradation of organic substances.

The hydrolysis of organic catalyzed by bacteria and extracellular hydrolytic enzyme, allow to transform complex substances (carbohydrates, protein, fat, cellulose) into simple molecules. In this way, it's possible to penetrate the cellular membrane through the active enzymatic transport. The

aerobic degradation of organic substances convert the molecule, hydrolyzed before into CO_2, water, nitrates and sulfates. Anaerobic degradation is described as a series of processes involving microorganisms to break down biodegradable material in the absence of oxygen. The overall result of anaerobic digestion is a nearly complete conversion of the biodegradable organic material into methane, carbon dioxide, hydrogen sulfide, ammonia and new bacterial biomass.

In this chapter the various phases of waste stabilization process and the waste degradation sequences that occur in a landfill are described. Additionally a sub-chapter on the factor that affect the anaerobic degradation are briefly discuss.

4.1 Biological degradation processes

4.1.1 Aerobic degradation

Hydrolysis or aerobic degradation is the first process and generally occurs during or after waste has been disposed at a landfill site. The availability of a solid substrate is a prerequisite for its solubilization in an aqueous phase (Aguilar-Juarez, 2000).The organic fraction of the waste is metabolized by aerobic organisms, in particular complex substances are converted into simple molecule:

-   proteins are transformed into amminoacids and CO_2, H_2O, nitrate and sulfate,
-   cellulose and hemicellulose, are degraded into glucose, thanks to extracellular enzyme which are then used by bacteria and converted into CO_2 and H_2O
-   Carbohydrate are hydrolyzed in monosaccharaides and after converted into CO_2 and H_2O
-   Fats are transformed into fatty acids and glycerol.

Intense metabolism (exothermic reaction) generates heat which leads to an increase in temperature, of up to 60-70 °C. Well compacted waste result in a low availability of O_2 which in turn results in low temperatures (Andreottola and Cannas, 1996). Lu et al., 1995, states that the length of the aerobic phase depends on the compacted of the landfill and since the O_2 penetration is low in high density landfills, the anaerobic processes usually dominate. The duration of this stage depends on the availability of O_2 and can also be influenced by the management practices of the landfill site (e.g. air injection after landfill disposal (Stegmann and Ritzkowski, 2007).

During this phase, there is not a net gas production. If we consider the degradation reaction of glucose:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + \text{biomass} + \text{heat}$$
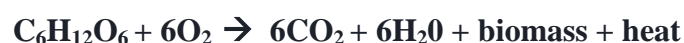
The major decomposition products are CO_2 and H_2O. CO_2 can be released as gas or is absorbed into water to form carbonic acid which gives acidity to the leachate.

The CO_2 produced has approximately the same moles as the O_2 used with very little displacement of N_2 (Christensen and Kjenldsen, 1989). The odors emitted at this stage is due to the formation of organic esters. As the concentration of O_2 decreases creating an anaerobic condition, aerobic microorganisms are replaced by facultative anaerobes and consequently obligate anaerobic microorganism (Loukidou and Zouboulis, 2001).

4.1.2 Anaerobic degradation

The predominant part of the landfill waste will soon after disposal become anaerobic, and a different group of bacteria will start degrading the organic carbon. The processes converting organic carbon are complex and a short presentation is need to understand the overall process.

The figure 1.5 represent the result of the most important interaction between bacterial groups, the involved substrate and the intermediate products. Anaerobic degradation can be viewed as constituted of three stage. In the first step the solid and complex, dissolved organic compounds are hydrolyzed and fermented by the fermentative bacteria to volatile fatty acids, alcohol, carbon dioxide, hydrogen. In the second step, acetogenic bacteria degrade the fermentation products into acetic acids, hydrogen and carbon dioxide. Finally there is the methane production by the methanogenic bacteria, that can be used as substrate both acetic acids (acetophilic bacteria) and Hydrogen and carbon dioxide (hydrogenophilic bacteria).These stages will be discussed in detail in the following sections.
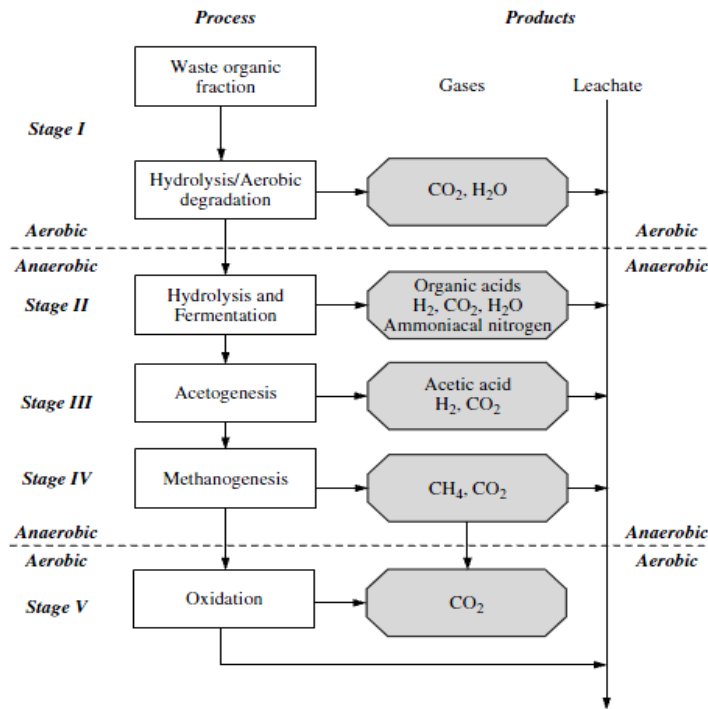
Figure 1.5 Major stage of waste degradation in landfills. (Waste management paper 26B, 1995)

Anaerobic degradation processes occurs whit a net consumption of water, as result by follow general formulation (Christensen and Kjeldsen, 1989):

$$C_n H_a O_b + \left(n - \frac{a}{4} - \frac{b}{2} \right) H_2O \rightarrow \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4} \right) CO_2 + \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} \right) CH_4$$
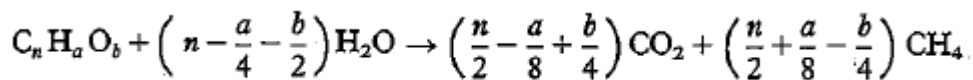
It's important to underline the role of moisture, because create the ideal condition to bacterial metabolism. In particular for the hydrolytic processes where the solid organic substances must be solubilized before the microorganism can convert it. After the smaller, easily soluble part of the organic matter has been converted, the hydrolysis may prove to be the overall rate-limiting process in the landfill environment (Cristensen and Kjeldsen, 1989). The fermenters are a large heterogeneous group of anaerobic and facultative anaerobic bacteria. The acetogenic bacteria are also a large heterogenic group, instead, the methanogenic bacteria are obligate anaerobic and require very low redox potential. Finally, the sulphate-reducing bacteria is mentioned. This group in many ways resembles the methanogenic group and since is a major compound of many waste types. The sulphate-reducing bacteria are obligate anaerobic and may convert hydrogen, acetic acid and high volatile fatty acids during sulphate reduction. However, the organic carbon s always oxidized to CO_2 as opposed to the conversion by the methanogenic group (Cristensen and Kjeldsen, 1989).

4.2 Waste degradation sequences

The combination of the various degradation reactions and the variability of inhibition abiotic factors have led to the speculation on a theoretical sequence of the involved anaerobic degradation

processes and their consequences as to gas and leachate composition. Figure 1.6 illustrate the development in gas and leachate in a landfill cell (Cristensen and Kjeldsen, 1989).

Hydrolysis

This is a short aerobic phase immediately after landfilling the waste. Here the easily degradable organic matter is aerobically decomposed, hence the oxygen tend to zero, while there is a CO_2 formation and a very little displacement of N_2 occurs. In this phase compound such us polysaccharides, proteins and lipids (fats and greases), cellulose (that is the major part of organic waste) are hydrolyzed by extracellular enzyme in soluble products (increase in COD). In the liquid phase we aspect an increase in ammonia nitrogen due to the accumulation of the hydrolysis of organic nitrogen.

Iron and zinc are solubilized and we have the formation of sulphate. The duration of this phase is limited in a few days.

Fermentation

As a result of the depletion of O_2 from the previous stage, anaerobic condition develops. During this stage the monomers produced during the hydrolysis, such us simple sugars, amino acids, glycerin and fatty acids are consequently decomposed to CO_2, H_2, NH_3 and organic acids with soluble intermediates like acetone, inorganic salts and sulphates (Peavy et al., 1985). The organic acids are mainly propionic (CH_3CH_2COOH), butyric ($CH_3C_2H_4COOH$), acetic (CH_3COOH) and formic acids ($HCOOH$) and their formation, that depends on the composition of the waste, tend to decrease the pH. The content of nitrogen in the gas is reduced due to the generation of CO_2 and H_2 and there is no formation of CH_4 at this stage. The leachate derived at this stage is rich in ammonia nitrogen (due to the hydrolysis and fermentation of proteinases compound). Lignin on the contrary is not degraded by anaerobic bacteria and does not decompose significantly.

The temperature in the landfill drops to between 30°C and 50°C. CO_2 and H_2 concentration at this stage may rise by 80 % and 20 % respectively.

When the redox potential tend to decrease, sulphates (SO_4^{2-}) are reduce in sulphites. Iron and Zinc could also be precipitate whit sulphate, such us other metal. Leachate pH is around 5.5 and 6.5. The fermentative processes are summarized below:

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + H_2 + 2CO_2$$
$$C_6H_{12}O_6 \rightarrow CH_3C_2H_4COOH + 2H_2 + 2CO_2$$
$$C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2$$
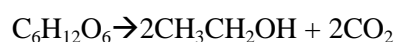
Acetogenesis

In this stage, acetogenic bacteria, convert the products of the previous phase to simple organic acids (mainly acetic acids), CO_2 and H_2 in anaerobic condition. Leachate contain very high level of COD due to the presence of carbossilic acids.

Some other bacteria convert carbohydrates, to acetic acid in the presence of H_2 and CO_2. H_2 and CO_2 concentration decrease throughout this stage, as methane producing bacteria use it at a rapid rate. The low H_2 concentration promotes the formation of methanogens, which generate CH_4 and CO_2 from organic acids and organic acids derivatives produced in stage two.

The increased acidic conditions in this stage cause metal ions to be more soluble, increasing their concentration in leachate. Also organic acids, chlorides ions, ammonium ions and phosphates ions are all in high concentration, forming complexes with metal ions increasing their solubility (Neil,2005). There is a possibility for the formation of hydrogen sulphide (H_2S) in this stage because the sulphate compounds found in the waste are reduced to H_2S by sulphate reducing microorganisms. The presence of organic acids generates an acidic solution with a pH of 4 or lower (Christensen at al., 1996).

$$CH_3CH_2COOH + 2H_2O \rightarrow CH_3COOH + CO_2 + 3H_2$$
$$CH_3C_2H_4COOH + 2H_2O \rightarrow 2CH_3COOH + 2H_2$$
$$CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 2H_2$$
$$C_6H_5COOH + 4H_2O \rightarrow 3CH_3COOH + H_2$$
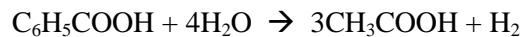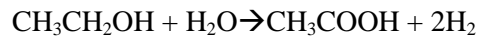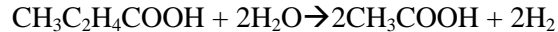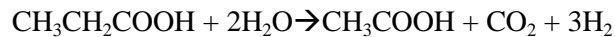
Methanogenesis

As the concentration of H_2 produced in stage three decreases it promotes the formation of methanogenic microorganisms which produce CO_2 and CH_4 from organic acids and their derivatives.

CH_4 can also be formed directly by microorganisms conversion of CO_2 and H_2 to CH_4 and H_2O. This causes the concentration of H_2 produced in stage two and three to fall in stages four (Dahab and Woldt, 1994). Throughout this stages two classes of microorganism are active, the mesophilic bacteria, active in the temperature range of $20 - 45\ °C$, and the thermophilic bacteria, active between $45 - 65\ °C$. Therefore landfill gases are generated at a temperature range of $30 - 65\ °C$, with an optimum temperature of gas production between $30 - 45\ °C$ (Rovers and Farquhar, 1972).

At very low temperature, for example $15\ °C$, biological degradation decreases. Organic acids produced from stage two and three are degraded by the methanogens microorganisms (Castaldi et

al., 2005). As the acids are depleted the pH rises to about 7 – 8. However the ideal pH range for the action of methanogens is between 6.8 and 7.5 (Gerardi, 2003).

The sulphate-reducing bacteria is mentioned, since this group of bacteria in many ways resembles the methanogenic group and since sulphate is a major compound of many waste type (demolition waste, fly ashes). This type of bacteria are obligate anaerobic and may convert H_2, acetic acid and VFA during sulphate reduction. Methanogenesis is the longest stage in all the landfill processes taking from six months to several years for this process to commence after the waste

has been land filled , depending on the water content and the water circulation. Most often, a considerable amount of CH_4 is produced only after three to twelve months depending on the development of the anaerobic organisms and waste degradation products. Other author suggested that stages one to four occurs in approximately 180 days, or a time of approximately 250 days or 500 days (Asah M.K,, 2007). Methanogenic and sulphate reducing processes are reported below:

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \qquad\qquad 4H_2 + SO_4^{2-} + H^+ \rightarrow HS^- + 4H_2O$$
$$CH_3COOH + 3H_2 \rightarrow CH_4 + CO_2 \qquad\qquad CH_3COOH + SO_4^{2-} \rightarrow CO_2 + HS^- + HCO_3^- + H_2O$$
$$HCOOH \rightarrow CH_4 + 2H_2O \qquad\qquad 2CH_3C_2H_4COOH + H^+ + SO_4^{2-} \rightarrow 4CH_3COOH + HS^-$$
$$CH_3OH + H_2 \rightarrow CH_4 + H_2O$$
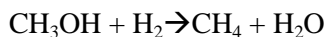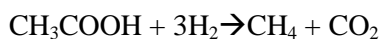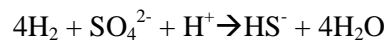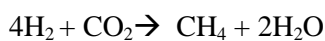
Final Oxidation phase

When the biodegradable organic substances were totally degraded, the production of methane and the concentration of fatty acids tend to zero. Only the more refractory organic carbon remaining the landfilled waste (Humic acid, fulvic acids, ecc) that give a residual COD around hundred mg/l. At this stage new aerobic microorganisms slowly replace anaerobic forms and aerobic conditions are re- established (USEPA, 1998). Nitrogen start to appear in the landfill gas again to the diffusion from the atmosphere. In cases where waste has a high concentration of sulphate, hydrogen sulphite gas may be formed. All the processes in a landfill site can be described diagrammatically as in Figure 1.6. It is important to underline that this ideal sequences is dealing whit a homogeneous waste volume, and the length of each phase should be estimated based on the abiotic factor, local condition, waste composition and landfill procedure.

Gas composition, vol %

Leachate

Leachate

Phase I II III IV V
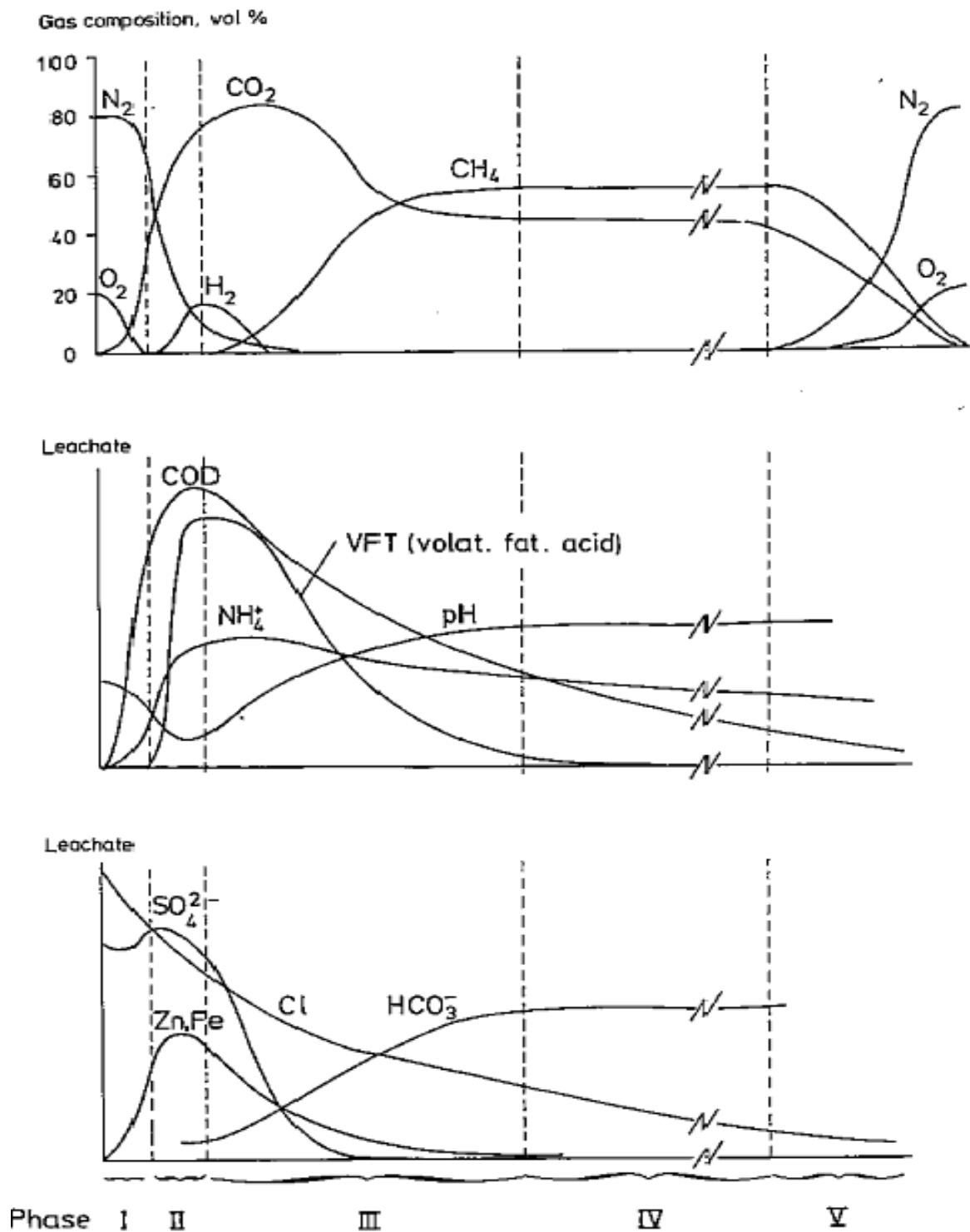
figure 1.6 : Illustration of developments in gas and leachate composition in a landfill cell (Kristensen and Kjeldsens 1989)

4.2.1 Factors affecting anaerobic waste degradation

Several factors can affect the performance of the anaerobic digestion, either by process enhancement or inhibition, influencing parameters such as specific growth rate, degradation rates,

biogas production or substrate utilization. This sub-chapter will briefly discuss those factors namely: pH, temperature, substrate, and inhibitory substances.

- pH is the driving force that makes possible to start the methanogenesis process (Valencia et al.,2009). Methanogenic bacteria are more susceptible to pH variation than other microorganisms in the microbial community (Khanal, 2008),and operate efficiently only within a narrow pH-range of 6 and 8as suggested by Zehnder et al., (1982), whit an optimal value around 7 – 7.2 (Pfeffer, 1980). The pH is influenced by the volatile acids (VFA) that tend to acidify the solution and ammonia (NH_4^+) that tend to basificate. Both, in the dissociated form (eg, CH_3COOH, NH_3), are inhibitory. The pH range of fermentative and acetogenic bacteria is much wider than methanogenic one. If methanogenic bacteria are stressed by other factor, their conversion of Hydrogen and acid acetic decrease, leading to an accumulation of volatile organic acid and a decrease in pH which may inhibit the methane formation and lead a further decrease in pH until pH value of 4.5 – 5, where the methane production may stop (Christensen at al., 1996). Recent studies had shown that the methanogenesis favored within a range of pH of 6.4 – 7.2 (Chughet al., 1998; Yuenet al., 2001).
In agreement with Gerardi, (2003), the metanogenic process is established starting from pH6.3, with an optimal performance when pH reach range of 6.8 – 7.2. Values of pH below 6 or above 8 are restrictive and somewhat toxic to methane-forming bacteria. Although anaerobic digester efficiency is satisfactory within the pH range of 6.8 to 7.2, it is best when the pH is within the range of 7.0 to 7.2 (Gerandi, 2003). To maintain a stable pH, a high level of alkalinity is required.

- Alkalinity: Sufficient alkalinity is essential for proper pH control. Alkalinity serves as a buffer that prevents rapid change in pH, and must be sufficient to buffer the production of VFAs in the acidogenic phase, to have an optimal biological activity (Ozturk, 1999). Agdad and Sponza (2005) recommend a range of alkalinity from 1000 to 5000 mg$CaCO_3$/ L. Ozturk (1999) concludes that in anaerobic systems, the total value of alkalinity required for optimal production of methane is 2000 – 3500 mg$CaCO_3$/ L. Alkalinity values encountered by Sekman et al (2011) in samples of leachate from waste in reactors with anaerobic and aerobic show that always remains above the 3500 mg$CaCO_3$/ L for the whole period of observation. Other authors suggest that would be need to satisfy of a ratio VFA/mg$CaCO_3$ below 0.8 (Farquhar and Rovers, 1973).

- Moisture Content: Having adequate moisture is an essential requirement in a functional bioreactor. Gas production rates increased whit the moisture content whit maximum production occurring at moisture content from 60% to 80% (Farquhar and Rovers, 1973). The main effect of the increased water content, is probably the facilitated exchange of substrate, nutrients, buffer, and possibly dilution of inhibitors and spreading of micro-organisms between the micro-environment (Christensen at al., 1996). Moreover, the water limiting the oxygen transport from the atmosphere to landfill, and his presence it's fundamental for hydrolysis and acid fermentation stage. As regard the first phase, an excess of moisture can lead to high acid formation and a consequent a decrease of pH whit an inhibition of methanogenic bacteria (Cossu, 2001).
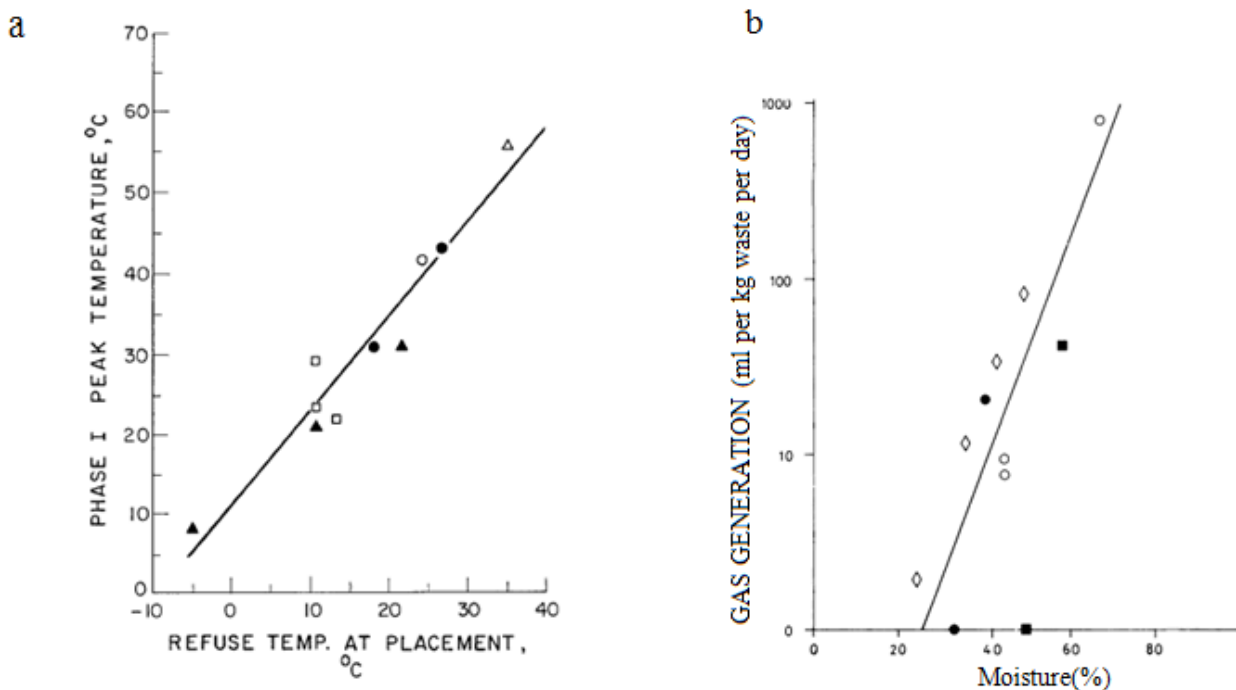
figure 1.7 : a) Phase I peak temperature as a function of refuse temperature at placement (Farquar, G.J. and Rovers, F.A (1973). b) Gas generation rate as a function of moisture content (Kristensen and Kjeldsen 1989)

- Temperature: The anaerobic waste degradation process is affected by temperature from both kinetic and thermodynamic point of view; the rate and yield are increasing with the temperature (Mata-Alvarez, 2003). Most methane-forming bacteria are active in two temperature ranges. The mesophilic group with a maximum rate of gas production at around 35 – 40 °C of temperature range and thermophilic group with a maximum around 55 °C (Mata-Alvarez, 2003; Khanal, 2008). At temperatures between 40 °C and 50 °C, methane-forming bacteria are inhibited. Generally in anaerobic digester, whenever temperature falls below 32 °C, close attention should be paid to the volatile acid to alkalinity ratio. Volatile acid formation continues at depressed temperatures, but methane production proceeds slowly. Volatile acid production

can continue at a rapid rate as low as 21 °C, whereas methane production is essentially non-existent. Therefore, 32 °C is the minimum temperature that should be maintained, and 35°C is the preferred temperature. Similar observation have been made concerning gas production in sanitary landfills. Some author observed maximum gas production between $30 - 35$°C, and both found that gas production rates reduced with deviations from these optimal temperature. Moreover, the temperature achieve a peak value immediately after the refuse placement, as a result of aerobic decomposition . The figure 1.7a show that the magnitude of this temperature is dependent in part, upon the refuse temperature at placement. The time require to achieve this peak should be equal to the duration of Phase I. The maintenance of aerobic condition in landfills creates sustained temperature. However, if the transition to anaerobiosis is made, the temperature reduces (Rovers and Farquhar, 1972).

- Nutrients: Organic and inorganic substances are required for anaerobic waste degradation. In addition to the organic carbon substrate, there is a need for macro nutrients such as nitrogen and phosphorous and micro nutrients such as calcium, magnesium, potassium, nickel, iron, zinc, copper, cobalt, and some vitamins. Various researchers have suggested different ratios of C (expressed as COD), N, and P based on biodegradability of waste, for example, COD:N:P ratio of 100:0.44:0.08 (McCarty, 1964; Christensen and Kjeldsen, 1989) and 350:7:1 (Khanal, 2008). However, an average ratio of COD:N:P of around 100:1.2:0.2 can be recommended for a substrate to be anaerobically degraded (Mata-Alvarez, 2003). However the mixed waste landfill will not be limited by nitrogen and phosphorus, but insufficient homogenization of the waste may result in nutrient-limited environments. Phosphorus is, if any, the nutrient most likely to limit the anaerobic degradation processes (Christensen at al., 1996).

- Inhibitors: The absence of oxygen is an essential condition for the anaerobic bacteria to grow. There are some substances that at a given concentration inhibit the bacterial activity; ammonia-nitrogen above 1500 mg/L (Khanal, 2008) and hydrogen sulphide above 200 mg/ L (Mata-Alvarez, 2003) are inhibitors, while if ammonia is present between 50 and 200 mgN/L guarantee a stimulation effect on methane production. However, the presence of some substances can act as stimulants at their low concentrations or inhabitants at high concentrations (McCarty, 1964). For example, sodium is a stimulant when the concentration ranges between $100 - 200$ mg/L while it is an inhibitor when the concentration is higher than 3000 mg/L.

- The production of VFA during the acidogenic phase (fermentation) is the main responsible for the lowering of the pH. The VFA are oxidized by the acetogenic into CH_3COOH, H_2, CO_2, which are excellent substrates for the methanogenic bacteria. The concentration of VFA and the

performance of anaerobic digestion are closely related (Asah, 2007). The VFA are important intermediates in the pathway of microbial fermentation and can cause stress if they are present in high concentrations, resulting in a lowering of the pH and the failure of digestion. In a correctly designed and well-operated digester, the concentration of total VFA is typically below 500 mg/L as acetic acid. However, if the digester is undersized for the organic load this concentration can be higher. At VFA concentrations over 1.500 – 2.000 mg/L, biogas production might be limited by inhibition (Labatut and Gooch, 2012). Wang et al. , (1999) have conducted analysis to investigate the effect of VFA (court chain for the most part) on the methanogenesis, and concluded that until the VFA not exceed a value that inhibits the methanogenic phase, they are used as excellent substrate by methanogenic bacteria and that inhibition of their degradation is also dependent on the concentration of VFA In particular, it must be < 1400 mg / l. However, other study confirm that the inhibitory effect were not observed up to 6000 mg/l of total concentration of VFA (Christensen and Kjeldsen, 1989).

- Oxygen: the absence of free oxygen is a must for the anaerobic bacteria to grow and perform the above mentioned processes. The methenogenic bacteria are the most sensitive to oxygen, they require a redox potential below -330 mV (Christensen and Kjeldsen, 1989), or what suggest other author below -200 mV or better below -100 mV (Rovers and Farquhar, 1972).

Table 1.2 : Summary of influencing factor on landfill anaerobic degradation

Influencing factors	References	criteria
Temperature	35 – 40 °C (Mata-Alvarez, 2003), maximum around 55 °C (Khanal, 2008)	30-40 ° C
Alkalinity	1000-5000 mgCaCO3/L (Agdad and sponza 2005), 2000-3500 mgCaCO3/L (Ozturk 1999), >3500 mgCaCO3/L (ElifSekmann2011)	1000- 5000 mgCaCO$_3$/l
pH	approx. 7 (Christensen and Kjeldsen,1989), 6-8 Zehnder et al., (1982), 7 – 7.2 (Pfeffer, 1980), 6.4 – 7.2(Chughet al., 1998; Yuenet al., 2001), 7.0 to 7.2. (Gerandi, 2003)	>6,5 , < 7,5
VFA	VFA< 1400 (Wang), VFA 1.500 – 2.000 mg/L (Labatut and Gooch, 2012), up to 6000 mgVFA/l (Christensen and Kjeldsen,1989)	<6000 mgVFA/l
Moisture content	60% to 80% (Farquhar and Rovers, 1973)	70%
Ammonia	< 1500 mg/L, stimulation effect 50 and 200 mgN/L (Khanal, 2008)	>50mgN/l, < 3000 mgN/l

4.3 Leachate

Leachate from a landfill site is formed as a result of liquid that percolates through the waste and may contained dissolved or suspended material from the refuse (Cossuet al., 1995). The composition and nature of the leachate varies in concurrence to the composition and type of waste which is in contact with the liquid (MSW, industrial waste, bottom ashes), the state of biodegradation, the moisture content of the waste and the procedures used in operating the landfill.

Leachate contains great quantities of organic contaminants usually measured as chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), ammonia, suspended solid, heavy metals and inorganic salts. This means that leachate is composed of different organic and inorganic compounds that may be either dissolved or suspended and which are biodegradable and non-biodegradable. The different fraction of leachate COD are illustrated in Figure 1.8.
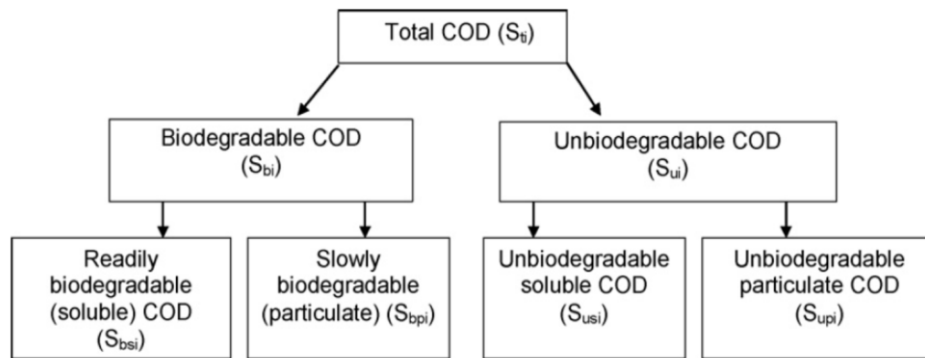
figure 1.8 :Fractionantion of influent COD into its constituent fractions (Bilgili et al 2008).

Due to the different processes taking place into the landfills, the leachate characterization changes along time, so its composition is not constant. This must be taken into consideration in relation to the treatment that must be designed for its management. The phases of leachate are reported in the table 1.3. From these different steps, the liquid contains different constituents; therefore, young leachate tend to be acidic due to the presence of volatile fatty acids. The ammonia concentration does not vary that much during the years.

Table 1. 2 : Leachate characterization over the time (Kostova, 2006).

Leachate constituent	Transition phase (0-5 years)	Acid-formation phase (5-10 years)	Methane fermentation (10-20 years)	Final maturation phase (>20 years)
BOD_5	100-11000	1000-57000	100-3500	4-120
COD	500-22000	1500-71000	150-10000	30-900
TOC	100-3000	500-28000	50-2200	70-250
Ammonia	0-190	30-3000	6-430	6-430
NO_2^- -N	0.1-500	0.1-20	0.1-1.5	0.5-0.6
TDS	2500-14000	4000-55000	1100-6400	1460-4640

Leachate treatment for sanitary landfills depending on the discharge limits and contaminants present, in particular

• Leachate, once collected, must undergo a treatment process

• If a sewer line is available in the vicinity of the site, leachate can be fed into the sewer system and undergo treatment at the sewer treatment works.

• Alternatively, there are various methods of treating leachate on site

    o   Sequencing Batch Reactor

    o   Leachate recirculation

    o   Aerobic Lagoons

4.4 Biogas

Gases arising from the biodegradation of biodegradable wastes in landfills consist of hydrogen and carbon dioxide in the early stages, followed by mainly methane and carbon dioxide in the later stages (figure 1.6). What is known as 'landfill gas' is a product mainly of the methanogenic stage of anaerobic degradation of biodegradable wastes. Landfill gas is produced from municipal solid waste which contain a significant proportion of biodegradable materials. Municipal solid waste is permitted to be deposited into non-hazardous waste landfills under the EC Waste Landfill D (1999). The main gases are methane and carbon dioxide and are odourless, but a wide range of other gases can potentially be formed. In addition, the gas is usually saturated with moisture. Table 4 shows the composition of the major constituents of landfill gas (Waste Management Paper 27, 1994;). The main chemical compounds found in landfill gas can be broadly categorised into saturated and unsaturated hydrocarbons, acidic hydrocarbons, organic alcohols, aromatic hydrocarbons, sulphur compounds (such as hydrogen sulphide, organic esters and the organo-sulphur compounds which give landfill gas a malodorous smell) and inorganic compounds (Allen et al 1997).

During the 4th stage of biodegradation, the production of carbon emissions is highest: 50 - 70 % of CH_4 and 30- 50 % of CO_2. Studies on landfill sites in Hong Kong are minimum concentration of 0-69.1 mg/m3 and maximum of 69-10 mg/m3 of CH_4 . This corresponds well with 66 % of CH_4 and 34 % of CO_2 for the gas produced in other experiments e.g. (Christensen and Kjeldsen, 1996). Small amounts of N_2 and H_2S may also be present. Studies have shown that if the amount of CH_4 produced is below 50 %, the production of CH_4 is only being retarded particularly because of detected of H_2 and abrupt environmental changes (Mclnerney and Bryant, 1983).

There are three types of system used to control landfill gas migration:

▪ passive venting;

▪ physical barriers;

▪ pumping extraction systems

Table 1.3 Main landfill gas composition (Waste management paper 27, 1994)

Component	Typical value (% by volume)	Observed maximum (% by volume)
Methane	63.8	88.0
Carbon dioxide	33.6	89.3
Oxygen	0.16	20.9
Nitrogen	2.4	87.0
Hydrogen	0.05	21.1
Carbon monoxide	0.001	0.09
Ethane	0.005	0.0139
Ethene	0.018	—
Acetaldehyde	0.005	—
Propane	0.002	0.0171
Butanes	0.003	0.023
Helium	0.00005	—
Higher alkanes	<0.05	0.07
Unsaturated hydrocarbons	0.009	0.048
Halogenated compounds	0.00002	0.032
Hydrogen sulphide	0.00002	35.0
Alcohols	0.00001	0.127

The gas production in a landfill site can also be affected by factors which affect the microbial activity of the landfill processes discussed above.

5. S.An.A. landfill model

Landfilling represent the last phase of the integrated waste management, because it has the function to store permanently the residual fractions which have already been pretreated which there is no further alternative available. The target is to build a landfill designed based on the principle of sustainability, in order to give to next generations an environment in the same conditions as it is characterized of nowadays (Cossu, 1995). A landfill can be defined as sustainable if it ensures, at the end of the post-management sustainable emission and impacts from the natural surroundings. To ensure this, several methods are applicable, including the technologies of aeration in situ, that is the release of forced air into the landfill body, allowing the establishment of aerobic conditions. These conditions are characterized by significantly faster and versatile kinetics than anaerobic and aspire to stabilize in a shorter time the residual organic substance present in the landfill before the management period (fixed in 30 years). Numerous laboratory tests, to investigate the different technologies to decrease the long-term impacts, were carried out by Cossu et al, (2003) through a system called PAF which comprises a step of pre-treatment of waste (such as to decrease the organic matter content), a phase of natural ventilation of the waste and a final phase of Flushing, designed to flush the waste through the entry of water into the landfill through permeable top cover and recirculation of leachate. From these models, it is developed a system called S.AN.A., which provides for a period of management and post-closure management in three distinct phases:

- Semi-aerobic (S) pre-treatment of waste by means of natural air flow (method semi-aerobic) or if necessary also forced, with the aim of improving the buffer capacity of the waste and consequently to accelerate the subsequent phase methanogenic.

- Anaerobic treatment of waste (AN) for the production and utilization of biogas energy, as long as this practice to be cost effective.

- Aeration in situ of the waste (A) (when the biogas exploitation is finished), by means of forced ventilation and using the extraction wells of biogas already prepared, in order to definitively stabilize the landfill until to achieve the final storage quality (FSQ concept described by Cossu, 2007) in order to obtain an environmental equilibrium, without negative impact for the environment before the 30 years (D.Lgs 36/2003).

Below follow a technical description of the phases constituting the S.AN.A. model. For each single phase is carried out a general overview on the principles of technology and the experiences made by other authors.

Semi-aerobic phase

Semi-aerobic landfill works exploiting the temperature difference between the waste (warm, due to the temperature reached during the aerobic degradation, about (50-70)°C) and the outside air (cold), so the oxygen is naturally flowing into the waste mass through convection. It enters from the leachate collection pipes placed on the bottom of the landfill and through some vertical pipes in the refuses mass itself; in this way it is possible to increase the overall area covered with oxygen flux. This is the so called Fukuoka method (Matsufuji e Tachifuji, 2007). This type of landfill produce limited methane (CH_4) and H_2S production – only in those parts of the waste mass where the air is not able to arrive through convection. The reduction of COD and BOD in the produced leachate, that, consequently, results less charged help to reduce the costs needed for the leachate treatment. Moreover we have the reduction of environmental impact because of the methane is controlled and oxidized in the capillary top cover.
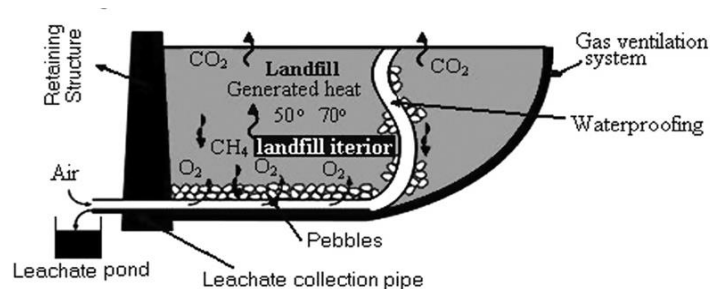
figure 1.8 : Schematic diagram of semi aerobic landfill (Aziz et al 2010).

According to which described before, the aims of the semi aerobic phase is to degraded via aerobic pathway the readily biodegradable fraction of waste, allowing to anticipate and optimize the subsequent methane production via anaerobic degradation. Whit the onset of aerobic condition during the first phase of the landfill, allow to limit the acetogenic phase (due to a less accumulation of volatile fatty acids that would lower the pH until the inhibition of methanogenic bacteria) and to achieve the optimal temperature for the growth of methanogenic bacteria (Cossu et al.,2003; Green et al.,2005; Berge et al.,2007).

Specific laboratory tests has been made on MSW and sewage sludge, testing a semi aerobic treatment before anaerobic phase. Limited aeration can be used as a pre-treatment prior to anaerobic digestion to enhance the digestibility of different types of wastes. Limited aeration has been tested as a pretreatment prior to anaerobic digestion of municipal organic solid waste by Nguyen et al. (2007) and Juangaet al. (2005).According to these two studies, waste bed reactors which were effectively partially aerated by sending air through the bed (flow rate 0. 4 L/kg. hr.) in a "2 hr. run 4 hr. stop" mode for a 5 day period before inoculation and anaerobic digestion phase started, showed a considerably improved methanogenic stage performance compared to the reactors which were not aerated. Not only did the pre-aerated reactor produce a higher biogas volume but it also reached the active methane phase (50% methane in gas) quicker than the rest of the reactors. This is a clear indication of a positive effect that partially aerated pre-treatment can pose on anaerobic digester performance. The rapid increase in gas generation observed just after the lag phase may suggest that partial aeration could have also resulted in better acidification providing enough substrate for methanogens. Akashi et al. (2000) reported a significant increase in biogas generation as a result of partially aerated pre-treatment. They observed an impressive 1.5 times higher biogas generation from biological sludge when pretreated by partial aeration than the anaerobic operation alone. Gerassimidou et al. (2013)study the effect of aerobic biological pretreatment on the emissions of MSW after landfilling. MSW was first pretreated aerobically for three different time periods (8, 45 and 90 days) resulting in organic matter reductions equal to 15%, 45% and 81% respectively and after placed in anaerobic bioreactors. The control anaerobic bioreactors contained untreated MSW. Results showed that the biogas production from untreated MSW was 372 NL dry kg-1 after 530 days. The MSW that was pretreated aerobically for 45 days and 90 days yielded 130 and 62 NL dry kg-1 of biogas after 310 days and 230 days respectively. However, the 8-day (very short-term) pretreatment period led to an increase of the biogas yield (550 NL dry kg- 1 after 340 days) compared with that of raw refuse. All three runs with aerobically pretreated MSW reached the steady methanogenic phase faster than raw MSW. This fact confirm that a limited pre-aeration

period, where have a little loss of organic substances, increase the star up period of methanogenesis, and result in a less acidic leachate and more high biogas yield if compared whit anaerobic.

The duration of this preliminary phase could be established through the monitoring of specific parameter, such us the concentration of volatile fatty acids in the leachate, temperature of body waste (Green et al.,2005).

Anaerobic phase

Since the anaerobic waste degradation process is affected by various parameters, a well-controlled environment needs to be maintained throughout the process. During this phase, the prevention of the intrusion of the air is fundamental in order to established the condition for anaerobic degradation in the waste mass. The production of methane results anticipated (due to semi-aerobic pretreatment) respect a traditional landfill, and this allow to optimized the treatment and the energy use. The most important process-based technique used to accelerate the gas production from bioreactor landfills are leachate recirculation and enhancements (Morris et al., 2003; Bilgili et al., 2004; Sponza and Agdad., 2004; Francois et al., 2007). Leachate recirculation (LR) offers the best potential in terms of accelerating waste degradation and gas production (Francois et al., 2007), as well known by the "Bioreactor landfill" concept.

During LR, leachate collected at the base of the landfill is recirculated through waste matrix several times instead of a single pass. LR enhances the microbial activity by supplying the optimum moisture requirements, reintroducing the nutrients, homogenizing the environment allowing better contact between the microbes and substrate, and diluting the inhibitory compounds (Suna-Erses and Onay, 2003). As a result, the process of conversion of organic matter to methane is enhanced.

Many researchers consider LR alone as a method to increase the moisture content of the waste. This only accelerates early hydrolysis and acidogenesis stage, which results in a high acid concentration in leachate (Yuen, 2001). The modification of leachate before recirculation, that may aid the biodegradation process, has received relatively less attention. The available studies related to leachate manipulation process include addition of sludge (Barlaz et al., 1990; Warith et al., 1999; Alkaabi et al., 2009), addition of supplemental nutrients and buffer (Warith et al., 1999), replacement of present landfill leachate with old landfills leachate (Suna-Erses and Onay, 2003). Among these techniques, the addition of sludge is shown to be the most common and oldest practice. LR is also effective in enhancing gas production and improving leachate quality, especially in terms of leachate COD. Results from Chan et al (2002) indicate that LR can maximize the efficiency and waste volume reduction rate of landfill sites.

LR enhances the degradation of MSW, as it provides an aqueous environment that facilitates the provision of nutrients and microbes within landfill cells. It is also an effective way to mobilize nutrients and microorganisms in waste, together with improved mass transfer to prevent the development of stagnant zones in landfill cells (Chugh et al., 1998). The results from Chan et al. (2002) provided evidence that LR can shorten the transitional period to active methane production and boost the methanogenesis of a landfill cell containing MSW. In leachate recirculated columns, maximal gas production was observed 9 weeks after the commencement of anaerobic digestion
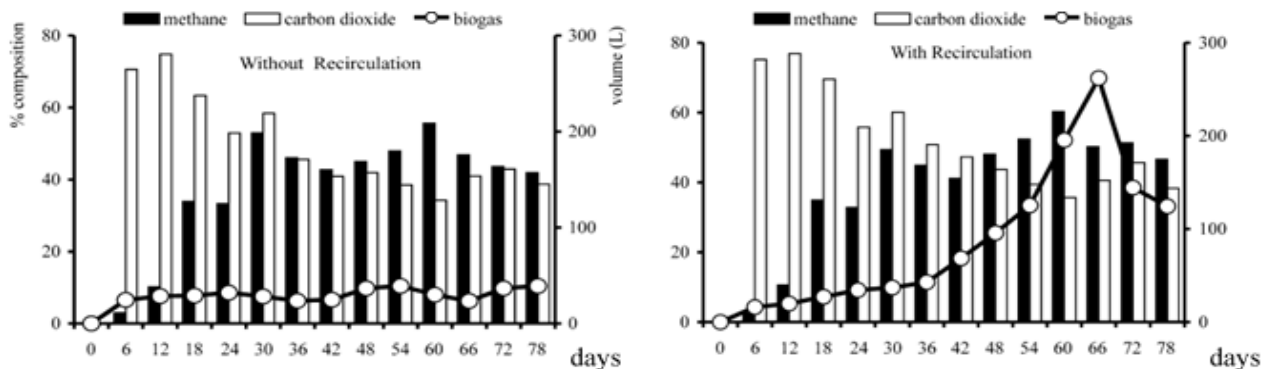
figure 1.8: Gas production and compositions of methane and carbon dioxide (%) collected from treatment with and without leachate recirculation (Chan et al., 2002)

In columns without LR, the gas generation was slow and peak generation rate could not be detected within the 11 week experimental period (Figure 1.8).

Research by Bilgili et al. (2007), Francois et al. (2007), Sponza and Agdad (2004) successfully reported effect of LR in laboratory scale. In particular the influence of leachate recycle on aerobic and anaerobic decomposition of solid waste and the impact of LR and recirculation volume on stabilization of MSW in simulated anaerobic bioreactor. Bilgili et al.(2007) compared the traditional anaerobic landfill (AN2) with landfill whit recirculation(AN1), landfill aeration (A2) and aeration with LR (A1). Aerobic leachate recirculated landfill appears to be most effective option in the removal of organic matter and ammonia.

All reactor had the same initial COD concentration value around 40000mg/L. After reaching to maximum value, COD began decrease rapidly. After 120 and 250 days was measured, whit this values 6500-5000 forA1 and 45000-17200 for AN1. The last concentrations determined in AN1 and AN2 reactors on day 500 were1600 and 2400 mg/L respectively. Cossu et al. (2003) found in their column study that the COD values of leachate from aerobic dry and wet reactors were lower than from anaerobic reactor. They found that after 120 days of operation the COD value of the anaerobic landfill reactor was approximately 20000, while equivalent value were 3000 and 800 in aerobic dry

and wet bioreactor. The result of Bilgili et al are similar to those of Cossu et al. (2003) and show that the aeration and LR has a positive effect on the rate of solid waste degradation in landfill.

On the other side, Recirculation is more effective on anaerobic degradation of solid waste than aerobic degradation (see the value after 500 day), these facts was highlighted by Francois et al (2007) in their study.

Moreover, The evolution of ammonia and TKN in aerobic and anaerobic bioreactor was measured. The ammonia concentration were measured to be 120 and 1900 respectively for A1 and AN1 after250 days. This differences show the nitrification effect. The most of nitrogen in aerobic and anaerobic landfill reactor is in the ammonia for following the degradation of protein and ammino acids (Agdad and Sponza, 2004). Thus, the same evolution for TKN concentrations is observed. Another important factor that take into consideration is the recirculation volume and its impact on stabilization of MSW. This aspect was investigated by Sponza and Agdad (2004). A single pass reactor (SP) was operated without LR while the other two reactors were operated whit LR. The LR rate was 9 L/day (13% of reactor volume) in reactor 9 (R9)and 21 L/day(30% of reactor volume) in reactor 21 (R21). After 220 day of anaerobic incubation, it was observed that the pH, COD, VFA concentration, CH4 gas production and percentages in R9 were better than the single pass reactor and R21. When the leachate recirculation rate was increased three time, a decrease in pH and accumulation of VFA and COD concentrations were observed in R21.After 220 day of anaerobic incubation, the value of COD was 47000, 39000, and 52000 while the VFA concentrations were 15 000, 13000 and 21000respectivelyin SP, R9, R21. The mean methane percentages of SP, R9, R21 were 30, 50, 40 % respectively after 50 day of incubation. However LR was not effective in removing ammonia from the leachate. The amount of COD recovered by methane were 62.9, 162.3 and94.6 gr for SP, R9 and R21at the end of anaerobic incubation. Finally, high recirculation volumes may deplete the buffering capacity and remove the activity of methanogens. Therefore, an optimum leachate recirculation volume contributes to COD, decreasing VFA and effective methane gas production.

Aerobic phase

The finally aerobic phase started when the production of biogas become negligible and it's impossible to exploit it for energy use.
The main objective of Landfills aeration is to accelerate the processes of stabilization, taking advantage of the increased speed of the aerobic reactions (about 10 times higher than that anaerobic one).

In the aerobic landfill the release of biodegradable carbon in the gaseous form is maximized, thus reducing significantly the pollution load in the leachate. Because that the carbon is released primarily as CO_2 , landfills aeration will also reduce the impacts related to the greenhouse effect.

In addition to oxidation of the substance organic to carbon dioxide and water, the aeration favors the transformation of the fraction more hardly biodegradable in humic substances (humin, humic and fulvic acids), consisting refractories that can remain in the landfill or be removed through the leachate.

The processes of aeration can be applied to new landfills, designed to be aerobic, both old anaerobic landfill, in order to accelerate the stabilization and reduce the period of post-management.

The technique used in the two cases, called in situ aeration, is the same: it provides for the insufflations of air at low pressure in the landfill body via a system of wells, connected to one or more compressor stations.

The amount of air to be supplied is continually adjusted, so as to ensure a supply of sufficient oxygen and optimize energy consumption. The exhausted air is extracted by a system of wells connected to extractor fan and sent to treatment, which can be achieved through bio-filters, activated carbon adsorption or non- catalytic thermal methods (Heyer et al., 2005b).

Since it is not necessary to provide additional energy to maintain the optimal temperatures, the process can be considered relatively economic.

Figure 1.9 shows a simplified diagram of the in situ aeration process and major effects on the characteristics of the leachate, biogas and residual waste .

The results of an experimental study conducted by Prantl et al. (2006) , Ritzkowski and Stegmann (2007), Heyer et al. (2005b), and Cossu et al. (2004) (as indicated in the table 1.5), to assess quantitatively the positive effects of aeration of landfills. In particular the composition of biogas was evaluated for different old landfill after an aeration period of 2, 22, 10, 6 month respectively . Biogas composition in all the case tend to decrease and the carbon in biogas is released into CO_2.

table 1.5: biogas composition for different old landfill after forced aeration

	Prantl (2006)	Ritzkowski and Stegmann (2007)	Heyer (2005b)	Cossu (2004)
CO2	15 %	5 – 10 %	10 – 20 %	2 – 15 %
CH4	0 % circa	< 1 %	2 – 10 %	0 – 5 %
O2	5 – 15 %	15 – 20 %	1 -5 %	5 -20 %

In Prantl (2006) The degree of stabilization of the waste , finally, is increased: this is demonstrated by the reduction TOC by about 10-25 % and the value of the final respirometric index ($0.5mgO_2/gTS$).

The analysis of the humic and fulvic acids extractable showed an increase of fulvic acids during

the first aeration period , followed by an increase of humic acids , due to the conversion

the first in more stable molecules of humic acids . However, with the increase of the period of

aeration , humic acids has started to decrease , probably due to the conversion into substances

humic high molecular weight , non-extractable and therefore not measurable with the method used .

The observation of old landfills , where it was performed a remedial treatment of by aeration in situ

led to the results presented below .

In Cossu (2004) are also reported observations on the quality of the leachate at the end of

aeration period : the COD is equal to 2662 mgO_2/l , BOD5 to 260 mgO_2/l , nitrogen

ammonia at 1400 mg / l, TKN to 1449 mg / l, and nitrate to 3.7 mg / l. These values deviate

significantly from those evaluated in the course of the experimental tests of Prantl et al. (2006) ,

resulting in much higher ; in this case , also , not having the initial characteristics of the leachate, is

difficult to assess the effectiveness of treatment .

As regards the characterization of the waste after treatment, was assessed the final IR4. The value

decreased from IR4 1.83 mgO_2/gTS to IR4 0.55 mgO_2/gTS sign that the refusal has high degree of

stabilization. On the other hand,B21 indicates a residual potential of biogas production still

significant result was 7.1 Nl /KgTS. The eluate analysis give the following values: COD 219 mgO_2

/l, BOD5 of 31 mgO_2 /l, TKN of 26 mg /l, ammonia nitrogen of 17 mg /l nitrate equal to 0.27 mg/ l.

Finally Ritzkowski et al. (2006) report the results of analyzes carried out on the eluate of waste

collected from an old landfill, after 22 months of aeration . In this case the BOD5 lies between 15

and 34 mgO2 / l (before aeration was in the range $28 - 877$ mgO2/ l) , the TOC between 58 and

775 mg / l (before aeration was in the range of 71-153 mg / l), Ammonia-nitrogen between 26 and

55 mg / l (before aeration was in the range of 10-55 mg / l); however within the parameters of

BOD_5 and ammonia nitrogen , these results are therefore comparable with those reported in Cossu

(2004).
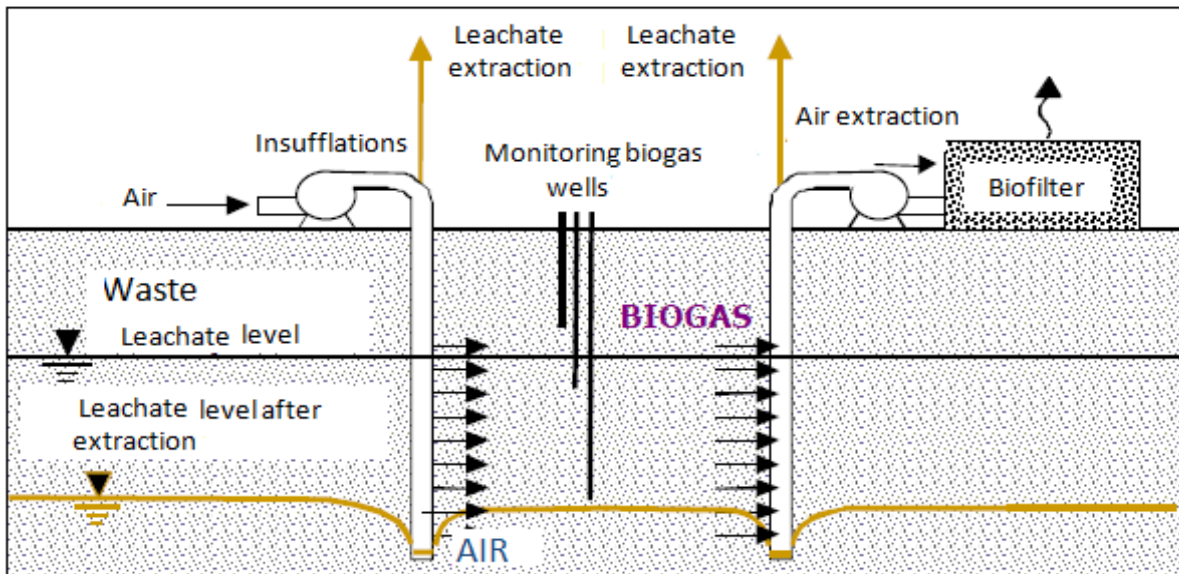
figure 1.9: In situ aeration scheme process and major effects on the characteristics of the leachate, biogas and residual waste

6. Technical approach

6.1 Columns for simulated landfill

Generally landfill generate emission over a long periods, often longer than a lifetime. Leachate is the longest lasting emission from landfill. Hence it will determine the required time for emission treatment and control (Kylefors et al., 2003). Moreover landfill is very heterogeneous, the waste mass change during the age of filling and could be present a stability problem. For this reason it's difficult to take a direct measures of a certain phenomenon in the real scale, resulting inaccurate.

In order to predict the behavior of MSW landfills and the time required for leachate treatment, different methods are apply today. Methods ranging from small scale test and simulator test (columns or lysimeter) to large-scale field test. All methods show a specific advantages and disadvantages and have been used for various purposes and time scale (e.g. assessing after care period or evaluating factor determining gas generation rate).

A methodology often applied for predicting emission from landfill is based on laboratory experiments. In particular landfill simulator reactor are necessary in order to increase the control of the most important parameters and to decrease the time of experimentation. Obviously it is reasonable to assume that the more similar the test is to the full scale application, the closer the result of the test will be to the future real emissions of landfill (Kylefors et al., 2003).

In the past, different lab-based experiments have been conducted to assess the predicted operation period of full-scale measures. In order to reliably predict field operation performance derived from

lab-based tests, it is very important to observe and consider all the specific landfill-site properties, to adapt pre-or concomitant investigations, such as column or lysimeter tests continuously to varying and changing field conditions, and finally to find site-specific, tailor-made technical solutions for efficient full-scale measures. (Hrad et al., 2013). Column landfill simulators were cylindrical plastic or glass containers some kilos of waste (10-20 kg). Their dimensions allow the placement inside a building and it's easily to carefully monitor the parameter that we want; such as water, temperature and air supply. The emissions, such as leachate and biogas are cached and it's possible to change management and operate very fast.

The main disadvantage of columns is that they cannot consider the heterogeneity of waste. The result indicate that, due to the preferential pathways, the flow of water in field-scale landfills is less uniform than in laboratory reactors. Consequence of the difference in water flow and moisture distribution are that the leachate emission from full scale landfills decrease faster than predicted by lab experiments and the stock of materials remaining in the landfill body, and thus emission potential, is likely to be underestimated by laboratory landfill simulator (Fellner et al., 2009).

The problem of homogeneity is solved by having more columns in a test campaign. The advantage is that these reactors allow very fast test thanks to the ideal conditions in which they operate and to the possibility to increase the liquid solid ratio very much in a short time.

In order to design leaching test that are reliable for long term predictions, it's essential to know what factor influence leaching and how they influence the leaching. Those factor have been defined as: water withdrawal, biological processes, recirculation, duration, particle size, temperature and sample preparation (Kylefors et al., 2003).To relating the laboratory results to full scale landfill, L/S ratio are commonly used (amount of water given in liter passing through a given waste mass given in kg of dry waste). L/S is also used to determine the remaining pollution potentials of MSW in a landfill (Allgaier and Stegmann, 2003) and consequently to estimate the time necessary for after care measure. However the transformation of the columns results to full scale landfill implies a similar water distribution within landfills and column because the kinetics of metabolic reactions largely depend on the water content and its distribution within the waste (Fellner et al., 2009). Liquid-solid ratio consist in evaluate the cumulate leachate emissions for every time and substitute this values to the timescale. The accuracy of this method is due to the strict bond between all reaction and all emission processes with water circulation, except in the aerobic case where it is only sufficient the water presence (Ritzkowski and Stegmann, 2013). Despite this, the direct comparison between lab tests and field data must be always managed with caution and experience. In case of aeration, the lag-factor between lab and field performance depends mainly on the differences between the calculated (lab) and the real (field) aeration rate, the deviating aeration

efficiency, the L/S ratio evaluation, the temperature and moisture differences and the higher heterogeneity of landfill (Hrad et al., 2013)

6.2 waste samples

The waste used for the test come from the MSW collection plant in central Italy, and were intended to be stored without any previous treatment. A sample of 200 Kg of waste have been sieved (80 mm) and the under sieve was used to fill the 6 column reactors. Before to fill the reactors, the under sieve (107 Kg) was previously homogenized to ensure as much as possible comparable results. Waste composition analysis was carried out considering the following categories : Garden waste (15%), putrescible waste (30%), paper and cardboard (12%), textile (7%), composites (10%), metals (4%), glass (2%), plastic (10%) and other (10%). Values were approximated. A sample of 2 kg of weight was extract and shredded (3 mm of size) with a mill for solid analysis. In the solid analysis, the following parameters were analysed: Total solids (%), Volatile solids (%), moisture content, TOC, TKN, N-NH4, Respiration index. Leaching test was performed according to standard UNI EN12457-2, to understand how the waste release or not its constituents under the influence of the condition of exposure. In this way it is possible to characterize leachate in the long-term period.

6.3 Columns equipment

Six Plexiglas column reactors were set up for the experiment and filled whit the waste described before. The waste put in the reactors have been compacted manually in order to obtain layers of homogeneous density from 10 cm to ensure the correct distribution of the air and of the liquids placed inside. The mains reactors characteristics are reported in table 1.6

The reactors having internal height of 106 cm and diameter of 25 cm (figure 1.10). Each column is closed at the top and the bottom by means of bolted flanges, provided with double rubber seals, to ensure a perfect seal. The upper and the lower part is equipped whit inox valve. In particular the upper part had 4 valve, for the introduction of air in the reactor, to collect the gas formed during the processes, for sampling and extraction gas and one for the introduction of water or recirculation of leachate (figure 1.11). The lower part is equipped whit a valve that allows the leachate to flow by gravity into a 5 liter collection container.

Table 1.6: Characteristics of wastes placed in each reactor

Parameters	Group first (sana)				Group second (anaerobic)	
	S1	S2	S3	S4	AN5	AN6
Quantity of waste (Kg)	18,4	18,4	18,4	18,4	15,6	18,4
Moisture content (%)	45	45	45	45	45	45
Density (Kg/l)	0,5	0,5	0,5	0,5	0,5	0,5
Quantity of Total solids (Kg TS)	10,12	10,12	10,12	10,12	8,58	10,12

Figure 1.10: Column reactors placed in L.I.S.A. laboratory, I.C.E.A. Department, University of Padua.

The liquid has been recirculated in the upper part of the reactor using peristaltic Heidolph PD 5001 pumps operated by means of an analogical timer (figure 1.11). This pump allows to dose a variable flow analogy between 0.7 and 729 ml / min. The range of speed of the pump is adjustable between 10 and 120 rev / min.On the surface and a bottom layer, respectively, 10 cm and 5 cm of fine gravel (10 mm) and coarse are guaranteed to facilitate the distribution, drainage and leachate collection.

The pump used for leachate recirculation has been carefully chosen according to the objectives of use and guaranteed performance. In fact the liquid is not contaminated since it is only in contact with the tube (type Tygon ® standard); that have an excellent durability under conditions of variable temperature between -50 ° C and 75 ° C.
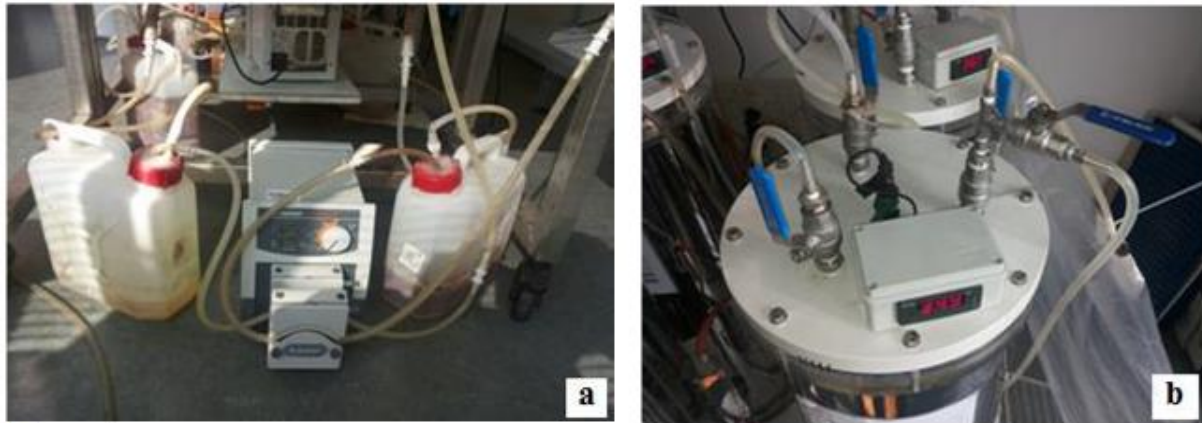
Figure 1.11: a) Leachate storage container and recirculation pump detail. b) – Particular of the valves installed on the superior flange of every column.

Inside the column, before the filling whit waste, has been situated at the center of the reactor a bottom-sealed vertical PVC tube fed by a compressor and controlled by means of a flow meter. This tube, whit side perforations guarantees the homogeneous distribution of the air throughout the reactor. In this phase play an important role the degree of compaction of the waste.

Reactor gas emissions are bubbled through an acid scrubber (figure 1.12) in order to reveal and quantify the release of ammonia nitrogen from the system.

The acid scrubber consists of a glass bottle containing 500 ml of boric acid and dye solutions (methylene blue, methyl red). The gas exiting from the columns is bubbled from below upward within the solution. Ammonia possibly present in the gas, come back in liquid phase in acid environment and accumulates within the solution, which changes color going from purple to green. By titration with sulfuric acid it is therefore possible quantify the amount of ammonia exiting the system in the gas phase. Inside the waste mass has been situated a Thermo System TS100 temperature probes. Whit this devices, it's possible to monitoring the temperature using a display located outside the column (figure 1.12)
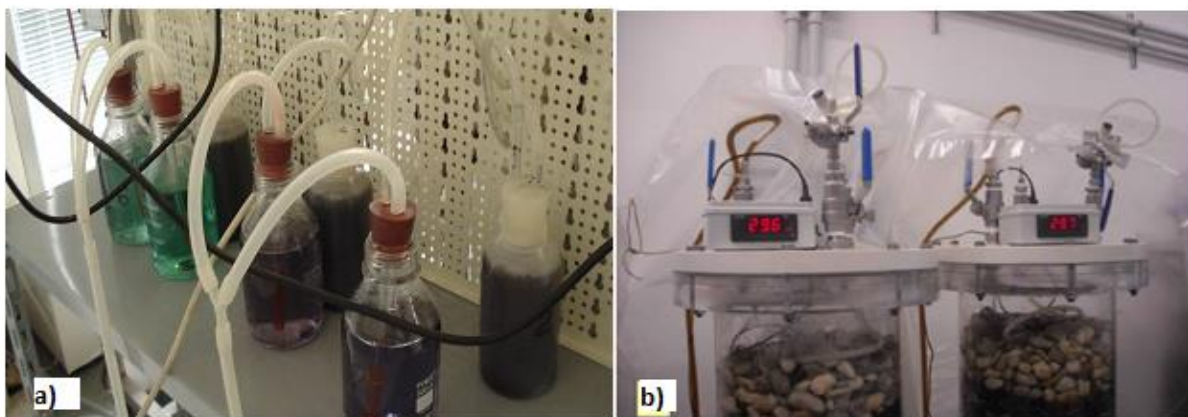
Figure 1.12: a) Scrubbers filled with boric acid for the outflowing gas washing in order to quantify the content of ammonia-nitrogen. b) particular of temperature display.

The reactors may be operated both in aerobic and anaerobic condition. In anaerobic condition no air influx is supplied and the biogas produced is collected in 10-l bags (LindePlastigas). Additionally, it's possible to control enabled the temperature by using a purpose built thermo-regulated insulation system covering all reactor lateral surface.

In aerobic condition air is introduced into the system by a Prodac Air Professional pump 360; airflow is regulated by a Sho-Rate GT1335 flow meter (Brooks Instruments). Unfortunately it's impossible to simulate semi-aerobic condition because the bottom valve don't allow the natural convection of the air.

6.4 Test description

The thesis test conducted in the columns is only the first phase of a more complete management regarding always the same waste. The entire simulation test is made up and start whit the first semi-aerobic phases (Phase 1), follow the second anaerobic phase (Phase 2), and finish whit the third aerobic phase (Phase 3). When the complete stability will be achieved, It's possible to perform a flushing test. Two of the six columns start anaerobic and finish aerobic, in order to simulate the traditional landfill and to verify the efficiency of the first phase on the second. All these phases are better described.

- Semi-aerobic phase : in this step, the reactors S1, S2, S3, S4, received an air flux in different mode. We chose to blow as much air as required to ensure the only presence of oxygen in the waste. According to the previous study, the duration of this first phase is estimated to be two weeks.

  Moreover, into S1, S2 and AN6 columns the addition of water is related to the moisture content of the waste, or better guarantee the moisture that the waste needs (60-80%). Is also carried the recirculation of leachate to ensure a better distribution of nutrients and moisture, which are essential for a good degradation of the organic substance . It is not expected at this stage any extraction of leachate, which is then stored in the column of waste.

SEMIAEROBIC PHASE	S.AN.A.				TRADIZIONAL ANAEROBIC	
	S1	S2	S3	S4	AN 5	AN 6
Water added [liter]	6	6	5	5	5	6
Leachate recirculation [times/day]	1/day	1/day	1/day	1/day	1/day	1/day
Aeration methodologie	Intermittent	Continue	Intermittent	continue	0	0

- The anaerobic phase will begin, therefore, the achievement of predetermined parameters

or within a certain predetermined time given by previous experiences (table 1.2 chapter 4). During the anaerobic phase the presence of air is stopped and the amount of biogas produced is continuously monitored. During this phase, the columns are kept at a constant temperature of 35 ° C inside thermo-regulated insulation system. It will be interesting to note the different probable methane production between the four columns S.An.A. mode due to the different air injection in the first semi-aerobic stage. In this phase, there is a extraction of leachate. The release of water will have to decrease in order to prevent a saturation of the porosity of the waste body and a complete inhibition of the methanogenic processes. Consequently, the recirculation of leachate play an important role and will not be total, but respect the range expected from the literature (10-30%) in order to accelerate the processes of degradation and biogas production while providing the necessary moisture (Sandip et al., 2012, Francois, 2007). The transition to the third phase will determine during the analysis, when the production of methane is insufficient for its eventual energy use.

ANAEROBIC PHASE	S.AN.A.				TRADIZIONAL ANAEROBIC	
	S1	S2	S3	S4	AN 5	AN 6
Water added [liter]	6	6	5	5	5	6
Leachate recirculation [times/day]	1/day	1/day	1/day	1/day	1/day	1/day
Aeration methodologie	0	0	0	0	0	0

- Aerobic phase : During this phase the injection of air in the waste body is carried out. In this way, the degradation of the last most recalcitrant organic compounds is achieved, whit a complete stabilization of the waste. At this point the recirculation of leachate and the injection of air will be more consistent, as they will allow a good leaching of the compounds still present and the degradation of hardly biodegradable substances.

AEROBICA PHASE	S.AN.A.				TRADIZIONAL ANAEROBIC	
	S1	S2	S3	S4	AN 5	AN 6
Water added [liter]	6	6	5	5	5	6
Leachate recirculation [times/day]	1/day	1/day	1/day	1/day	1/day	1/day
Aeration methodologie	Airflow	Airflow	Airflow	Airflow	Airflow	airflow

6.5 Management of first semi aerobic phase

The process was started by dosing water to each reactor. Reactors S1, S2, AN6, were saturated with 6 liters, while S3, S4, AN5 with 5 liters. The water was dosed to the top of the reactors to start the leachate production. Has been also carried recirculation of leachate every day. Throughout the first phase was recirculated 100% of the leachate outgoing for all columns. During the 14 weeks of the study, the only water introduced was for replaced the extracted leachate. There is a wide range of aeration rate used in pilot and full-scale aerobic landfill studies in the literature (Sekman et al. 2011, Cossu et al. 2005). Cossu et al. 2003, set up lab scale test to investigate different options for reducing long term landfill emissions and they used for "semi-aerobic like" condition an aeration rate of 200Nl/day. Again, Cossu et al. 2005, used the same columns to simulate semi-aerobic landfill and aerobic one using an aeration rate of 1 Nl/h and 5 Nl/h respectively. During the first phase of the entire research, the reactors S1 S2 S3 S4 was aerated in different way with a very low intensity, just to ensure the presence of oxygen proper in semi aerobic landfill.

The test for the first phase was conducted in three different and subsequent step.

In the first step, reactors S1 and S3 are aerated in intermittent way. For the first ten days were guarantee a flow of 14 l / 12h, then for the next two days was used a flow of 28 l / 12h. From the 14th day onwards we used a flow rate of 50 l / 12 h. Reactors S2 and S4 are aerated in a continuous way. For the first ten days were guarantee a flow of 14 l / day, then for the next two days was used a flow of 28 l / day. From the 14th day onwards we used a flow rate of 50 l /day.

After the first step, a second anaerobic step was performed for all reactors. Here, the temperature was set at 35° and leachate recirculation has been stopped for 2 weeks for all reactors. At the end of the second step (2 week after the 37 days), a check-up of interested parameter (pH, VFA, TOC, NH_4) has been made. If these parameters were around or respect the literature range (table 1.2), the aeration was stopped definitively, otherwise aeration continued until reached the range. For reactors S3, S4 the aeration was stopped after 37 days.

In the third step, the recirculation has been reactivated. Reactors S3, S4, AN5, AN6, continue to be anaerobic. Reactor S1 and S2 the aeration was switched on again. Reactor S1 has been aerated for additional 14 days (51 days in total) . Reactor S2 has been aerated for the entire duration of the test. The columns AN5 AN6 have never been aerated for the duration of the experiment except on days 21, 25,29 July, with respectively 100, 40, 40 l / h to favor the hydrolysis of the organic substance complex. The control of processes parameter was effect by means of periodic leachate samplings. After sampling an additional amount of distilled water was added to replace the extracted leachate. Leachate samples was extracted 3 times a week during the first37 days of operations, and then once a week. During the first 37 days, the leachate quality was initially tested 3 days a week, in

particular, FOS/TAC ratio and ammonia. Temperature and pH was measuring every day, instead COD, TOC, SO4, SO2, Cl once a week. Heavy metal, BOD, humic and fulvic acid every month; TKN, NO2, NO3 twice a week. The leachate production was measured and recirculated completely once a day. O2, CH4, CO2 concentration in the landfill gas, as well as the quantity of produced gas were measured every days by LFG20 analyzer.

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Part 2

Scientific article

Abstract

Numerous lab-scale tests were set up to investigate different options to achieve sustainability by reducing long-term landfill emission. The options which have been studied and compared with the traditional anaerobic landfill for unprocessed refuse were: landfill aeration with natural advective air flow (semi-aerobic), anaerobic condition for biogas exploitation, in situ aeration of landfill by means of forced ventilation (Aerated). Combination of different option has been experimented. The synergy between these three options seems to enhance the effect of individual option. Starting from these considerations, Spinoff Srl, in collaboration with the University of Padua, has developed an innovative system of landfilling: the S.An.A. ® landfill model, which provides for a period of management and post-closure management in three distinct phases: Semi-aerobic, Anaerobic, Aerated conditions. In this study, a pre-aeration step was investigated as a pre-treatment for anaerobic digestion of municipal solid waste. Pilot scale columns experiments were carried out under different aeration combinations to obtain detailed information regarding the influence of aeration modes on leachate characteristics. It was found that intermittent pre-aeration of waste was the most effective to achieve a pH, VFA, alkalinity and temperature values for the start-up of anaerobic digestion without the need for an external source (buffer, inoculums etc…) when compared with continuous aeration. Moreover the volume of methane collected from the intermittent aerated reactors was much greater than that anaerobic and continuous reactor. The experiments were carried out with focus on carbon balance in the reactors. Intermittent aeration exhibited positive results in term of enhancing hydrolysis and acidification, showing a positive effect in methane phase performance. It is hoped that this study will stimulate further investigations in this field.

1. Introduction and goals

Prognosis from the United Nations (2007) show that, the world population will likely increase by 2.5 billion over the next 40 years, passing from the current 6.7 billion to 9.2billion in 2050. As a consequence to the increasing number of population and the improvement of living quality since the past three decades, the total amount of municipal solid waste is continuously rising. In Europe alone, it is estimated that more than 3,000 million tons of waste are generated annually (EEA, 2003). Out of this number, 60 million tons of recyclable organic wastes are collected from households and food industries (Gallert and Winter, 2002). Due to the environmental problems caused by solid waste generation, during the last 30 years solid waste management has become a major concern around the world. The main tool of integrated solid waste management is solid waste

management hierarchy. This management hierarchy consists of a comprehensive waste reduction, recycling, resources recovery (commonly known as 3R strategies) and final treatment/disposal (Bagchi, 2004; Cheriminisoff, 2003). When the solid waste cannot be prevented or minimized through 3R strategy, the next strategy is reducing solid waste volume and/or its toxicity before ultimate disposal. One way to reduce the volume of solid waste is through combustion. The ultimate disposal of solid waste is to place it in landfills. In Europe the introduction of the European Landfill Directive (EC, 1999) has stimulated European Union Member States to develop sustainable solid waste management strategies, including collection, pretreatment and final treatment methods. According to the Directive, it is compulsory for the Member States to reduce the amount of biodegradable solid waste that is deposited on landfills.

The target is to build a landfill designed based on the principle of environmental sustainability and provide multi-barrier system, with a coherent long-term strategy for the control of emissions and climate change issues, in order to give to next generations an environment in the same conditions as it is characterized of nowadays (Cossu, 1995). A landfill can be defined as sustainable if it ensures that, the accumulation of organic substances level and the amount of emissions (leachate and biogas) reach sustainable value from the natural surroundings, within the maximum time of one generation (30 years). In this period, the landfill must be monitored by a multi-barrier system that avoid or minimize the emission to negligible levels. In this context is defined barrier not only the physical one (characterized by limited duration), but also the quality of the waste (modified by mechanical-biological pretreatment, different collection, thermal pretreatment), the landfill construction and operation procedure (such us aerobic, semi aerobic, leachate recirculation), the choice of top cover (that allow the necessary infiltration of water), the drainage and collection system, the landfill site.

Numerous laboratory tests, to investigate the different technologies to decrease the long-term impacts, were carried out by Cossu et al., (2003) through a system called PAF which comprises a step of pre-treatment of waste (such as to decrease the organic matter content), a phase of natural ventilation of the waste and a final phase of Flushing, designed to flush the waste through the entry of water into the landfill through permeable surface cover and recirculation of leachate. From these models, it is developed a system called S.An.A., which provides for a period of management and post-closure management in three distinct phases:

- Pre-aerobic (S) treatment of waste mass (phase 1) by means of natural air flow (semi-aerobic method) or if necessary also forced, (Matsuto et al., 1991; Matsufuji et al., 2000; Chong et al., 2005) with the aim of improving the buffer capacity of the waste and

consequently to accelerate the subsequent phase methanogenic (Cossu et al.,2003; Green et al.,2005; Berge et al.,2007).

- Anaerobic treatment of waste (AN) whit leachate recirculation (phase 2) for the production and utilization of biogas energy (landfill bioreactor concept) (Morris et al., 2003; Bilgili et al., 2004; Sponza and Agdad., 2004; Francois et al., 2007; Chan et al., 2002), as long as this practice to be cost effective.

- In Situ Aeration of the waste (A) (phase 3) when the biogas exploitation is finished, by means of forced ventilation and using the extraction wells of biogas already prepared (Prantl et al. (2006), Ritzkowski and Stegmann (2007), Heyer et al. (2005b), and Cossu et al. (2004), in order to completely stabilize the landfill until to achieve the final storage quality (FSQ concept described by Cossu, 2007) in order to obtain an environmental equilibrium, without negative impact for the environment before the 30 years (D.Lgs 36/2003).

The main purposes of this research study are:

- Check the effects of pre-aeration (phase 1) on the subsequent anaerobic phase. This can be done by different type of aeration on the waste just deposited until pH, temperature, VFA do not reach optimal range.

- Assess the conditions for the achieving of the Final Storage Quality (FSQ) in a Sustainable way (within 30 years, simulated). Through of in situ aeration and flushing process, we want to accelerate the process of stabilization and leaching of the remaining potentially contaminating substances, taking advantage of the increased aerobics kinetics reaction.

- Perform a mass balance for the most important elements such as Carbon, Nitrogen, Chlorides, Sulfates and heavy metals. Particular attention will be placed on carbon speciation (focus on non-reactive and slowly biodegradable substances) and nitrification and denitrification pathways.

The research study is currently in progress; the present paper refers to the result obtained respect to quality of emission as observed after 90 days for lab column. In this paper will be analyzed the first part (phase 1) of the S.An.A. landfill model, managed in 3 different step. In particolar the goal are:

- First, to investigate the effect of pre-aeration on the subsequent anaerobic phase, in order to achieve optimum values of pH, VFA, alkalinity and temperature that can enhance the methanogenic phase in simulated bioreactor landfill (S.An.A.).

- Refine the transition parameter between first and second phase, set a significant aeration period and investigate which pre-aeration method is the most appropriate.

- Analyzing mobility-stability of compounds by a mass balance approach. Focus on the first phase of the experiment, carbon mass balance has been used to allow understanding how a specific element has been distributed during the time among the principal emission form, such as leachate, biogas and residual waste.

The wastes used for the test come from the MSW collection plant in central Italy, and were intended to be stored without any previous treatment.

This article summarized the first part of a series of preliminary studies on the feasibility of the S.An.A. landfill model in real scale.

2. State of art and experimental references

The efficiency of waste degradation can be expressed by the rate of waste decomposition in individual phase. The durations of degradation phases of untreated solid waste in anaerobic laboratory reactors was investigated by several authors. The beneficial effects of aerobic pretreatment of waste before landfilling on reducing the duration of hydrolysis and acidic phase, and speeding up the start of stable methane phase are well documented. A specific laboratory test has been made on MSW, testing a semi aerobic treatment before anaerobic phase.

Limited aeration has been tested as a pretreatment prior to anaerobic digestion of municipal organic solid waste by Nguyen et al. (2007) and Juanga et al. (2005). According to these two studies, waste bed reactors which were effectively partially aerated by sending air through the bed in intermittent mode for a 5 day period before anaerobic digestion phase started. Reactors showed a considerably improved methanogenic stage performance, higher biogas volume and reach active methane phase quicker than the rest of reactor that were not aerated. Gerassimidou et al. (2013), study the effect of aerobic biological pretreatment on the emissions of MSW. Its studies confirm that, for a waste with high putrescible content, a limited pre-aeration period (8 days), lead to a little loss of organic substances, increase the star up period of methanogenesis, and result in a less acidic leachate and more high biogas yield if compared whit anaerobic. Other study conducted by Xu et al. 2014, Mali et al.,2012 confirm that temporary aeration respectively of 70 and 14 days result in a lower COD and BOD concentrations and that methane production was improved within a short period of time.

Time interval of aeration varies with the waste age, compositions and other factors, and it is not clear what is optimum range. This study aims to provide an appropriate pre aeration time interval for this kind of waste.

3. Materials and methods

3.1. Waste material

The research was conducted on MSW unprocessed biologically and mechanically, collected from collection plant in central Italy. Grain size distribution analysis was performed on 200 kg of MSW sample using 80 mm mesh size sieves. The under-sieve, used to fill the 6 reactors, was previously homogenized to ensure as much as possible comparable results. Waste composition analysis was carried out on under-sieve, considering the following categories: Garden and kitchen waste, wood, paper and cardboard, textile, composites, metal, glass, plastic and other. The values were approximated. The composition of waste was presented as the share of respective fractions in the total mass of waste, in % (m/m).

Table 2.1: Waste characterization and percentage composition of waste. Merceological analyses were carried out on under-sieve, before filling the reactors.

Fraction	Kg	Percentage %
Over sieve	93	47
Under-sieve	107	53
Total initial waste weight	200	100
Under-sieve characterization		
Garden waste	16,05	15
Putrescible waste	32,1	30
Paper and cardboard	12,84	12
Textile	7,49	7
Composites	10,7	10
Metal	4,28	4
Glass	2,14	2
Others	10,7	10
Plastic	10,7	10
Overall	107	100

3.2. Equipment

Six Plexiglas column reactors with an internal height of 106 cm and diameter of 25 cm (figure 2.1) are used for the test. Each column is closed at the top and the bottom by means of bolted flanges, provided with double rubber seals, to ensure a perfect seal. The upper and the lower part is equipped whit inox valve. In particular the upper part had 4 valves, for the introduction of air in the reactor, to collect the gas formed during the processes, for sampling and extraction gas and one for the introduction of water or recirculation of leachate. The lower part is equipped whit a valve that allows the leachate to flow by gravity into a 5-liter collection container. In each reactor 18 Kg of under-sieve described before (table 2.1) were placed. Waste layers with a height of 10 cm were placed in the reactors and were thickened manually to a density of 0,5 Kg/l to ensure the correct

distribution of the air and of the liquids placed in the reactor. The surface and the bottom of the waste was covered with a 10 cm and 5 cm layer of fine and coarse gravel respectively, to facilitate the distribution, drainage and leachate collection. The liquid has been recirculated in the upper part of the reactor using peristaltic Heidolph PD 5001 pumps operated by means of an analogical timer. Inside the column, before the filling whit waste, has been situated at the center of the reactor a bottom-sealed vertical PVC tube fed by a compressor and controlled by means of a flow meter. This tube, whit side perforations, guarantees the homogeneous distribution of the air throughout the reactor. Inside the waste mass has been situated a Thermo System TS100 temperature probes. Whit this devices, it's possible to monitoring the temperature using a display located outside the column. The reactors may be operated both in aerobic and anaerobic condition. In anaerobic condition no air inlet is supplied and the biogas produced is collected in 20-l bags (LindePlastigas). Additionally, it's possible to control the temperature by using a purpose built thermo-regulated insulation system covering all reactor lateral surfaces. In aerobic condition air is introduced into the system by a Prodac Air Professional pump 360; airflow is regulated by a Sho-Rate GT1335 flow meter (Brooks Instruments). Unfortunately it's impossible to simulate semi-aerobic condition directly because the bottom valve doesn't allow the natural convection of the air.
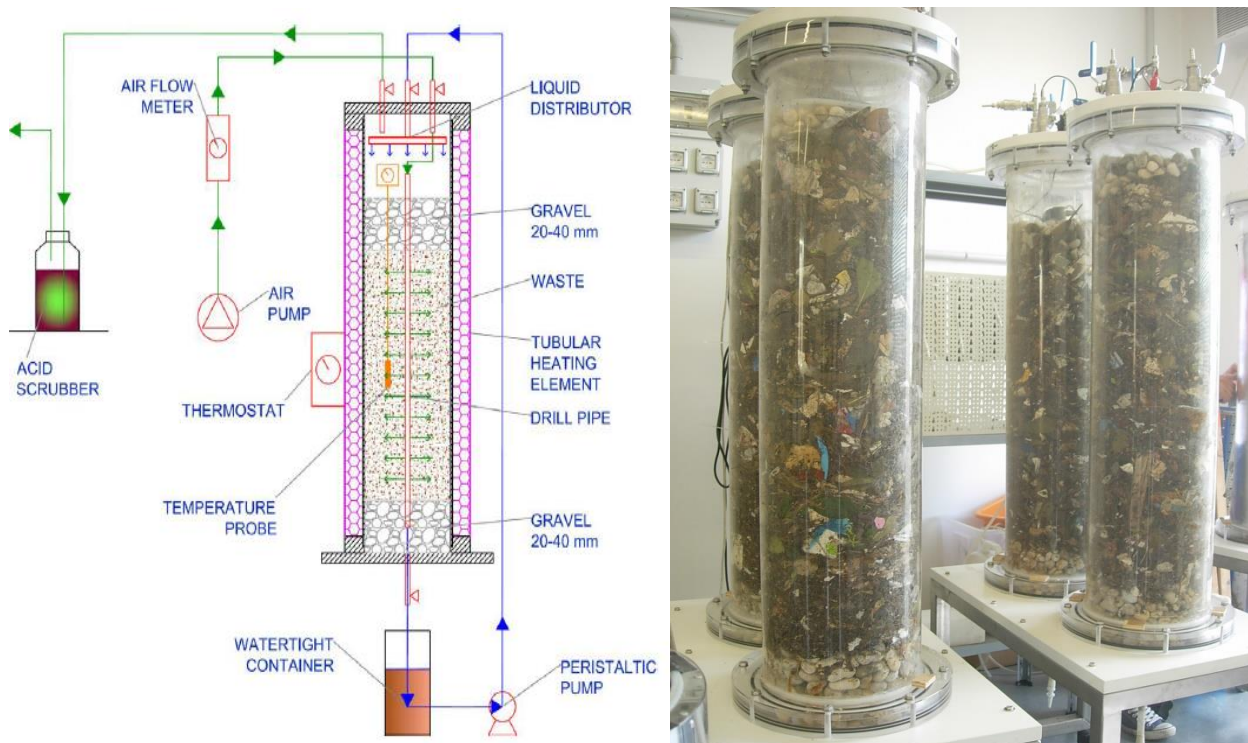
Figure 2.1: (a) sketch of the test reactor under aerobic conditions. Under anaerobic conditions no air influx is supplied and a gas bag is connected for periodic biogas sampling. (b) Columnar tests. These columns are placed in LISA laboratory in "Voltabarozzo ", ICEA department in Padua University.

3.3. Sampling and analysis

Solid waste samples have to be characterized at the beginning and at the end of life. The respiration activity was determined in a Sapromat by measuring the oxygen uptake continuously over a period of 4 and 7 days (IR4, IR7). The analysed parameter for solid samples are conducted according to international standards and reported in table 2.2. Leaching test was performed according to standard UNI EN12457-2, to understand how the waste release or not its constituents under the influence of the condition of exposure. In this way it is possible to characterize leachate in the long-term period. The control of processes parameter was effect by means of periodic leachate samplings. After sampling (approx. 250 ml) the same amount of distilled water was added to replace the extracted leachate. International standard methods, used for the determination of the most important parameter on leachate quality are reported in the table 2.2. The test was performed for 90 days. Leachate samples was extracted 3 times a week during the first 37 days of operations, and then once a week for the remaining 53 days.

During the first 37 days, the leachate quality was initially tested 3 days a week, in particular, FOS/TAC ratio and ammonia (NH_3-N). Temperature and pH was measuring every day, instead COD, TOC, SO_4^{2-}, Cl^- once a week. Heavy metal, every month; TKN, NO_2, NO_3 twice a week. The leachate production was measured and recirculated completely once a day; leachate recirculation was performed during the whole test, while O_2, CH_4, CO_2 concentration in the landfill gas, as well as the quantity of produced gas were measured every days by LFG20 analyser. Analyses presented in this paper included COD, pH, TOC, (NH_3-N), Cl^-, FOS/TAC.

Table 2.2: Analytical standards for leachate and solid sample analysis.

Analytical standards for leachate	
Parameter	Analitic methodologie
pH	IRSA CNR 29/2003, Vol1, n.2060
Total organic carbon (TOC)	IRSA CNR 29/2003, Vol1, n.5040
Ammonia (NH3-N)	IRSA CNR 29/2003, Vol1, n.4030 C
Total KjeldahNitrogen (TKN)	IRSA CNR 29/2003, Vol1, n.5030
Nitrates (NO3-)	IRSA CNR 29/2003, Vol1, n.4040 A1
BiologicalOxygenDemand (BOD5)	IRSA CNR 29/2003, Vol1, n.5120 B2
ChemicalOxygenDemand (COD)	IRSA CNR 29/2003, Vol1, n.5130
Sulphates (SO4--)	IRSA CNR 29/2003, Vol1, n.4140 B
Chlorine (Cl-)	IRSA CNR 29/2003, Vol1, n.4090 A1
FOS/TAC	Federal Agricultural Research Centre (FAL) Nordmann-Methode)
Metals	IRSA CNR 29/2003, Vol1, n.3010+3020
Analytical standards for solid	
Total solids (TS)	IRSA CNR Q.64/84 vol.2 n°2
Total volatile solids (TVS)	IRSA CNR Q.64/84 vol.2 n°2
Total organic carbon (TOC)	UNI-EN 13137
Ammonia (NH3)	IRSA CNR Q.64/86 vol.3 n°7
Total Kjeldah Nitrogen (TKN)	IRSA CNR Q.64/85 vol.3 n°6
Respirometric index	ANPA 3/2001 n.12.1.2.3.

3.4. Bioreactor configuration

The test for the first phase was conducted in three different and subsequent step graphically represented in the figure 2.2.

Six pilot simulated bioreactors were used in two groups: The first group simulates as a traditional anaerobic landfill (AN5, AN6). The second group represent the S.An.A. landfill model management (S1, S2, S3, S4). The mains characteristics are reported in the table 2.3.

In the first step, reactors S1, S3 are aerated in intermittent way. For the first ten days were guarantee a flow of 14 l/12h, then for the next two days was used a flow of 28 l/12h. From the14th day onwards we used a flow rate of 50l /12h. Reactors S2 and S4 have the same management of reactor S1, S3 but whit a continuous air influx. Anaerobic columns were not been aerated except in an initial phase to starting.

In the second step, (37 days later), the temperature was set at 35°C and leachate recirculation has been stopped for 2 weeks for all reactors. At the end of the second step, a check-up of interested parameter (pH, FOS/TAC, TOC,NH$_3$) has been made, if these parameters were around or respect the literature range (table 2.4), the aeration was stopped definitively (S3 and S4), otherwise aeration continued until reached the range (S1 and S2).

In the third step, the recirculation has been reactivated. Reactors S3, S4, AN5, AN6, continue to be anaerobic. Reactor S1, after further 14 aeration days, was switched anaerobic. For reactor S2 the aeration continued until the end of test. The columns AN5 and AN6 were maintained under anaerobic conditions for the entire duration of the experiment and were used as controls. The values of pH, VFA, alkalinity, temperature and ammonia, that have been achieved by the columns for which it has the onset of the second anaerobic phase was reported in table 2.5. After filling the reactors, the process was started by dosing water to each one (table 2.3). The water was dosed to the top of the reactors to start the leachate production. During the 90 days of the study, the only water introduced was for replaced the extracted leachate. Has been also carried recirculation of leachate every day. Throughout the first phase was recirculated 100% of the leachate out going for all columns. There is a wide range of aeration rate used in pilot and full-scale aerobic landfill studies in the literature (Sekman et al. 2011, Cossu et al. 2005). Aeration rate has been chose according this value.

AN6	37	14	39
AN5	37	14	39
S4	37	14	39
S3	37	14	39
S2	37	14	39
S1	37	14	14	25

■ continuos aeration ■ anaerobic without LR ■ intermittent aeration ■ anaerobic with LR
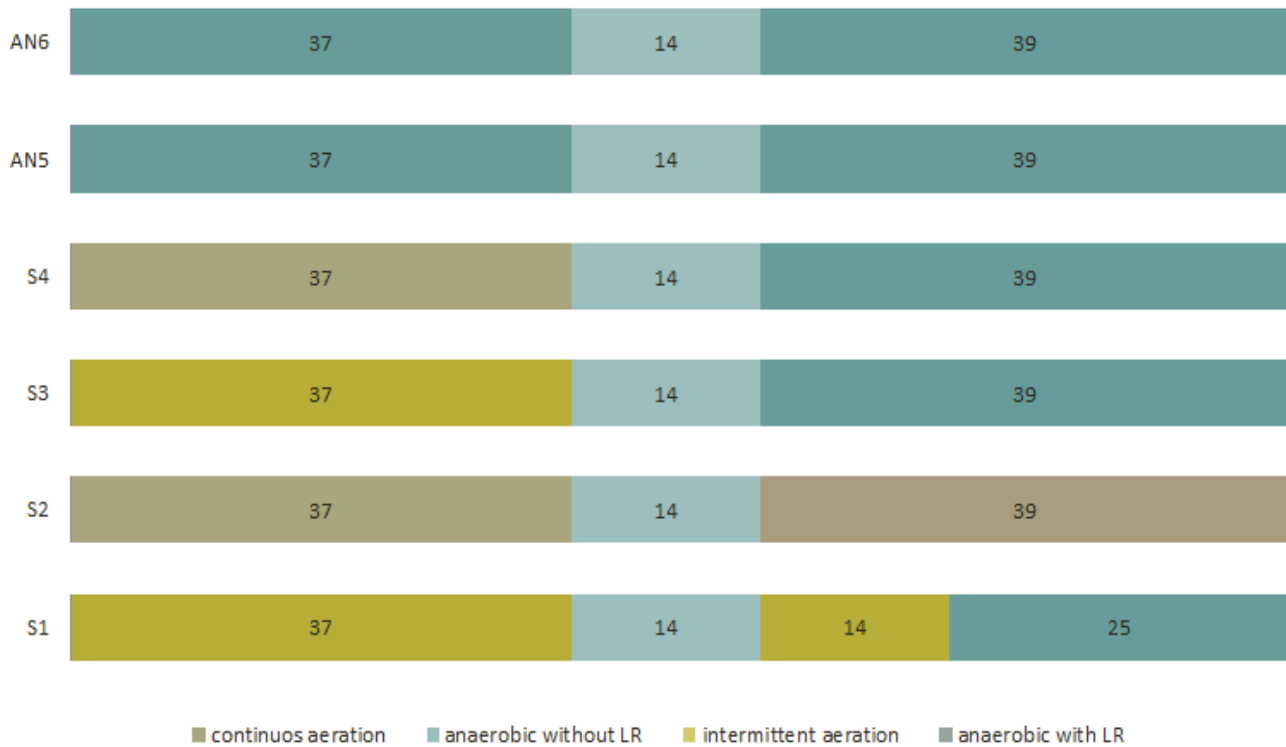
Figure 2.2: column's management scheme used for model application. 90 days overall. During the test the aeration was performed in this way: 10 days, 14 l/12h or 14 l/day; 2 days, 28 l/12h or 28 l/day; 58 days, 50 l/12h or 50 l/day respectively for intermittent and continuous aeration. LR stay for leachate recirculation.

Table 2.3: Operating condition and characteristics of wastes placed in each reactor.

Num	Parameters	Group first (S.An.A.)				Group second (anaerobic)	
		S1	S2	S3	S4	AN5	AN6
1	Quantity of waste (Kg)	18,4	18,4	18,4	18,4	15,6	18,4
2	Moisture content (%)	45	45	45	45	45	45
3	Density (Kg/l)	0,5	0,5	0,5	0,5	0,5	0,5
4	Quantity of Total solids (Kg TS)	10,12	10,12	10,12	10,12	8,58	10,12
5	Starting Water addition	6	6	5	5	5	6
6	Daily leachate recirculation %	100	100	100	100	100	100
7	Aeration method	Intermittent	Continue	Intermittent	Continue	-	-
8	Initial Semi aerobic phase (days)	51	76	37	37	-	-

The transition from phase 1 to phase 2 is performed when will be achieved the criteria set out in the table 2.4. In particular:

▪ pH : Methanogenic bacteria are more susceptible to pH variation than other microorganisms in the microbial community (Khanal, 2008), and operate efficiently only within a narrow pH-range.

- Alkalinity: sufficient alkalinity is essential for proper pH control. Alkalinity serves as a buffer that prevents rapid change in pH, and must be sufficient to buffer the production of VFAs in the acidogenic phase, to have an optimal biological activity (Ozturk, 1999).

- Moisture content: his presence it's fundamental for hydrolysis and acid fermentation stage. Gas production rates increased whit the moisture content whit maximum production occurring at moisture content from 60% to 80% (Farquhar and Rovers, 1973).

- Temperature: most methane-forming bacteria are active with a maximum rate of gas production at around 35 – 40 °C of temperature range (Mata-Alvarez, 2003; Khanal, 2008).

- VFA: organic acids are important intermediates in the pathway of microbial fermentation and can cause stress if they are present in high concentrations, resulting in a lowering of the pH and the failure of digestion. Inhibitory effect were not observed where the total concentration was arise up to 6000 mgVFA/l (Christensen and Kjeldsen, 1989).

- Inhibitor: there are some substances that at a given concentration inhibit the bacterial activity; ammonia-nitrogen above 1500 mg/L (Khanal, 2008) is inhibitor, while if ammonia is present between 50 and 200 mgN/L guarantee a stimulation effect on methane production.

Table 2.4: Summary of influencing factor on landfill anaerobic degradation

Influencing factors	References	criteria
Temperature	35 – 40 °C (Mata-Alvarez, 2003), maximum around 55 °C (Khanal, 2008)	30-40 ° C
Alkalinity	1000-5000 mgCaCO3/L (Agdad and sponza 2005), 2000-3500 mgCaCO3/L (Ozturk 1999), >3500 mgCaCO3/L (ElifSekmann2011)	1000- 5000 mgCaCO$_3$/l
pH	approx. 7 (Christensen and Kjeldsen,1989), 6-8 Zehnder et al., (1982), 7 – 7.2 (Pfeffer, 1980), 6.4 – 7.2(Chughet al., 1998; Yuenet al., 2001), 7.0 to 7.2. (Gerandi, 2003)	>6,5 , < 7,5
VFA	VFA< 1400 (Wang), VFA 1.500 – 2.000 mg/L (Labatut and Gooch, 2012), up to 6000 mgVFA/l (Christensen and Kjeldsen,1989)	<6000 mgVFA/l
Moisture content	60% to 80% (Farquhar and Rovers, 1973)	70%
Ammonia	< 1500 mg/L, stimulation effect 50 and 200 mgN/L (Khanal, 2008)	>50mgN/l, < 3000 mgN/l

Table 2.5: Value of influencing factor reached by the columns at the end of aeration period. For column S2 was reported the value of influencing factor achieved after 90 days of test.

Influencing factors	S.An.A.			
	S1	S2	S3	S4
Temperature	30	34,6	34,2	34,1
VFA (mgVFA/l)	5287	6130	6378	6838
Alkalinity	4163	4250	3712	4629
pH	6,46	6,25	6,05	6,18
Ammonia (mgN/l)	1596	1933	1263	1300

3. Results

3.1. Analytical results on solid waste sample

The data of the analysis carried out on solid waste sample at the beginning of the test are reported in table 2.6.

The respirometric index IR_4 and IR_7 was detected by Sapromat. The instrument requires a small amount of sample and an appropriate moisture range (45-65%), making insignificant the value obtained due to the heterogeneity of the waste.

The test was carried out on 3 waste samples comes from under sieve. The trend is shown in the figure 2.3:
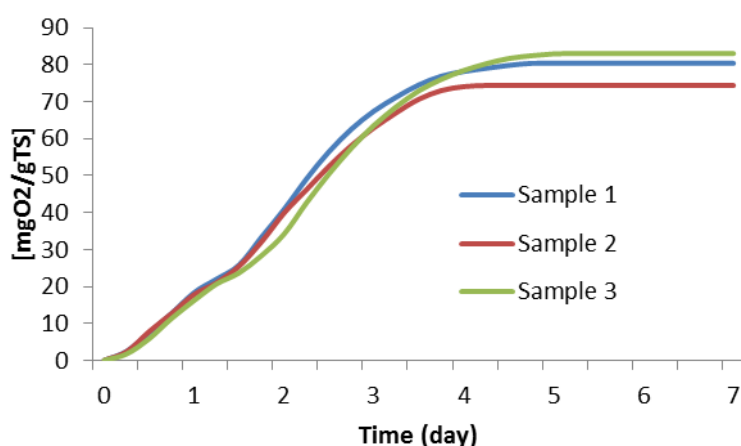
Table 2.6 analysis on solid sample.

Parameter	Unit of mesure	average value
TOC	mgC/KgTS	367740
NH_3	mgN/KgTS	1150
TKN	mgN/KgTS	10000
TS	(%)	0,55
RI_4	mgO$_2$/KgTS	76,94
RI_7	mgO$_2$/KgTS	79,31

figure 2.3: Respirometric index behavior. The value at day 4 and 7 was take into considerations.

The respirometric index, in this case, is used to assess the biological activity of a waste, that is the oxygen consumption due to the activity of bacterial degradation due to the organic carbon content of biodegradable material. The method used to estimate this index is dynamic, that is, the sample is subjected to continuous oxygenation for 4 or 7 days.

All samples have a high value of RI_4, respectively 78.2 mgO$_2$/KgTS 74.3 mgO$_2$/KgTS, 78.4 mgO$_2$/KgTS for the samples 1 and sample 2 and sample 3. After the fourth day the oxygen consumption stabilizes, providing values RI_7 equal to 80.4 mgO$_2$/KgTS, 74 mgO$_2$/KgTS, 80.3 mgO$_2$/KgTS respectively for sample1, sample 2, and sample 3. The values are those typical of a fresh waste and with a high percentage of organic substance. This fact is also confirmed by merceological analysis made at the beginning on solid sample (Table 2.1). Some authors state that values of RI_4 from 80 up to 150 mgO$_2$/KgTS are typical of a fresh refusal, while values RI_4 of 5 mgO$_2$/KgTS are typical of stabilized waste (Cossu and Raga, 2008). The values obtained of

respirometric index are also in agreement with the concentrations of COD, VFA, TOC measured in the leachate characteristics of a fresh waste.

The measurement of TOC on the solid waste sample was performed on four samples of shredded under sieve fractions. This data was also used to perform a mass balance on carbon. The average value was 367740 mgC/KgTS.

The TKN and ammonia were measured on two sample of under sieve previously shredded. The value of TKN results for both fractions of approximately 10000 mgN / kgST. Measuring the concentration of ammonia in the solid showed a similar value for the two samples 1130 mgN / kgTS.

3.2. Leachate characterization

- PH and temperature

The optimum pH range for microbial activity is generally between 6 and 8 (Bilgili et al.,2006). The trends of the pH within leachate generated from reactors S1, S2, S3, S4, AN5, AN6 were plotted in figure 2.5. The pH of leachates samples was maintained during the whole experimentation around weakly acidic conditions (between 5.5 and 6). Only in column S1and S3 after 50 days the value has risen to around 6.6 and 6.9 respectively.

The evolution of the internal temperature for the reactors S1, S2, S3, S4, AN5, AN6 were plotted in figure 2.4. The reactors S2, S3, S4, reached 35 degrees in the first 37 days. The final values of temperature columns AN5, AN6 and S1 are comprised between 28 and 30 degrees. After 37 days, the thermo insulating armor was attached and regulated at 35 degree.
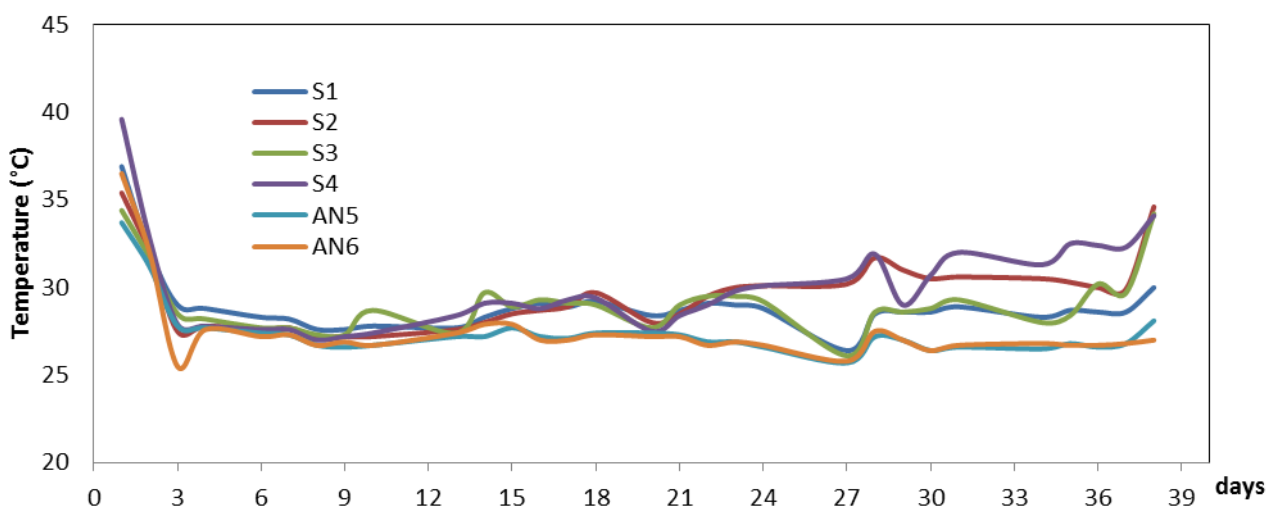
Figure 2.4: Evolution of internal temperature in the waste mass from the different columns.
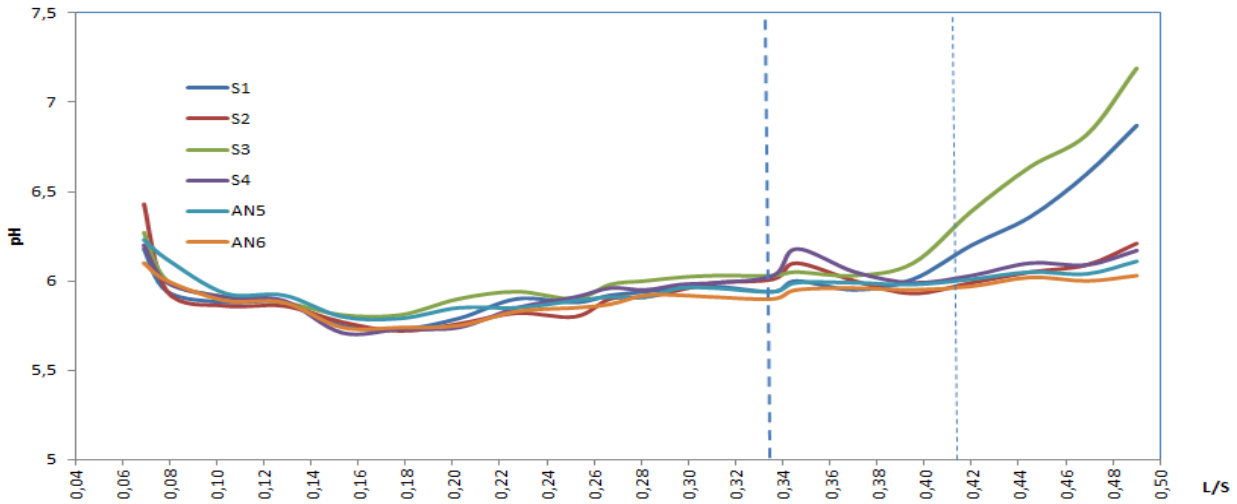
Figure 2.5: Evolution of pH in the leachate from the different columns. The trace thick line indicates the stop of aeration for columns S3 and S4 (37 days). The trace thin line indicates the stop of aeration for column S1(51 days).

- Total organic carbon (TOC)

The TOC expresses the dissolved organic carbon in the leachate. For leachates of all the columns it has been observed an increase during the first 20 days of this parameter with a maximum value of 18100 mgC/ l achieved by S1.

The organic carbon concentrations in the leachate have a constant trend for almost the entire duration of the test. After 50 days, the concentrations are seated around a constant value, approximately 14000 mgC/l in columns S1, S2, S3, S4 and around 15000mgC / l in anaerobic columns AN5 and AN6. The columns S1, S3 that compared to anaerobic and continuous aerated columns present TOC values decreasing and equal to 11060mgC/l and 12100 mgC/l.

A comparison between values of TOC detected in the leachate extracted from the columns S1, S2, S3, S4, AN5, AN6 were reported in the graph 2.6.
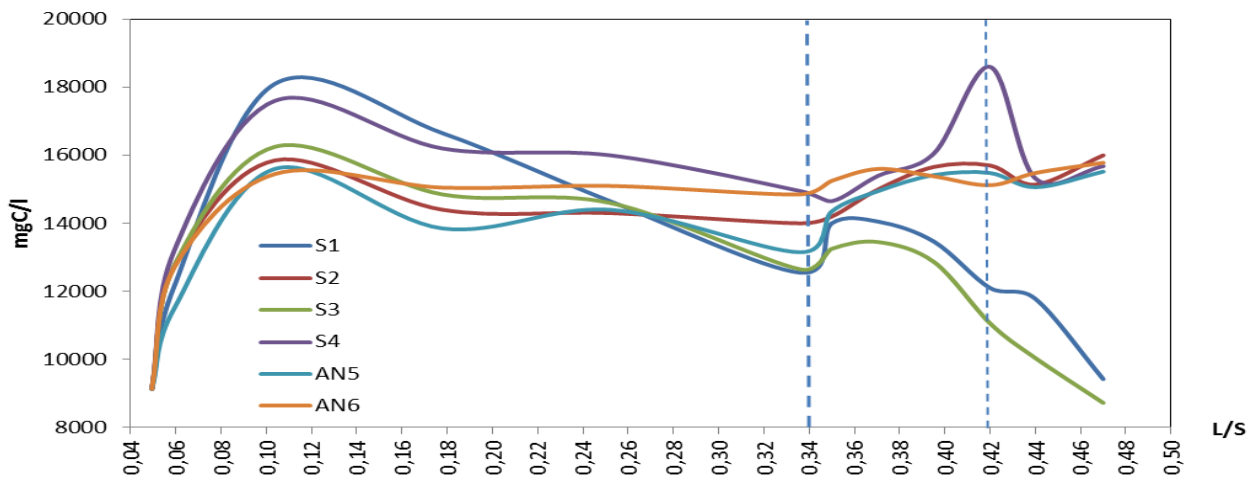
Figure 2.6: Evolution of TOC, expressed as mgC/l in the leachate from the different columns. The trace thick line indicates the stop of aeration for columns S3 and S4 (37 days). The trace thin line indicates the stop of aeration for column S1(51 days).

- Chemical Oxygen Demand (COD)

The COD is the oxygen required for complete chemical degradation of total organic compounds, both biodegradable and non-biodegradable . At the beginning of the test, in all the columns there was an increase of COD, with maximum values 98000 of mgO_2/l for S2, 100000 mgO_2/l for S4 and values between $60000mgO_2/l$ and $70000mgO_2/l$ for the anaerobic AN5, AN6 and intermittent aerated columns S1 S3.

The anaerobic columns AN5 and AN6 showed a constant trend, stopping on the final values around 60000 mgO_2/l . The continuous aerated columns S2, S4, have produced leachate with final values around 60000 mgO_2/l. Overall, after 50 days of management, the COD concentrations in all reactors show a slight tendency to decrease over time.
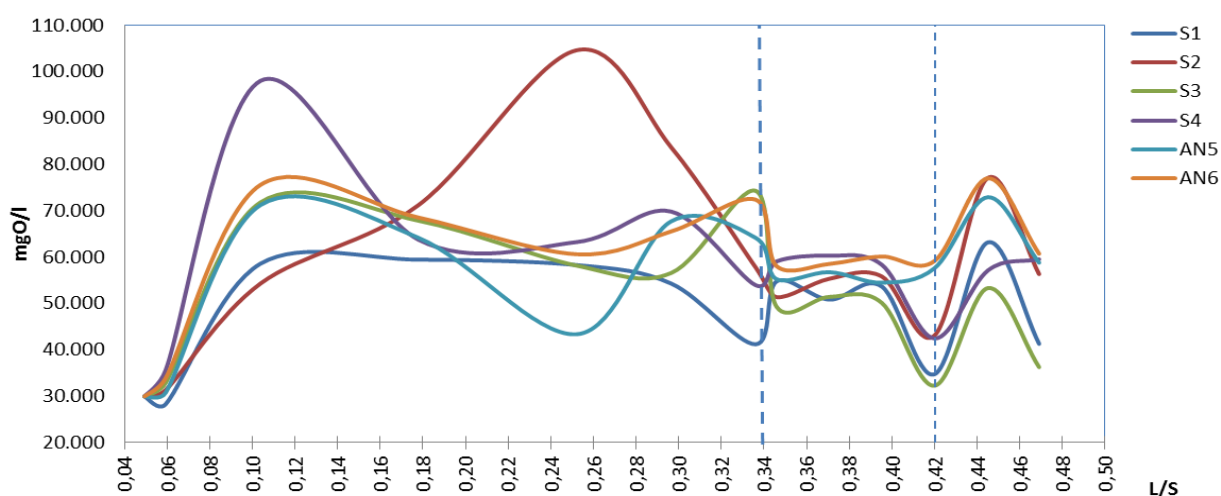
Figure 2.7: Evolution of COD, expressed as mgO2/l in the leachate from the different columns. The trace thick line indicates the stop of aeration for columns S3 and S4 (37 days). The trace thin line indicates the stop of aeration for column S1(51 days).

- FOS/TAC ratio

The FOS / TAC ratio is one of the tests for titration developed in Germany (Federal Agricultural Research Centre) for the determination of the acid concentration and the buffer capacity of the fermentation substrate starting by Nordmann-methode. FOS stands for Flüchtige Organische Säuren, i.e.volatile organic acids (VFA), and is measured in mg CH3COOH/l, while TAC stands for Totales Anorganisches Carbonat, i.e. total inorganic carbonate (alkaline buffer capacity), and is measured in mg CaCO3/l.

The trends of VFA in the leachates of the reactors S1, S2, S3, S4, AN5, AN6 were reported in the figure 2.8. For all reactors during the first 60 days was obtained an increase of volatile fatty acids, with maximum concentration values comprised between 6000-7600 $mgCH_3COOH / l$. The columns S1, S3 aerated intermittently, after reaching concentration values equal to 5900 $mgCH_3COOH / l$ and 6900 $mgCH_3COOH / l$, start to decrease to values that are around 5000 $mgCH_3COOH / l$. The. slowness of the of anaerobic reactions degradations is clear by looking at the graphs of column AN5

and AN6 that still have values around 6500 mgCH$_3$COOH / l. Similarly the columns S2 and S4 aerated continuously present similar trends to anaerobic one, with final concentration values around 6500 mgCH$_3$COOH / l.

The alkalinity concentrations value detected in the leachate from columns S1 S2 S3 S4 AN5 AN6 were reported in figure 2.9. For all reactors there was a slight increase in the alkalinity value than the initial one. At the beginning all the reactors had a value of about 3000 mgCaCO$_3$/l, after 70 days of test, the alkalinity has reached for all reactors values between 4000 mgCaCO$_3$/l and 3500 mgCaCO$_3$/l.
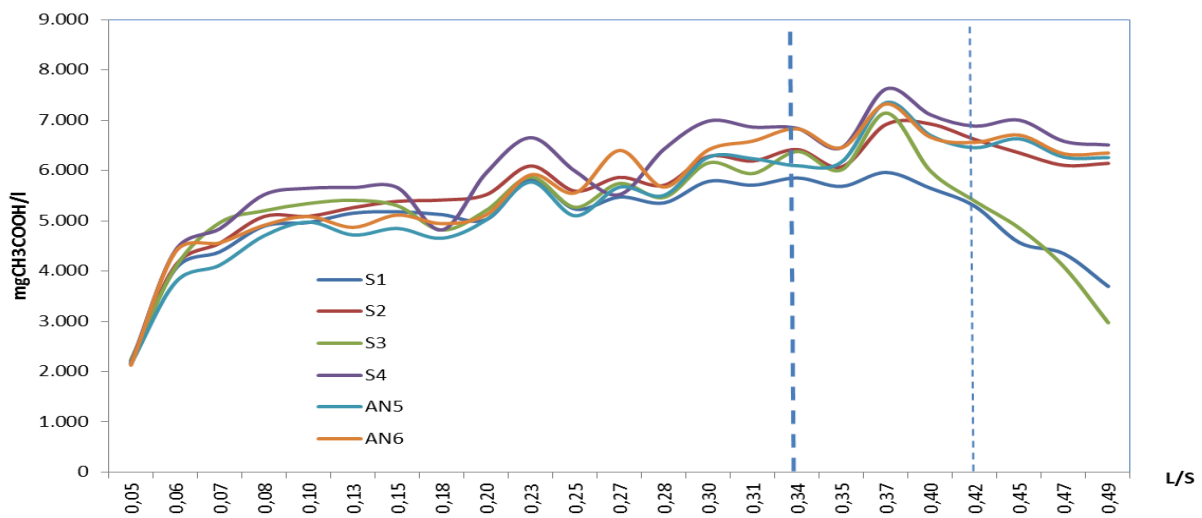
Figure 2.8: Evolution of VFA, expressed as mgCH3COOH/l in the leachate from the different columns. The thick line indicates the stop of aeration for columns S3 and S4 (37 days). The thin line indicates the stop of aeration for column S1(51 days).
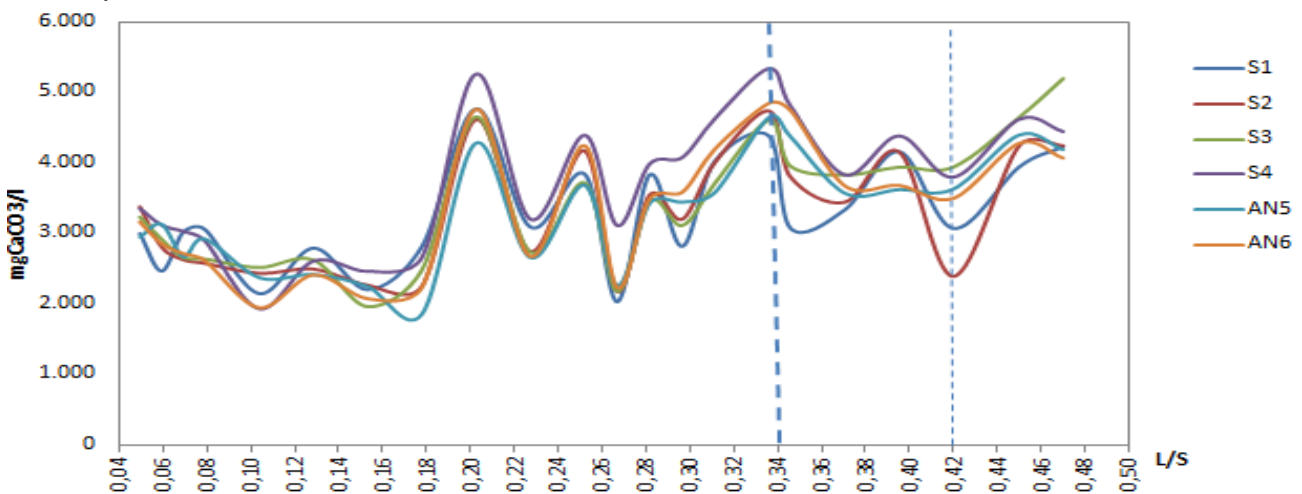
Figure 2.9: Evolution of alkalinity, expressed as mgCaCO3/l in the leachate from the different columns. The thick line indicates the stop of aeration for columns S3 and S4 (37 days). The thin line indicates the stop of aeration for column S1 (51 days).

- Ammonia

The trend of the NH$_3$ parameter expressed as mgN/l, of the leachate of the reactors S1, S2, S3, S4, AN5, AN6 were showed in figure 2.10. The ammonia for all the reactors has a linear increasing

trend. For anaerobic reactor, the final concentration was around 1200 mgN/l for AN5, AN6. The aerated reactors S3, S4, show a final ammonia value around 1700 mgN/l, the reactor S1, S2 around 1500 mgN/L.
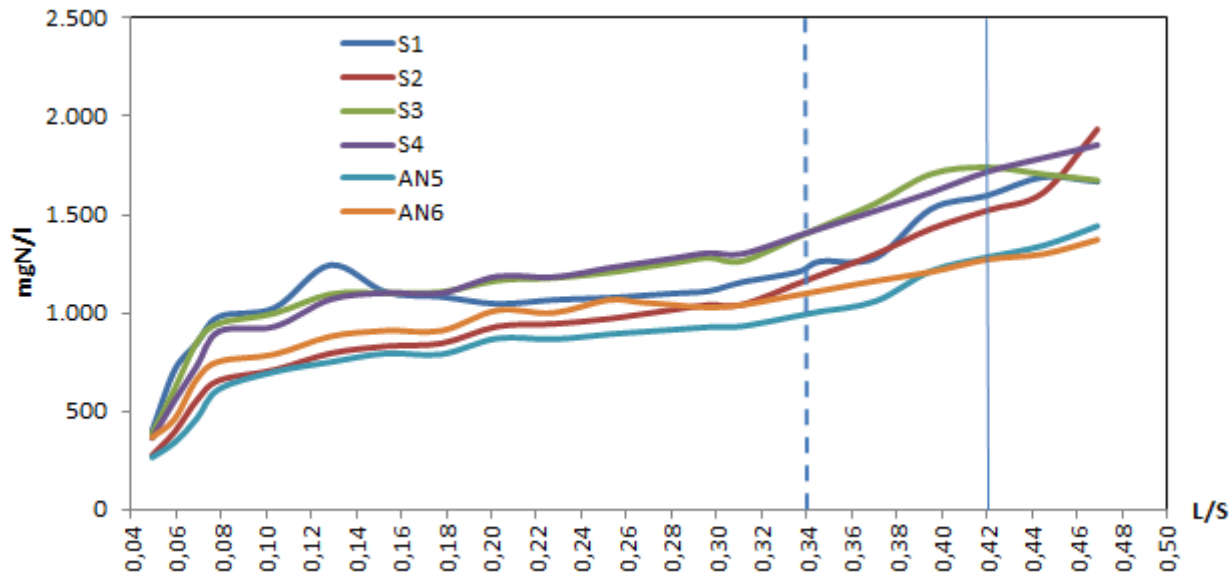
Figure 2.10: Evolution of ammonia-nitrogen, expressed as mgN/l in the leachate from the different columns. The thick line indicates the stop of aeration for columns S3 and S4 (37 days). The thin line indicates the stop of aeration for column S1(51 days).

- Chlorine

The trend of chloride is almost independent of the reactor management mode (Bilgili et al., 2007). Chloride represent a non-degradable conservative parameter, the change of chloride concentration is commonly used to asses variation in leachate dilution. Figure 2.11 shows variation of chlorine in the reactor S1, S2, S3, S4, AN5, AN6. They reported a linear constant trend, whit final value around 2500 mgCl⁻/l for AN5 and AN6, and between 3200-3500 mgCl⁻/l.
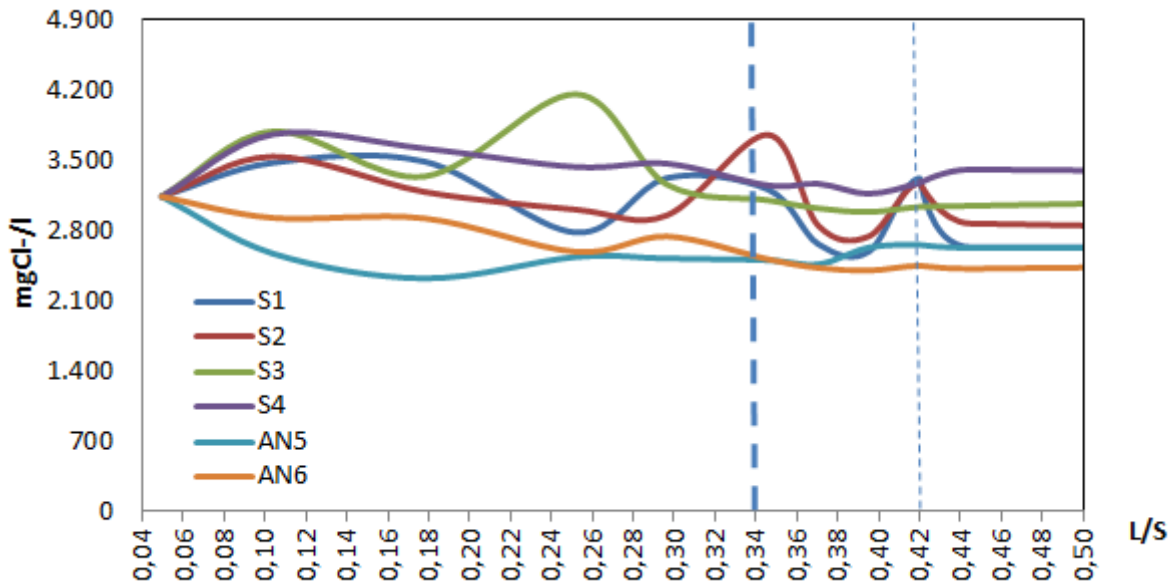
Figure 2.11: Evolution of Chlorine, expressed as mgCl⁻/l in the leachate from the different columns. The thick line indicates the stop of aeration for columns S3 and S4 (37 days). The thin line indicates the stop of aeration for column S1(51 days).

3.3. Biogas characterization

The determination of composition of the biogas was performed with the LFG 20 analyzer. It is measuring the percentage by volume of methane gas, carbon dioxide and oxygen. The methane percentages behaviors for reactors S1, S2, S3, S4, AN5, AN6, were plotted in graph 2.12.

The first methane production occur after 40 days from the start of the test. In reactors AN5 and AN6 the methane percentage range between 8% and 10%. Aerated reactor present much higher value. Reactors S1 and S3 aerated in intermittent way show mean methane percentage around 40% with a peak value around 60%. Instead reactor S2 and S4 aerated continuously present percentage value between 10% and 20%.

Carbon dioxide percentages trend relative to all reactors were showed in figure 2.13.

A the beginning of the experiment, high CO_2 percentage values (95%) have been evaluated for anaerobic reactors AN5 and AN6. This percentages start to decrease after ten days, but remain around 60% - 80% for about 40 days. For aerated reactors has been measured constant percentage of CO_2 , around 30%. At the end of management period, the CO_2 percentage start to increase.
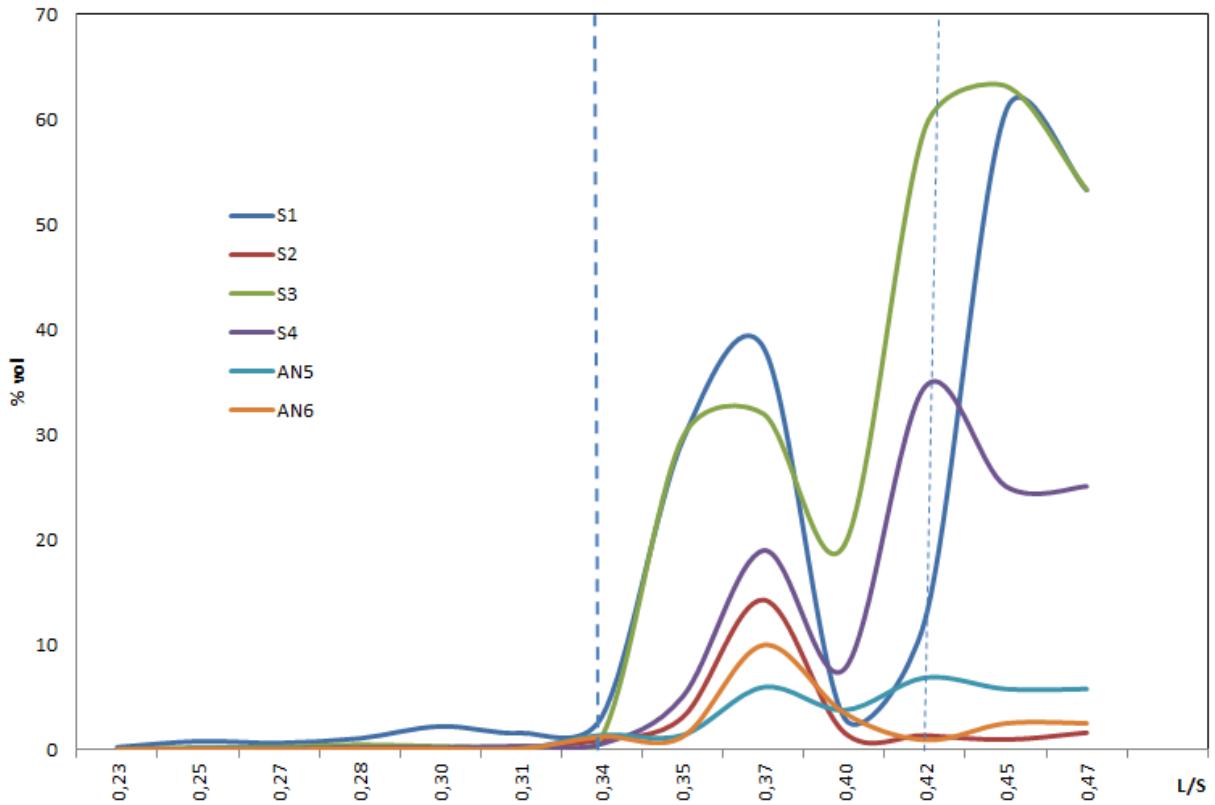
Figure 2.12: Behavior of CH4 percentage in all reactors. The trace thick line indicates the stop of aeration for columns S3 and S4 (37 days). The trace thin line indicates the stop of aeration for column S1(51 days).
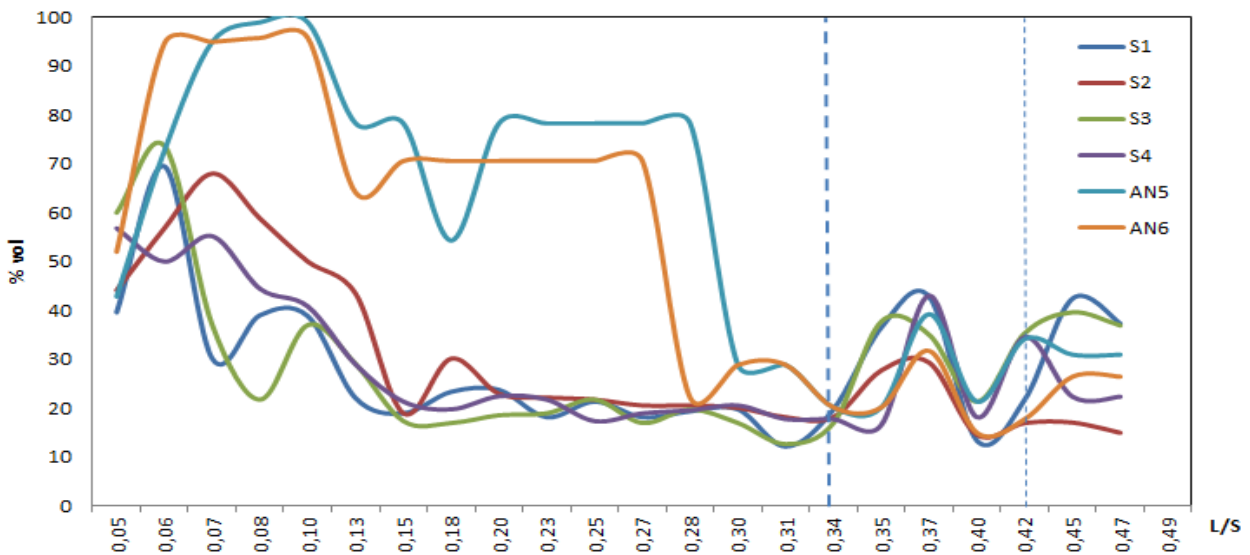
Figure 2.13: Behavior of CO2 percentage in all reactors. The trace thick line indicates the stop of aeration for columns S3 and S4 (37 days). The trace thin line indicates the stop of aeration for column S1(51 days).

An important indicator of the methane fermentation phase is CH_4/CO_2 ratio. Usually, during stable methanogenic phase the percentage of CO_2 and CH_4 ranging between 35-40 % and 65-60% respectively. The maximum value in percentage by volume that is possible to achieve ranged

between 1,5-1,8. The CH_4/CO_2 ratio trend has been plotted respect to maximum value in figure 2.14. When the ratio is stable, around 1.5-1.6, the fermentation is well established.
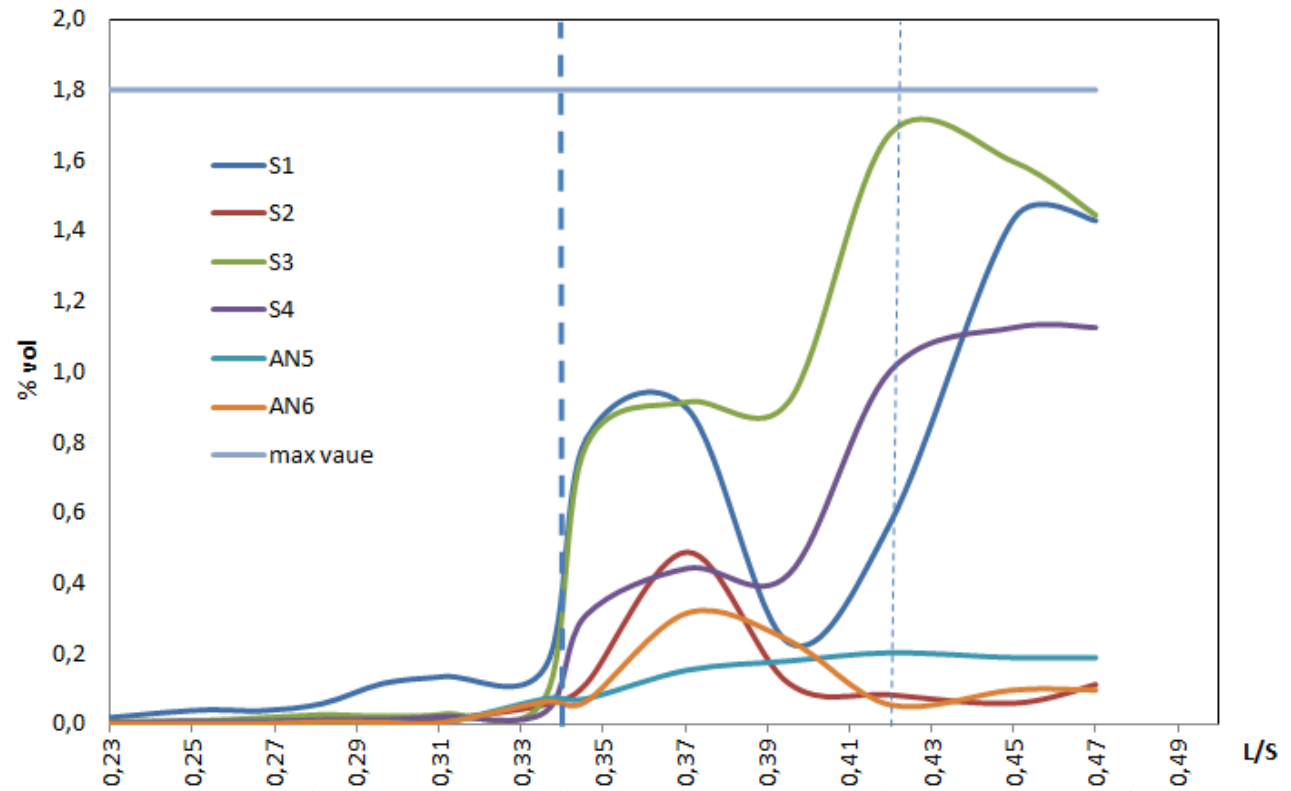
Figure 2.14: Trend of CH_4/CO_2 ratio for all the reactors. The trace thick line indicates the stop of aeration for columns S3 and S4 (37 days). The trace thin line indicates the stop of aeration for column S1(51 days).

4. Discussion

4.1. Leachate characterization

The leachate of aerated columns is characterized by a slight reduction of TOC during the time. This is an indication factor of the decreasing of the availability of organic carbon for effect of degradation and leaching processes. This effect is related also to the dilution effect of the water introduced for replaced the extracted leachate.

In anaerobic columns, TOC and COD concentrations remain almost constant, around 15000 mgC/l and 65000 mgO_2/l respectively for the whole experimental period. This fact could be related to slight acidic pH of AN5 and AN6 reactor, around 5.75-6.1. The accumulation of organic acids (around 6500-7000 mg$_{CH3COOH}$/l), due to the hydrolysis of complex organics from solid waste to the leachate, is favoured by low pH value, that tend to remain at the same high concentrations until the end of experiment. This reflecting the evidence of a strong acid phase in the anaerobic degradation of the raw waste, characterized by a higher content of putrescible.

For S1, S2, S3, S4, columns, the aeration stopped after 37 days, where has been made a check-up of the established parameters (Table 2.4). Concentration of VFA, alkalinity, pH value, temperature and organic carbon were evaluated. The bioreactors were operated under anaerobic condition, without recirculation for 2 week.

In the aerated bioreactors, S3 and S4, the achieved pH value in 37 days were 6.1 and 6.2 respectively, that remain still slightly acidic, but far to value suggested by literature (6,5). Concentration of VFA tend to slowly increased, and remain around high value, 6500 mg$_{CH3COOH}$/l in reactor S4 and 6000 mg$_{CH3COOH}$/l for S3. Also COD and TOC value still remain constant. For both reactors, S3 and S4, the aeration was definitively stopped. During the 2 anaerobic week the recirculation was switched off, and all parameter concentrations still remain stable. Despite the value of pH and VFA, in the S3 columns, the pH quickly increased from 6.1 to over 7 within 20 days when the recirculated was reactivated.

With continuous aeration in column S4, there were different results. During the remaining part of the test, pH and VFA remained constant (6.2 and 6500 mg$_{CH3COOH}$/l), but nevertheless begins to form methane. With similar value of pH (around 6) and VFA (around 6000 mg$_{CH3COOH}$/l) for both columns achieved by different type of aeration, in anaerobic phase, pH in S3 increase sharply and reach stable methanogenic phase early than S4, where the pH increase very slowly until the end of test.

For S1, S2, columns, the aeration stopped after 37 days. The VFA concentrations and pH value were similar to S3 and S4 columns (5000- 6000 mg$_{CH3COOH}$/l and 6-6.1). For this reason, after the 2 anaerobic weeks, the aeration was replaced in order to obtained further distinction between columns. Intermittent aeration was restarted and stopped when the pH of leachate achieved 6.3 (further 17 days) for column S1. After 51 aeration days, the VFA concentration start to decrease until value around 4000 mg$_{CH3COOH}$/l. PH value reach 6.4. According to pH and VFA value, the TOC and COD concentrations decreased quickly during the second aeration. Aerobic microorganisms might grow in the aerated bioreactor during the aeration process. The aerobes could quickly consume organic acids in the recirculated leachate and neutralizing the pH of leachate. The decreasing of VFA, COD and TOC concentrations are the confirm. In this way, the upper aeration layer probably functioned as a buffer layer and helped increase leachate pH in aerated bioreactor. The results indicated that pre aeration could shorten the acidic phase in the waste biodegradation process.(Xu Q. Et al. 2014). Similar observation are also found elsewhere (Erses et al.,2008; Sang et al., 2009).   After ceasing aeration, anaerobic condition for landfill gas generation was set up, and

the COD and TOC concentrations continued decreasing to 40000 mgO$_2$/l and 9000 mgC/l at the end of the test.

The column S2 was maintained under continuous aeration throughout the test. Unfortunately pH value doesn't increase and ammonia, COD, VFA, TOC concentrations start to accumulated in the reactor.

Nitrogen, which has potential to pollute water and soil, is another major constituent in the leachate. Ammonia nitrogen (NH$_3$-N) concentration in anaerobic and pre aerated bioreactors, accumulated and reach 1500 mgN/l for AN, 1800 mgN/l for aerated at the end of experiment. Initial concentrations of NH$_3$-N in leachate in both type of reactor were found to be similar, indicating uniformity in waste composition in the reactors. The variation of NH$_3$-N in leachate of aerated reactor showed a similar trend with that of the Anaerobic bioreactors.

During the aeration process, as a result of decomposition of organic matter containing nitrogen, initial NH$_3$-N concentration start to increased rapidly from 500 mgN/l to near 1000-1500 mgN/l for all reactors. After aeration ceased, NH$_3$-N concentration kept increasing slightly and fluctuated around.

Under anaerobic condition, protein fraction of biodegradables waste release ammonia nitrogen and they may accumulate in the leachate, due to the lack of ammonia degradation pathways (Long et al.2009). The recirculation practice in the anaerobic reintroduces ammonia to the system, keeping its value almost constant throughout experiment. Several researches indicated that NH$_3$-N is a significant long term pollution problem in landfill (Erses et al.,2008). The increased ammonia concentrations intensify the toxicity of the leachate, that it is better to remain below 2000 mgN/l (Khanal, 2008).

During the whole phase1 the NH$_3$-N concentration of the aerated bioreactors were slightly greater than those of AN bioreactor. For this reactors, it is considered that the aeration facilitate the degradation of waste, resulting in more NH$_3$-N dissolved in leachate. However, due to the relatively low air flow rate during the aeration and the slightly acidic pH doesn't allow the conversion of ammonia-nitrogen via nitrification or volatilization. This fact is underlined by the absence of nitrite and nitrate in the leachate. The elevate presence of readily biodegradable organic substances, confirmed by the high TOC concentrations in solid waste, and high IR$_4$ (76 mgO$_2$/gTS) and BOD/COD value (0,9), tend to rapidly consumed the oxygen available, due to heterotrophic bacteria.

Nitrate production occur by autotrophic bacteria, that nitrified ammonia and organic nitrogen in presence of oxygen and carbon dioxide. Their presence in the leachate, is due to the combination of aeration and organic substance degradation by heterotrophic bacteria. Their absence in the leachate during the whole experiment is related to the high organic content of the waste and the low airflow rate.

Chloride was monitored as a conservative tracer in order to estimate the dilution and washout effect. The chloride concentrations of aerated and anaerobic reactor indicated similar decreasing trend because the same amount of water and the same recirculation ratio was applied to the reactors. Decreasing in chloride concentrations caused by the dilution effect of water used for replaced the leachate sample. Initial chloride concentration were 3000 mgCl/l for aerobic and anaerobic reators, after 90 days of test, chloride concentration still remain constant.

4.2. Biogas characterization

Cumulative biogas and methane production per kilogram of waste in anaerobic and aerated reactor have been given in figure 2.15 and 2.16 respectively. In the start-up period, organic matters in the reactors are hydrolyzed and the produced organic acids cease gas production. During the intermediate anaerobic degradation stage, methanogenic bacteria slowly start to appear and gas production rate increases (Murphy et al., 1995). In this study, the anaerobic reactor exhibited some retardation in terms of gas production, because the acidogenesis period lasted a long time, confirmed by high COD concentrations and low pH values (5,5-6) in the reactor. Methane production was always under 16% by volume for both AN5 and AN6 during 90 days of operation (figure 2.16). The methane production rate per waste mass in the anaerobic bioreactor was 1.5 and 1.2 l_{CH4}/KgTS for AN6 and AN5 respectively, over 3 month of the experiment. The anaerobic bioreactor could not reach the stable methanogenic phase during that period. This result could largely be attributed to the long period of acid phase (figure 2.8). Those confirm the inhibition effect of acidic condition for methangenesis (Christensen and Kjeldsen, 1989). The value of TOC remains around 15000 mgC/l, related to the high organic substance content that indicate an high potential of methanization. The value of pH (around 6) doesn't allow this conversion.

In the Column S4, with a pH around 6,25, slightly greater than S2, methanogenesis was established successfully, with methane percentage around 30%.

Interesting result show S3 and S1 aerated column. For S3 aeration was stopped at 37 days, and the system was switched to an anaerobic bioreactor with a pH 6.1. The temperature was around 35 degree as confirm the exothermic aerobic degradation (Christensen and Kjeldsen, 1989). During the first 2 weeks, without recirculation the methane concentration of gas was 30%. When recirculation

has been restarted, the percentages sharply increased to over 60% whit a short time (5 days) and remain around this value

As shown in figure 2.16, the methane production rate increase quickly after aeration ceased with a peak value of 0.6 l_{CH4}/KgTS day.

In the column S1 was aerated again after 2 anaerobic week, to reach pH 6.5 (limit value). During this week started a low methane production, which is maintained also during the aeration restart period. This confirms the presence of anaerobic zone in the refuse mass also when aeration is performed. When methane production started, VFA concentration starts to decrease (4000 $mg_{CH3COOH}$/l) facilitate an increasing of ph. Stable methane conditions occur after 54 aeration days. The application of micro aeration during the first stage showed an positive result on hydrolysis/acidification enhancement. Micro aeration during pre-stage may have a positive effect in methanogenesis since an active methane phase was reached early compared to anaerobic reactors
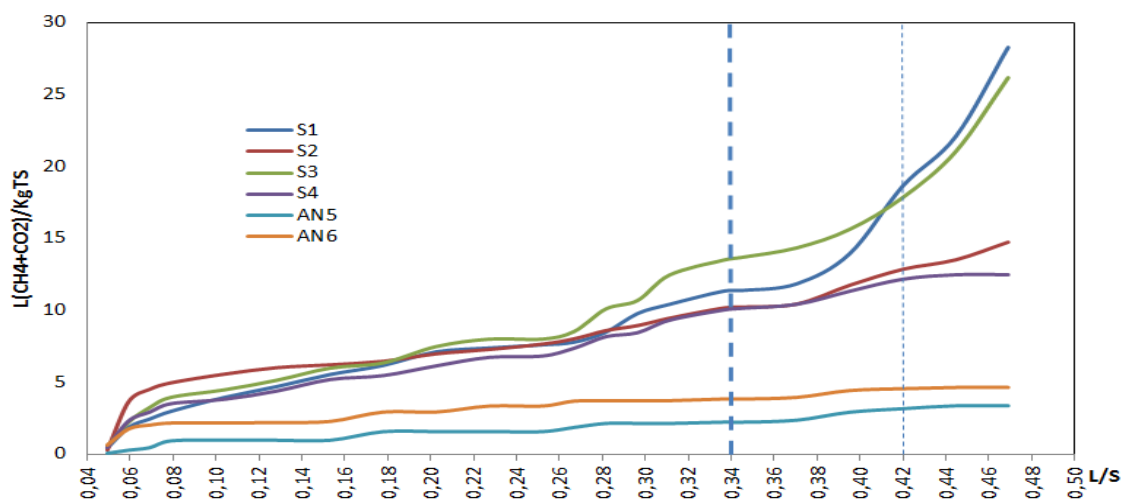
Figure 2.15 : Biogas yield trend for all the columns. The trace thick line indicates the stop of aeration for columns S3 and S4 (37 days). The trace thin line indicates the stop of aeration for column S1(51 days).

As regard the graph 2.16, methane production for Column S1, started on 37 days, respect anaerobic column where the effect is still negligible. Intermittent aeration benefit is evident also respect to continuous aeration. The first one lead to more readily stable methanogenic condition with gas percentage around 60% and 40 % for CH_4 and CO_2 respect to the continuous aerated columns.

Intermittent aeration is apparently the most practical strategy to support the established anaerobic condition. An intermittent aeration strategy is favorable for separation of the acid formation phase and methane fermentation phase, reducing the acid formation time (Sang et al. 2009). With this kind of waste, the stimulation of nitrifying and denitrifying bacteria doesn't appear, because the oxygen is immediately consumed by heterotrophic bacteria. Intermittent aeration present, respect

continuous aeration, a double flux. The air exiting velocity, with the same input liter, results much greater than the continuous, and this fact allow to better distributing the air, interesting an wide zone of the intermittent reactor. For this reason, the degradation that occurs in S3 and S1 results more stimulate respect the S2 S4 and lead to a more fast decrease of TOC, COD concentration in leachate.
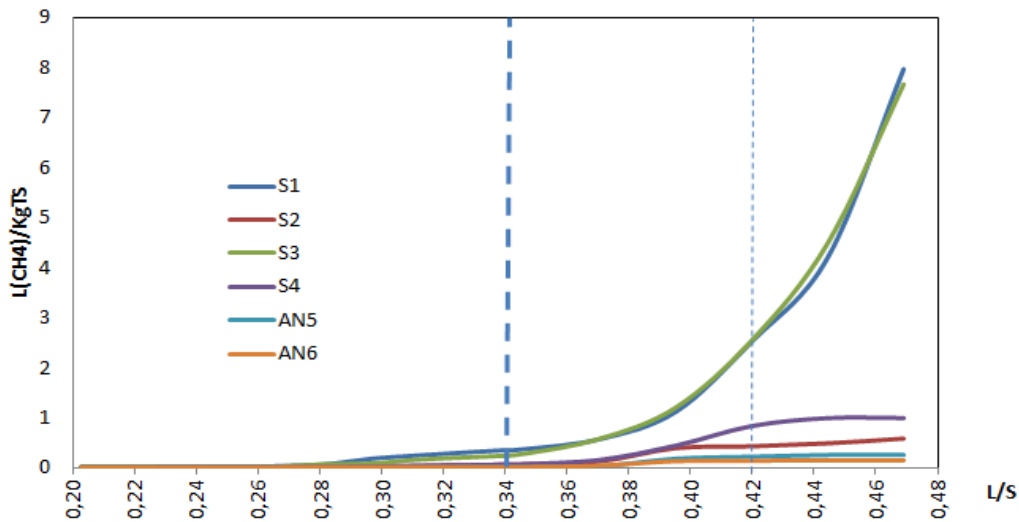
Figure 2.16 : Cumulative methane yield trend for all the columns. The trace thick line indicates the stop of aeration for columns S3 and S4 (37 days). The trace thin line indicates the stop of aeration for column S1(51 days).The methane production for S1 result to start before because during the calculation was taken into account also the methane produced during the second step. Moreover, the production does not begin exactly when the aeration was stopped. This fact is related to the sums of errors committed during the methane percentage measurement.

90

4.3 Carbon mass balance

The cumulative gasified and leachates carbon from the solid to the liquid and gas phase in the columns S1, S2, S3, S4, AN5, AN6, were plotted in the figure 2.17 and 2.18 respectively. The overall carbon mass transfer for all reactors operated under different test conditions, can be evaluated by means of monitoring of biogas flow rate and composition during the test, the measurements of TOC in waste samples at the beginning of the test (TOCi) as well as in the leachate extracted during the test (TOC$_L$). The mass balance referred to the entire duration of the experiment is shown in Table 2.7.Unfortunately, it was not possible to perform a total carbon mass balance, due to the lack of final characterization of solid waste sample. The lowest gasification occurred in the anaerobic column AN5, where the total amount of carbon measured in the gas phase was about 5,73 gC/kg TS in 90 days of test. Higher values, around 10,33 gC/kg TS respectively, were measured for the other anaerobic columns AN6. The highest gasification has been observed for intermittent pre aerated column S3 and S1 where the cumulative release of carbon in the gas phase was around 36,98 gC/kg TS and 34,87 gC/kg TS. A lower effect was observed in pre aerated continue column S2 and in the column S4, where values around 27,21 gC/kgTS and 25,05 gC/kgTS, respectively were calculated. The highest transfer of carbon into the leachate phase occurred for column S4, where a cumulated value of 7,18 gTOC/kg TS was calculated after 4.9 liter of leachate were extracted in 90 days. Considering the aerated columns and the anaerobic columns, the values for carbon transfer into the leachate phase ranged for all columns between 6-6.5 gTOC/kg TS after 4.9 l of leachate were   extracted in 90 days.
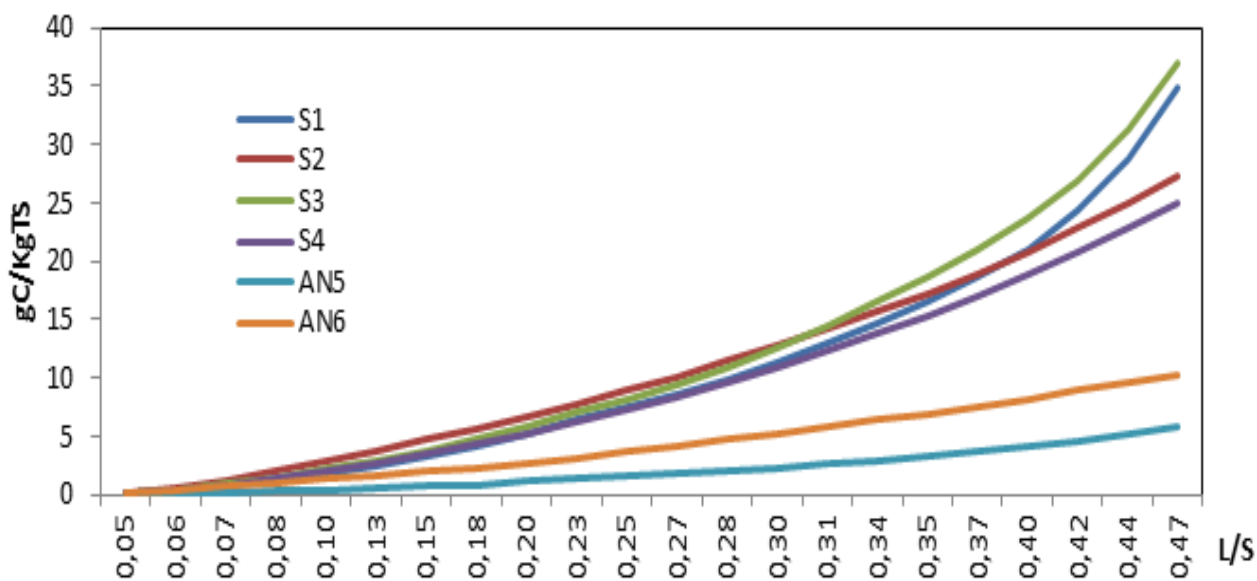
Figure 2.17: Evolution of cumulative gram of carbon per kilogram of total solids extracted through biogas from the different columns for the entire duration of the test.
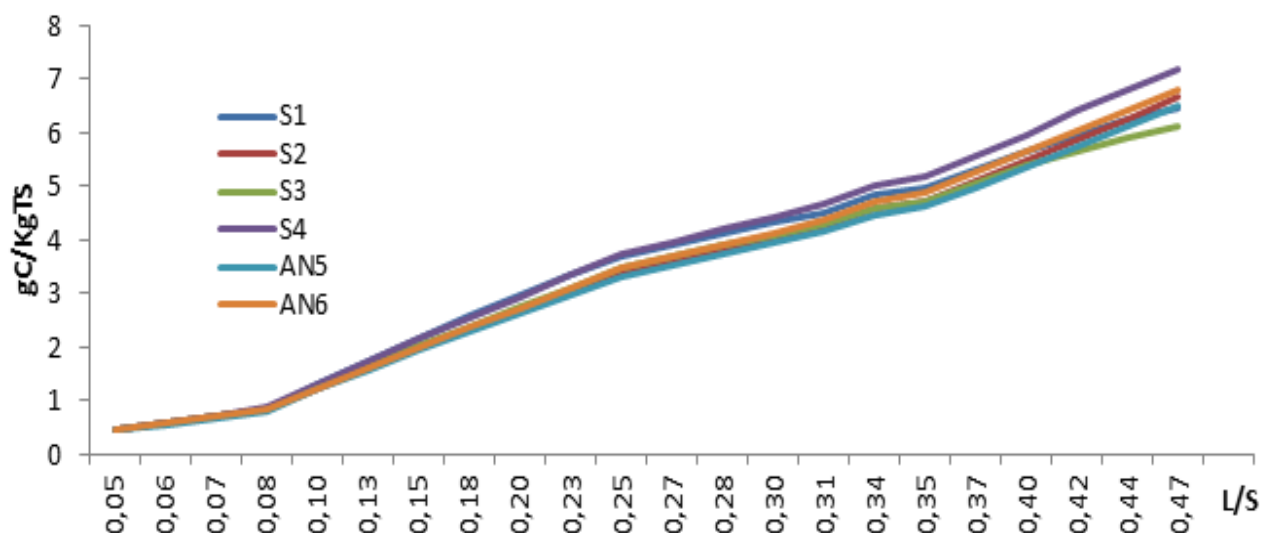
Figure 2.18: Evolution of cumulative gram of carbon per kilogram of total solids extracted through leachate from the different columns for the entire duration of the test.

Table 2.7: Carbon mass balance at the end of the experimental period. TOCi indicate the measurements on waste sample before the beginning of the test, Cg is the carbon in biogas, TOCl is the cumulative value for TOC measured in the extracted leachate, Cr is the total carbon removed after 90 days of test.

Carbon balance	S1	S2	S3	S4	AN5	AN6
TOC_i (gC/KgTS)	367,74	367,74	367,74	367,74	367,74	367,74
C_g (gC/KgTS)	34,87	27,21	36,98	25,05	5,73	10,33
TOC_l (gC/KgTS)	6,47	6,25	6,13	7,18	6,51	6,80
C_r (gC/KgTS)	41,34	33,46	43,11	32,23	12,24	17,13

Carbon removal percentage through gas and leachate respect the initial TOC (TOCi) are reported in table 2.8 and graphically showed in figure 2.19 to simplify the interpretation. Around 11% of the initial TOC in the waste samples was transferred into biogas and leachate altogether in intermittent aerated column S1and S3; values around 9 % were calculated for column S2 and S4 . The lower values for carbon transfer into biogas and leachate altogether were calculated for anaerobic column AN5 and AN6, around 3 and 4 % of the initial TOC in the waste samples, after 90 days of test.

Table 2.8: Carbon removal percentage through gas (Cgas. = gasified carbon) and leachate (Clea = leachated carbon.) respect the TOCi. Cr Is the total removal percentage sum of Cgas and Clea.

	S1	S2	S3	S4	AN5	AN6
$C_{gas.}$ (%)	9,84	7,40	10,06	6,81	1,56	2,81
$C_{lea.}$ (%)	1,76	1,70	1,67	1,95	1,77	1,85
C_r (%)	11,24	9,10	11,72	8,76	3,33	4,66
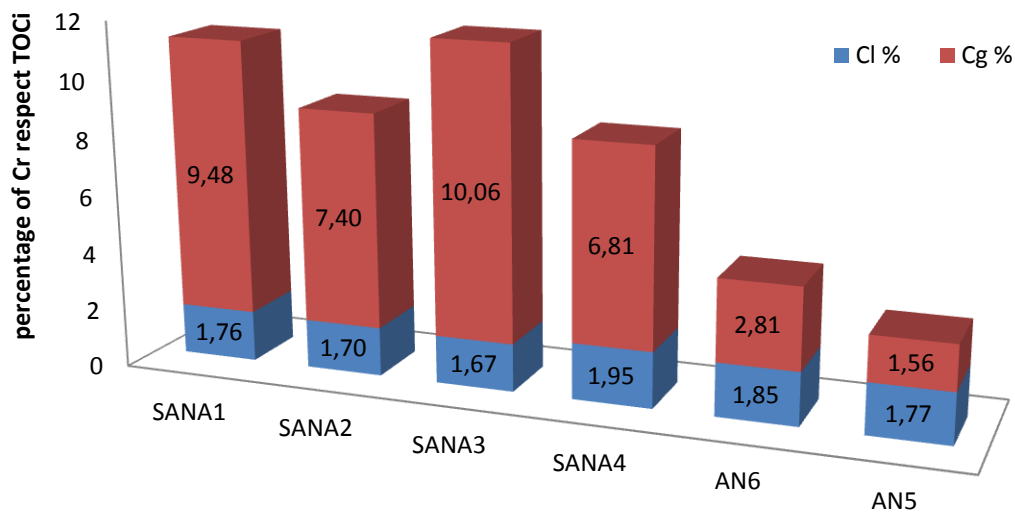
Figure 2.19: Carbon removal percentage through gas and leachate respect the initial TOC (TOCi) for all bioreactors during the entire duration of the test. Cgas. = gasified carbon, Clea = leachated carbon.

The carbon removal value during the first semi aerobic phase and the carbon removal through the anaerobic phase for reactors S1, S2, S3, S4, AN5, AN6 after 90 days of test are reported in table. Each fraction of carbon removed by leachate and by biogas in semi aerobic and anaerobic condition, expressed as gC/KgTS/day, are plotted in figure 2.20. The mean value of carbon removal percentage per day was also reported.

Table 2.9: Fraction of removal carbon during semi aerobic and anaerobic phase expressed in gC/KgTS/day. Cg ae./an., TOCl ae./an., indicate the carbon removal by gasification in aerated or anaerobic conditions, and the organic carbon removal by leaching in aerated or anaerobic conditions. Cgas. ae./an., Clea. ae./an. Indicate the carbon removal percentage through biogas in aerated or anaerobic conditions, and the organic carbon removal percentage through leaching in aerated or anaerobic conditions. Cr ae./an. are respectively the total carbon removal percentage in aerated and anaerobic condition.

	S1	S2	S3	S4	AN5	AN6
C removed in semi aerobic condition						
Cg ae.	0,40	0,31	0,45	0,37	-	-
TOCl ae.	0,11	0,08	0,12	0,14	-	-
Cr	0,50	0,39	0,57	0,51	-	-
Cgas. ae.(%) of day	0,12	0,09	0,12	0,10	-	-
Clea. ae. (%) of day	0,03	0,02	0,03	0,04	-	-
Cr ae. (%) of day	0,15	0,11	0,15	0,14	-	-
C removed in anaerobic condition						
Cg an.	0,40	0,24	0,39	0,21	0,06	0,11
TOCl an.	0,02	0,04	0,03	0,04	0,07	0,08
Cr	0,42	0,27	0,42	0,25	0,19	0,14
Cgas. an.(%) of day	0,11	0,06	0,11	0,06	0,02	0,03
Clea. an.(%) of day	0,01	0,01	0,01	0,01	0,02	0,02
Cr an. (%) of day	0,12	0,07	0,12	0,07	0,04	0,05
Cr (%) mean of day	0,14	0,1	0,13	0,01	0,04	0,05
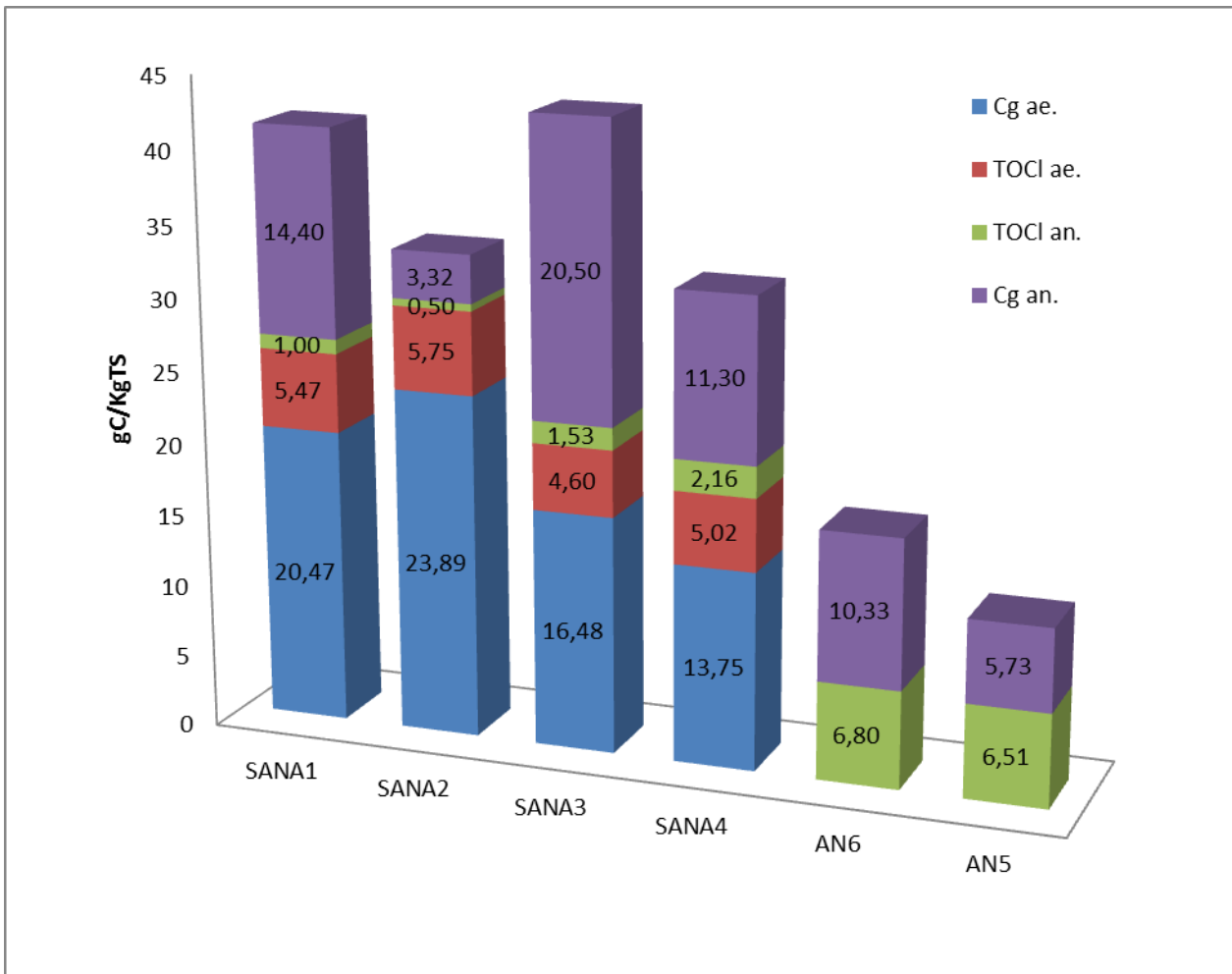
Figure 2.20: Fraction of removal carbon during semi aerobic and anaerobic phase. Cg ae./an., TOCl ae./an., indicate the carbon removal by gasification in aerated or anaerobic conditions, and the organic carbon removal by leaching in aerated or anaerobic conditions.

The duration of the Pre-aeration phase, play an important role during the gasification processes. In particular the intermittent conditions for reactor S3 and S1 showed a high carbon removal percentage of day (0,4-0,45 respectively) than the reactor pre-aerated continuously. The lower gasification occurs in anaerobic columns, with a mean carbon percentage removal of day around 0.02. The highest transfer of carbon into leachate phase was observed for all aerated reactor during the aeration phase, with value around 0,11. On contrary, during anaerobic phase the carbon removed through leachate decrease assuming values around 0,04. As seen before, intermittent aeration tends to facilitate the achievement of anaerobic condition rather than continuous aeration. This fact is related to the high carbon removal per day during the second phase for reactor S1 and S3 respect to reactor S1 and S2.

5. Conclusions and suggestions

A comparison of the emissions from the six lab columns, operating according to different landfill concept for a 90 days of test, indicate the following:

- The traditional anaerobic landfill with untreated MSW shows low changes in their pollution potential, with high TOC, COD, and ammonia concentration after 90 days of test respect to aerobically-pretreated MSW.

- Biogas production is delayed in the anaerobic columns by the initial acid phase, due to the low pH value caused by an accumulation of VFA.

- The application of semi aerobic phase as pre stage before anaerobic condition showed an equivocal result on hydrolysis/acidification enhancement. Pre aeration phase may have a positive effect in methanogenesis since an active methane phase was reached early compared to other reactor without pre aeration. This might have resulted in better hydrolysis/acidification during the start-up of methanization period providing substrate for methanogenesis.

- Intermittent aeration present, respect continuous aeration, a double flux (with the same input liter). The air exiting velocity through the waste mass, results much greater in intermittent than the continuous reactors. This fact allow to better distributing the air, interesting an wide zone of reactor.

- Methanogenesis is accelerated in reactors whit pre aeration phase. In particular reactors with intermittent aeration achieved readily stable methane condition than other reactors. The total gas production would seem to be much higher than that generally observed whit anaerobic reactors.

- Observing total carbon removal percentage, we can infer that anaerobic condition don't help at all the achievement of an acceptable impact in a short time. A semi-aerobic treatment at the beginning, should allow to saves time, anticipating methanogenic phase, and to achieve sustainable impact in short time.

- Mass balance seems to be a very useful tool to enable the quantification of the expected conversion of TOC with different management conditions. Carbon removal is significantly influenced by management method. Semi aerobic condition encourage removal of organic carbon through gasification.

- The intermittent aeration strategy, respect continuous aeration, was favorable for the initiation of solubilization of organic matter by aerobic bacteria and the reduction of acid formation phase. For achieve optimum range for anaerobic parameter, waste with high

content of organic fraction subject to continuous aeration need longer time respect to the same waste aerated intermittently.

- Careful consideration must be taken to avoid over aeration as this consumes substrate, which would otherwise be available to methanogens to produce biogas. For waste of high content of putrescible, as seen that a range of 40-50 days of intermittent aeration lead to favorable pH, VFA, and ammonia concentrations to established methanogenesis.

- Water addition and moisture content are essential in landfill. Water additions wash out organic substances through leachate and effect degradation kinetics inside the waste mass. Permeable top covers are essential to ensure this.

The effect of intermittent aeration on the performance of landfill bioreactors have never been studied systematically. The intermittent aeration performance is expected to be enhanced under optimize conditions on the intermittent aeration mode

Further study are in progress in order to optimize the operational conditions of the S.An.A. landfill model, as well as to investigate the dynamic behavior of oxygen and leachate in the waste mass.

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Da quando sono all'Università, sono riuscito a cambiare, 5 case, 8 bici e 17 coinquilini e 3 fidanzate. Tutto si può riassumere con una sola parola, Pizz. Indubbiamente una persona a me molto cara. Con lui si che ho fatto tutta la mia carriera universitaria, triennale e magistrale. Una persona autentica, di una semplicità disarmante. Mi fermo qui con i complimenti, lui lo sa che li voglio bene.

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Part 3

Annexes

Annex 1: Leachate and biogas results

Table 3.1: Analytical results of TOC concentration (Conc.) and cumulative mass extracted (Cum, mass) expressed as mgC/l and gC/KgTS respectively calculated on the leachate extracted from reactor S1, S2, S3, S4, AN5, AN6, during the experimental period. The day on which the aeration was stopped is marked in yellow; respectively 8-ago for S3 and S4, 8-set for S1.

Date	L/S (l/KgTS)	S1 Conc (mg/l)	S1 cum. mass (g/KgTS)	S2 Conc (mg/l)	S2 cum. mass (g/KgTS)	S3 Conc (mg/l)	S3 cum. mass (g/KgTS)	S4 Conc (mg/l)	S4 cum. mass (g/KgTS)	AN5 Conc (mg/l)	AN5 cum. mass (g/KgTS)	AN6 Conc (mg/l)	AN6 cum. mass (g/KgTS)
4-lug	0,05	9130	0,451	9130	0,451	9130	0,451	9130	0,451	9130	0,451	9130	0,451
7-lug	0,06	12150	0,571	12750	0,577	12750	0,577	13200	0,582	11500	0,565	12700	0,577
9-lug	0,07	13472	0,704	13439	0,710	13528	0,711	14178	0,722	12411	0,687	13311	0,708
11-lug	0,08	14794	0,850	14128	0,849	14306	0,852	15156	0,871	13322	0,819	13922	0,846
14-lug	0,10	18100	1,298	15850	1,241	16250	1,254	17600	1,306	15600	1,204	15450	1,227
16-lug	0,13	17617	1,733	15367	1,621	15783	1,643	17133	1,729	15017	1,575	15317	1,606
18-lug	0,15	17133	2,156	14883	1,988	15317	2,022	16667	2,141	14433	1,932	15183	1,981
21-lug	0,18	16650	2,567	14400	2,344	14850	2,389	16200	2,541	13850	2,274	15050	2,353
23-lug	0,20	15983	2,962	14367	2,699	14767	2,753	16133	2,940	14033	2,621	15067	2,725
25-lug	0,23	15317	3,341	14333	3,053	14683	3,116	16067	3,337	14217	2,972	15083	3,097
28-lug	0,25	14650	3,702	14300	3,406	14600	3,477	16000	3,732	14400	3,328	15100	3,470
30-lug	0,27	14279	3,914	14247	3,617	14256	3,688	15815	3,966	14179	3,538	15056	3,694
1-ago	0,28	13909	4,120	14194	3,828	13912	3,894	15629	4,198	13959	3,745	15012	3,916
4-ago	0,30	13538	4,321	14141	4,037	13568	4,095	15444	4,427	13738	3,948	14968	4,138
6-ago	0,31	13168	4,516	14088	4,246	13224	4,291	15259	4,653	13518	4,149	14924	4,359
8-ago	0,34	12550	4,826	14000	4,592	12650	4,604	14950	5,023	13150	4,474	14850	4,726
18-ago	0,35	14000	4,965	14200	4,732	13250	4,735	14650	5,167	14350	4,615	15250	4,877
25-ago	0,37	14050	5,312	15000	5,103	13450	5,067	15400	5,548	14950	4,985	15600	5,262
1-set	0,40	13460	5,644	15660	5,490	12860	5,385	16060	5,944	15420	5,366	15380	5,642
8-set	0,42	12100	5,943	15700	5,878	11060	5,658	18600	6,404	15480	5,748	15120	6,016
15-set	0,44	11780	6,234	15140	6,252	10040	5,906	15320	6,782	15060	6,120	15480	6,398
22-set	0,47	9420	6,473	16000	6,657	8720	6,127	15680	7,180	15520	6,513	15780	6,798

Table 3.2: Analytical results of SO_4^{2-} concentrations and Cl^- concentrations expressed as mg SO_4^{2-} /l and mgCl/l respectively calculated on the leachate extracted from reactor S1, S2, S3, S4, AN5, AN6, during the experimental period. The day on which the aeration was stopped is marked in yellow; respectively 8-ago for S3 and S4, 8-set for S1.

Data	L/S (l/KgTS)	S1 SO42- [mg/l]	S1 Cl- [mg/l]	S2 SO42- [mg/l]	S2 Cl- [mg/l]	S3 SO42- [mg/l]	S3 Cl- [mg/l]	S4 SO42- [mg/l]	S4 Cl- [mg/l]	AN5 SO42- [mg/l]	AN5 Cl- [mg/l]	AN6 SO42- [mg/l]	AN6 Cl- [mg/l]
04-lug	0,05	2.261,70	3.139,36	2.261,70	3.139,36	2.261,70	3.139,36	2.261,70	3.139,36	2.261,70	3.139,36	2.261,70	3.139,36
14-lug	0,10	2.000,20	3.475,00	1.917,80	3.538,00	1.999,50	3.787,00	1.706,00	3.758,00	1.680,70	2.571,00	2.607,60	2.927,00
21-lug	0,18	1.505,70	3.487,50	1.383,50	3.185,45	1.715,20	3.338,63	1.715,60	3.617,32	1.438,20	2.323,85	1.529,50	2.922,36
28-lug	0,25	2.824,70	2.780,53	1.232,32	3.009,60	1.562,90	4.157,68	1.237,60	3.434,40	1.271,85	2.537,30	882,35	2.588,36
04-ago	0,30	1.813,40	3.324,40	1.666,20	2.952,10	1.721,20	3.258,40	1.503,80	3.467,60	1.323,20	2.522,40	1.722,80	2.741,50
18-ago	0,35	1767	3210,27	1765,6	3754,8	1786,1	3101,77	1905,3	3250,69	1684,6	2504,68	1529,1	2515,31
25-ago	0,37	1.508,00	2.663,17	1.680,30	2.847,19	1.496,20	3.021,64	1.807,50	3.266,29	1.446,40	2.465,32	1.550,90	2.429,16
01-set	0,40	1.534,70	2.592,61	1.576,90	2.743,66	1.475,10	2.985,47	1.557,50	3.168,43	1.641,10	2.631,61	1.417,10	2.401,85
08-set	0,42	1.394,40	3.321,61	1.615,40	3.278,30	1.179,60	3.037,20	1.583,30	3.273,30	1.805,50	2.658,50	1.790,70	2.451,40
15-set	0,45	1.167,00	2.635,16	1.716,90	2.871,30	829,45	3.046,46	1.458,60	3.408,83	1.529,10	2.626,65	1.550,90	2.419,58
22-set	2,00	1.110,80	3.116,67	1.650,70	2.597,57	684,85	3.616,61	1.695,50	3.036,53	1.806,80	2.616,01	1.914,50	2.785,50
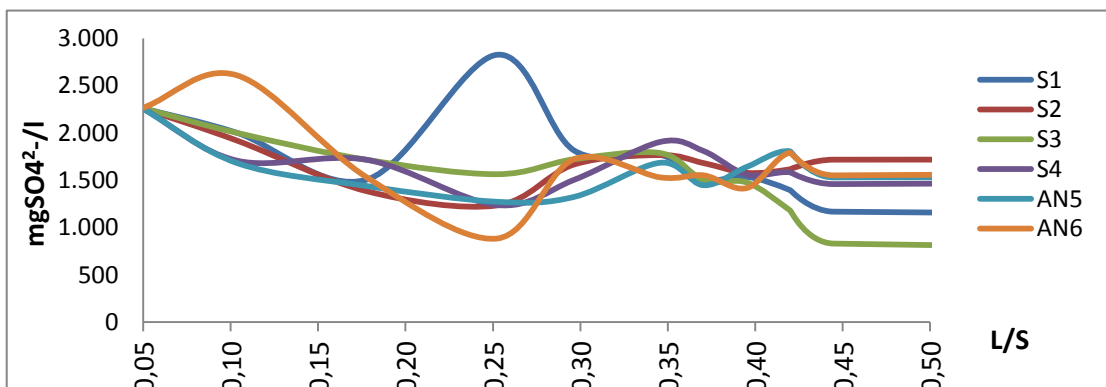
Figure 3.1: sulphates trend for all reactor during the test period.

Table 3.3: Analytical results of VFA concentration and alkalinity concentration expressed as mgCH3COOH/l and gCaCO3/l respectively calculated on the leachate extracted from reactor S1, S2, S3, S4, AN5, AN6, during the experimental period. The day on which the aeration was stopped is marked in yellow; respectively 8-ago for S3 and S4, 8-set for S1.

Data	L/S (l/KgTS)	S1 Alc [mg CaCO3/l]	S1 VFA [mg/l]	S2 Alc [mg CaCO3/l]	S2 VFA [mg/l]	S3 Alc [mg CaCO3/l]	S3 VFA [mg/l]	S4 Alc [mg CaCO3/l]	S4 VFA [mg/l]	AN5 Alc [mg CaCO3/l]	AN5 VFA [mg/l]	AN6 Alc [mg CaCO3/l]	AN6 VFA [mg/l]
04-lug	0,05	448	2.213	182	2.166	602	2.227	391	2.171	199	2.155	494	2.129
07-lug	0,06	3.000	4.045	3.384	4.109	3.235	4.073	3.358	4.411	2.953	3.776	3.167	4.385
09-lug	0,07	2.468	4.382	2.810	4.554	2.921	4.962	3.122	4.842	3.134	4.118	2.857	4.561
11-lug	0,08	3.024	4.895	2.631	5.087	2.660	5.200	3.032	5.520	2.674	4.703	2.717	4.910
14-lug	0,10	3.059	4.967	2.579	5.089	2.641	5.345	2.896	5.647	2.924	4.974	2.617	5.083
16-lug	0,13	2.150	5.152	2.438	5.262	2.520	5.407	1.935	5.662	2.375	4.717	1.949	4.868
18-lug	0,15	2.795	5.179	2.498	5.387	2.626	5.298	2.612	5.659	2.420	4.848	2.416	5.114
21-lug	0,18	2.207	5.123	2.271	5.413	1.965	4.817	2.466	4.817	2.250	4.652	2.078	4.944
23-lug	0,20	2.818	5.026	2.254	5.519	2.486	5.208	2.664	5.956	1.859	5.020	2.238	5.120
25-lug	0,23	4.770	5.827	4.619	6.090	4.656	5.868	5.265	6.653	4.286	5.772	4.765	5.915
28-lug	0,25	3.092	5.233	2.746	5.591	2.737	5.268	3.205	5.986	2.660	5.099	2.677	5.555
30-lug	0,27	3.848	5.473	4.175	5.864	3.722	5.742	4.398	5.522	3.688	5.669	4.250	6.400
01-ago	0,28	2.035	5.356	2.178	5.706	2.180	5.466	3.115	6.424	2.264	5.506	2.235	5.670
04-ago	0,30	3.836	5.784	3.548	6.278	3.461	6.151	3.989	6.984	3.433	6.265	3.496	6.410
06-ago	0,31	2.819	5.708	3.205	6.190	3.116	5.941	4.080	6.863	3.448	6.235	3.587	6.586
08-ago	0,34	4.024	5.852	4.006	6.418	3.712	6.378	4.629	6.839	3.582	6.095	4.197	6.829
18-ago	0,35	4.386	5.684	4.740	6.073	4.606	6.014	5.341	6.456	4.648	6.170	4.851	6.454
25-ago	0,37	3.074	5.962	3.800	6.917	3.953	7.144	4.807	7.622	4.373	7.351	4.745	7.325
01-set	0,40	3.339	5.646	3.446	6.925	3.830	5.988	3.834	7.108	3.573	6.697	3.678	6.661
08-set	0,42	4.163	5.287	4.159	6.617	3.944	5.389	4.386	6.883	3.624	6.454	3.685	6.559
15-set	0,45	3.075	4.566	2.394	4.792	3.945	4.853	3.802	7.002	3.633	6.631	3.501	6.704
22-set	0,47	3.948	4.346	4.250	6.103	4.651	4.087	4.623	6.582	4.400	6.266	4.282	6.332

Table 3.4: Analytical results of cumulative VFA concentration respect to TS and cumulative carbon concentration expressed as gVFA/KgTS and gC/KgTS respectively calculated on the leachate extracted from reactor S1, S2, S3, S4, AN5, AN6, during the experimental period. The day on which the aeration was stopped is marked in yellow; respectively 8-ago for S3 and S4, 8-set for S1.

Data	L/S	S1 g VFA/Kg	S1 gC/KgTS	S2 g VFA/Kg	S2 gC/KgTS	S3 g VFA/Kg	S3 gC/KgTS	S4 g VFA/Kg	S4 gC/KgTS	AN5 g VFA/Kg	AN5 gC/KgTS	AN6 g VFA/Kg	AN6 gC/KgTS
4-lug	0,05	0,11	0,044	0,11	0,04	0,11	0,04	0,11	0,04	0,11	0,04	0,11	0,04
7-lug	0,06	0,15	0,060	0,15	0,06	0,15	0,06	0,15	0,06	0,14	0,06	0,15	0,06
9-lug	0,07	0,19	0,077	0,19	0,08	0,20	0,08	0,20	0,08	0,18	0,07	0,19	0,08
11-lug	0,08	0,24	0,096	0,24	0,10	0,25	0,10	0,25	0,10	0,23	0,09	0,24	0,10
14-lug	0,10	0,36	0,145	0,37	0,15	0,38	0,15	0,39	0,16	0,35	0,14	0,37	0,15
16-lug	0,13	0,49	0,196	0,50	0,20	0,52	0,21	0,53	0,21	0,47	0,19	0,49	0,20
18-lug	0,15	0,62	0,248	0,63	0,25	0,65	0,26	0,67	0,27	0,59	0,24	0,61	0,25
21-lug	0,18	0,75	0,298	0,77	0,31	0,77	0,31	0,79	0,32	0,71	0,28	0,74	0,29
23-lug	0,20	0,87	0,348	0,90	0,36	0,89	0,36	0,94	0,38	0,83	0,33	0,86	0,35
25-lug	0,23	1,01	0,405	1,05	0,42	1,04	0,42	1,10	0,44	0,97	0,39	1,01	0,40
28-lug	0,25	1,14	0,457	1,19	0,48	1,17	0,47	1,25	0,50	1,10	0,44	1,15	0,46
30-lug	0,27	1,22	0,490	1,28	0,51	1,26	0,50	1,33	0,53	1,18	0,47	1,24	0,50
1-ago	0,28	1,30	0,521	1,36	0,54	1,34	0,53	1,43	0,57	1,26	0,51	1,33	0,53
4-ago	0,30	1,39	0,556	1,45	0,58	1,43	0,57	1,53	0,61	1,36	0,54	1,42	0,57
6-ago	0,31	1,47	0,589	1,55	0,62	1,52	0,61	1,63	0,65	1,45	0,58	1,52	0,61
8-ago	0,34	1,62	0,647	1,71	0,68	1,67	0,67	1,80	0,72	1,60	0,64	1,69	0,67
18-ago	0,35	1,67	0,670	1,77	0,71	1,73	0,69	1,87	0,75	1,66	0,66	1,75	0,70
25-ago	0,37	1,82	0,729	1,94	0,77	1,91	0,76	2,05	0,82	1,84	0,74	1,93	0,77
1-set	0,40	1,96	0,784	2,11	0,84	2,06	0,82	2,23	0,89	2,01	0,80	2,10	0,84
8-set	0,42	2,09	0,837	2,27	0,91	2,19	0,88	2,40	0,96	2,17	0,87	2,26	0,90
15-set	0,45	2,23	0,892	2,41	0,97	2,34	0,93	2,61	1,04	2,37	0,95	2,46	0,98
22-set	0,47	2,32	0,926	2,54	1,01	2,42	0,97	2,74	1,10	2,49	1,00	2,59	1,03

Table 3.5: Analytical results of cumulative VFA concentration respect to TS and cumulative carbon concentration expressed as gVFA/KgTS and gC/KgTS respectively calculated on the leachate extracted from reactor S1, S2, S3, S4, AN5, AN6, during the experimental period. The day on which the aeration was stopped is marked in yellow; respectively 8-ago for S3 and S4, 8-set for S1.

		S1	S2	S3	S4	AN5	AN6
Data	L/S (ll/KgTS)	FOS/TAC	FOS/TAC	FOS/TAC	FOS/TAC	FOS/TAC	FOS/TAC
04-lug	0,05	4,9	11,9	3,7	5,6	10,8	4,3
07-lug	0,06	1,3	1,2	1,3	1,3	1,3	1,4
09-lug	0,07	1,8	1,6	1,7	1,6	1,3	1,6
11-lug	0,08	1,6	1,9	2,0	1,8	1,8	1,8
14-lug	0,10	1,6	2,0	2,0	2,0	1,7	1,9
16-lug	0,13	2,4	2,2	2,1	2,9	2,0	2,5
18-lug	0,15	1,9	2,2	2,0	2,2	2,0	2,1
21-lug	0,18	2,3	2,4	2,5	2,0	2,1	2,4
23-lug	0,20	1,8	2,4	2,1	2,2	2,7	2,3
25-lug	0,23	1,2	1,3	1,3	1,3	1,3	1,2
28-lug	0,25	1,7	2,0	1,9	1,9	1,9	2,1
30-lug	0,27	1,4	1,4	1,5	1,3	1,5	1,5
01-ago	0,28	2,6	2,6	2,5	2,1	2,4	2,5
04-ago	0,30	1,5	1,8	1,8	1,8	1,8	1,8
06-ago	0,31	2,0	1,9	1,9	1,7	1,8	1,8
08-ago	0,34	1,5	1,6	1,7	1,5	1,7	1,6
18-ago	0,35	1,3	1,3	1,3	1,2	1,3	1,3
25-ago	0,37	1,9	1,8	1,8	1,6	1,7	1,5
01-set	0,40	1,7	2,0	1,6	1,9	1,9	1,8
08-set	0,42	1,3	1,6	1,4	1,6	1,8	1,8
15-set	0,45	1,5	2,0	1,2	1,8	1,8	1,9
22-set	0,47	1,1	1,4	0,9	1,4	1,4	1,5
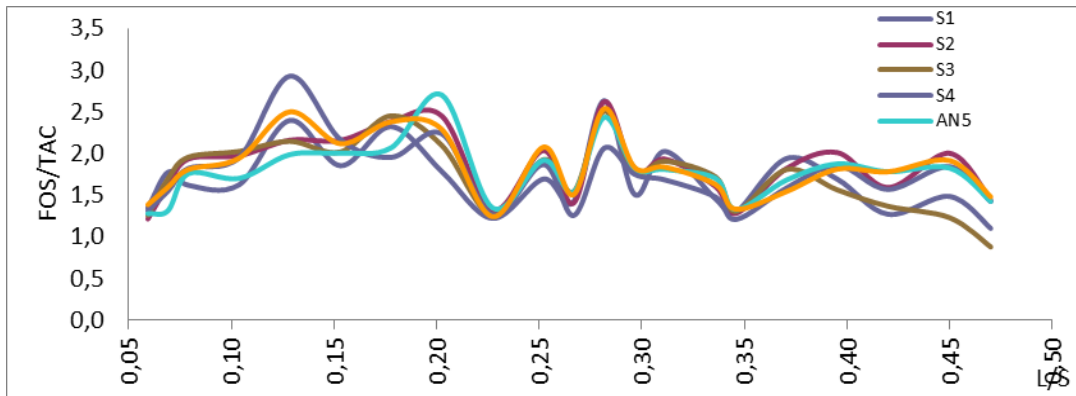
Figure 3.2: FOS/TAC trend for all reactor during the test period.

Table 3.6: Analytical results of COD concentration (Conc.) and cumulative mass extracted (Cum, mass) expressed as mgO/l and gO/KgTS respectively calculated on the leachate extracted from reactor S1, S2, S3, S4, AN5, AN6, during the experimental period. The day on which the aeration was stopped is marked in yellow; respectively 8-ago for S3 and S4, 8-set for S1.

	L/S	S1	S1	S2	S2	S3	S3
Data		Conc. mgO/l	Cum. Mass gO/KgTS	Conc. mgO/l	Cum. Mass gO/KgTS	Conc. mgO/l	Cum. Mass gO/KgTS
4-lug	0,05	30000,0	1,48	30000,0	1,48	30000,0	1,48
7-lug	0,06	28308,5	1,76	31361,4	1,79	32929,5	1,81
9-lug	0,07	35044,2	2,11	36467,6	2,15	41579,0	2,22
11-lug	0,08	41779,8	2,52	41573,8	2,56	58878,0	2,80
14-lug	0,10	58619,0	3,97	54339,3	3,91	71852,3	4,58
16-lug	0,13	58907,7	5,42	59979,7	5,39	70539,6	6,32
18-lug	0,15	59196,5	6,89	65620,1	7,01	69664,6	8,04
21-lug	0,18	59485,2	8,36	71260,5	8,77	67914,4	9,72
23-lug	0,20	59105,3	9,82	82403,9	10,80	64683,8	11,31
25-lug	0,23	58725,4	11,27	88289,8	12,99	62530,0	12,86
28-lug	0,25	58345,6	12,71	104690,8	15,57	58222,5	14,30
30-lug	0,27	57009,4	13,55	97707,1	17,02	57687,3	15,15
1-ago	0,28	55673,2	14,38	90723,5	18,36	57330,5	16,00
4-ago	0,30	54337,0	15,18	83739,8	19,61	56617,0	16,84
6-ago	0,31	49420,1	15,92	74041,4	20,70	63272,0	17,78
8-ago	0,34	41225,2	16,93	57877,2	22,13	74363,6	19,62
18-ago	0,35	54800,3	17,48	51411,2	22,64	49339,9	20,10
25-ago	0,37	50879,7	18,73	55358,2	24,01	51464,8	21,38
1-set	0,40	53679,2	20,06	55854,5	25,39	50156,5	22,61
8-set	0,42	34778,4	20,92	43150,0	26,46	32292,0	23,41
15-set	0,45	63230,3	22,50	77153,5	28,39	53354,2	24,75
22-set	0,47	41328,5	23,49	56372,3	29,74	36283,7	25,62

	L/S	S4	S4	AN5	AN5	AN6	AN6
Data		Conc. mgO/l	Cum. Mass gO/KgTS	Conc. mgO/l	Cum. Mass gO/KgTS	Conc. mgO/l	Cum. Mass gO/KgTS
4-lug	0,05	30000,0	1,48	30000,0	1,48	30000,0	1,48
7-lug	0,06	35631,1	1,83	30800,5	1,79	33915,5	1,82
9-lug	0,07	49511,5	2,32	39795,4	2,18	43183,9	2,24
11-lug	0,08	77272,2	3,09	57785,1	2,75	61720,6	2,85
14-lug	0,10	98092,8	5,51	71277,4	4,51	75623,2	4,72
16-lug	0,13	86662,6	7,65	68920,0	6,21	73279,3	6,53
18-lug	0,15	79042,5	9,60	67348,4	7,88	71716,7	8,30
21-lug	0,18	63802,3	11,18	64205,2	9,46	68591,5	10,00
23-lug	0,20	63630,1	12,75	57267,6	10,88	65952,2	11,63
25-lug	0,23	63515,3	14,32	52642,5	12,18	64192,7	13,21
28-lug	0,25	63285,8	15,88	43392,4	13,25	60673,7	14,71
30-lug	0,27	65479,9	16,85	51521,6	14,01	62315,9	15,64
1-ago	0,28	66942,7	17,85	56941,0	14,86	63775,5	16,58
4-ago	0,30	69868,3	18,88	67779,8	15,86	65600,2	17,55
6-ago	0,31	63915,8	19,83	66443,4	16,85	68172,3	18,56
8-ago	0,34	53994,8	21,16	64216,0	18,43	72459,2	20,35
18-ago	0,35	59121,0	21,75	55290,4	18,98	58107,6	20,93
25-ago	0,37	60344,6	23,24	56808,2	20,38	58574,6	22,38
1-set	0,40	58382,3	24,68	54518,1	21,73	60175,2	23,86
8-set	0,42	42489,6	25,73	57661,6	23,16	59211,1	25,33
15-set	0,45	57182,2	27,16	72978,4	24,98	77053,0	27,25
22-set	0,47	59586,6	28,59	58838,4	26,39	60756,1	28,71

Table 3.7 : Leachate volume extracted, recirculated and measured for columns S1 and S2 for the entire duration of the test

	column S1						column S2						
Data	W out (l)	W analysis (l)	W ricirc (l)	W in_new (l)	W cum (l)	W out cum (l)	W out (l)	W analisi (l)	W ricirc (l)	W in_new (l)	W cum (l)	W out cum (l)	L/S (l/Kg_TS)
03-lug	0	0	0	5	0	0	0	0	0	5	0	0	0,00
04-lug	2	0	2	1	0	2	2,25	0	2,25	1	0	2,25	0,00
04-lug	0,5	0,5	0	0,5	0,5	2,5	0,5	0,5	0	0,5	0,5	2,75	0,05
07-lug	2,25	0	2,25	0	0,5	4,75	1,5	0	1,5	0	0,5	4,25	0,05
07-lug	0,1	0,1	0	0,1	0,6	4,85	0,1	0,1	0	0,1	0,6	4,35	0,06
08-lug	1	0	1	0	0,6	5,85	2	0	2	0	0,6	6,35	0,06
09-lug	1,5	0	1,5	0	0,6	7,35	1,75	0	1,75	0	0,6	8,1	0,06
09-lug	0,1	0,1	0	0,1	0,7	7,45	0,1	0,1	0	0,1	0,7	8,2	0,07
10-lug	1,3	0	1,3	0	0,7	8,75	1,5	0	1,5	0	0,7	9,7	0,07
10-lug	0,15	0,15	0,15	0	0,7	8,9	0,15	0,15	0,15	0	0,7	9,85	0,07
11-lug	1,2	0	1,2	0	0,7	10,1	1,5	0	1,5	0	0,7	11,35	0,07
11-lug	0,1	0,1	0	0,1	0,8	10,2	0,1	0,1	0	0,1	0,8	11,45	0,08
14-lug	1,5	0,25	1,25	0,25	1,05	11,7	1,75	0,25	1,5	0,25	1,05	13,2	0,10
15-lug	1,1	0	1,1	1	1,05	12,8	1,5	0	1,5	1	1,05	14,7	0,10
16-lug	2	0,25	1,75	0,25	1,3	14,8	2,8	0,25	2,55	0,25	1,3	17,5	0,13
17-lug	1,6	0	1,6	0	1,3	16,4	2	0	2	0	1,3	19,5	0,13
18-lug	1,9	0,25	1,65	0,25	1,55	18,3	2,25	0,25	2	0,25	1,55	21,75	0,15
21-lug	2	0,25	1,75	0,25	1,8	20,3	2,5	0,25	2,25	0,25	1,8	24,25	0,18
22-lug	2,25	0	2,25	0	1,8	22,55	2	0	2	0	1,8	26,25	0,18
23-lug	2,1	0,25	1,85	0,25	2,05	24,65	2	0,25	1,75	0,25	2,05	28,25	0,20
24-lug	2	0	2	0	2,05	26,65	2	0	2	0	2,05	30,25	0,20
25-lug	2	0,25	1,75	0,25	2,3	28,65	1,9	0,25	1,65	0,25	2,3	32,15	0,23
28-lug	2,4	0,25	2,15	0,25	2,55	31,05	2	0,25	1,75	0,25	2,55	34,15	0,25
29-lug	2,2	0	2,2	0	2,55	33,25	2	0	2	0	2,55	36,15	0,25
30-lug	2,2	0,15	2,05	0,15	2,7	35,45	2	0,15	1,85	0,15	2,7	38,15	0,27
31-lug	2,1	0	2,1	0	2,7	37,55	2	0	2	0	2,7	40,15	0,27
01-ago	2,2	0,15	2,05	0,15	2,85	39,75	2	0,15	1,85	0,15	2,85	42,15	0,28
04-ago	2,25	0,15	2,1	0,15	3	42	2	0,15	1,85	0,15	3	44,15	0,30
05-ago	2	0	2	0	3	44	1,9	0	1,9	0	3	46,05	0,30
06-ago	2	0,15	1,85	0,15	3,15	46	1,8	0,15	1,65	0,15	3,15	47,85	0,31
07-ago	2	0	2	0	3,15	48	1,8	0	1,8	0	3,15	49,65	0,31
08-ago	2	0,25	1,75	0,25	3,4	50	1,8	0,25	1,55	0,25	3,4	51,45	0,34
18-ago	2,5	0,1	2,4	0,1	3,5	52,5	2,2	0,1	2,1	0,1	3,5	53,65	0,35
20-ago	2,5	0	2,5	0	3,5	55	2,1	0	2,1	0	3,5	55,75	0,35
25-ago	2,7	0,25	2,45	0,25	3,75	57,7	2,25	0,25	2	0,25	3,75	58	0,37
26-ago	2,5	0	2,5	0	3,75	60,2	2	0	2	0	3,75	60	0,37
27-ago	2,5	0	2,5	0	3,75	62,7	2	0	2	0	3,75	62	0,37
28-ago	2,4	0	2,4	0	3,75	65,1	1,9	0	1,9	0	3,75	63,9	0,37
29-ago	2,25	0	2,25	0	3,75	67,35	1,7	0	1,7	0	3,75	65,6	0,37
01-set	2,5	0,25	2,25	0,25	4	69,85	1,95	0,25	1,7	0,25	4	67,55	0,40
02-set	2,4	0	2,4	0	4	72,25	1,7	0	1,7	0	4	69,25	0,40
03-set	2,4	0	2,4	0	4	74,65	1,7	0	1,7	0	4	70,95	0,40
04-set	2,4	0	2,4	0	4	77,05	1,75	0	1,75	0	4	72,7	0,40
05-set	2,4	0	2,4	0	4	79,45	1,7	0	1,7	0	4	74,4	0,40
08-set	2,6	0,25	2,35	0,25	4,25	82,05	2	0,25	1,75	0,25	4,25	76,4	0,42
09-set	2,5	0	2,5	0	4,25	84,55	1,85	0	1,85	0	4,25	78,25	0,42
10-set	2,5	0	2,5	0	4,25	87,05	1,85	0	1,85	0	4,25	80,1	0,42
11-set	2,5	0	2,5	0	4,25	89,55	1,8	0	1,8	0	4,25	81,9	0,42
12-set	2,5	0	2,5	0	4,25	92,05	1,8	0	1,8	0	4,25	83,7	0,42
15-set	2,6	0,25	2,35	0,25	4,5	94,65	2	0,25	1,75	0,25	4,5	85,7	0,44
16-set	2,6	0	2,6	0	4,5	97,25	1,9	0	1,9	0	4,5	87,6	0,44
17-set	2,6	0	2,6	0	4,5	99,85	1,8	0	1,8	0	4,5	89,4	0,44
18-set	2,6	0	2,6	0	4,5	102,45	1,8	0	1,8	0	4,5	91,2	0,44
19-set	2,6	0	2,6	0	4,5	105,05	1,8	0	1,8	0	4,5	93	0,44
22-set	2,75	0,25	2,5	0,25	4,75	107,8	2	0,25	1,75	0,25	4,75	95	0,47

Table 3.8 : Leachate volume extracted, recirculated and measured for columns S3 and S4 for the entire duration of the test

Data	column S3						Column S4						L/S
	W out [l]	W analisi [l]	W ric [l]	W in_new [l]	W Cum [l]	W out cum (l)	W out (l)	W analisi (l)	W ric (l)	W in_new (l)	W Cum (l)	W out cum (l)	(l/Kg_TS)
03-lug	0	0	0	3	0	0	0	0	0	3	0	0	0,00
04-lug	0,25	0	0,25	2	0	0,25	1	0	1	2	0	1	0,00
04-lug	0,5	0,5	0	0,5	0,5	0,75	0,5	0,5	0	0,5	0,5	1,5	0,05
07-lug	1,5	0	1,5	0	0,5	2,25	2	0	2	0	0,5	3,5	0,05
07-lug	0,1	0,1	0	0,1	0,6	2,35	0,1	0,1	0	0,1	0,6	3,6	0,06
08-lug	0,5	0	0,5	0	0,6	2,85	1	0	1	0	0,6	4,6	0,06
09-lug	0,5	0	0,5	0	0,6	3,35	1,5	0	1,5	0	0,6	6,1	0,06
09-lug	0,1	0,1	0	0,1	0,7	3,45	0,1	0,1	0	0,1	0,7	6,2	0,07
10-lug	1	0	1	0	0,7	4,45	1,4	0	1,4	0	0,7	7,6	0,07
10-lug	0,15	0,15	0,15	0	0,7	4,6	0,15	0,15	0,15	0	0,7	7,75	0,07
11-lug	0,8	0	0,8	0	0,7	5,4	1,25	0	1,25	0	0,7	9	0,07
11-lug	0,1	0,1	0	0,1	0,8	5,5	0,1	0,1	0	0,1	0,8	9,1	0,08
14-lug	1,2	0,25	0,95	0,25	1,05	6,7	1,5	0,25	1,25	0,25	1,05	10,6	0,10
15-lug	0,7	0	0,7	1	1,05	7,4	1,25	0	1,25	1	1,05	11,85	0,10
16-lug	1,75	0,25	1,5	0,25	1,3	9,15	2,1	0,25	1,85	0,25	1,3	13,95	0,13
17-lug	1,5	0	1,5	0	1,3	10,65	1,9	0	1,9	0	1,3	15,85	0,13
18-lug	1,75	0,25	1,5	0,25	1,55	12,4	2	0,25	1,75	0,25	1,55	17,85	0,15
21-lug	2	0,25	1,75	0,25	1,8	14,4	2,2	0,25	1,95	0,25	1,8	20,05	0,18
22-lug	1,75	0	1,75	0	1,8	16,15	2	0	2	0	1,8	22,05	0,18
23-lug	1,7	0,25	1,45	0,25	2,05	17,85	2	0,25	1,75	0,25	2,05	24,05	0,20
24-lug	1,5	0	1,5	0	2,05	19,35	2	0	2	0	2,05	26,05	0,20
25-lug	1,5	0,25	1,25	0,25	2,3	20,85	2	0,25	1,75	0,25	2,3	28,05	0,23
28-lug	1,7	0,25	1,45	0,25	2,55	22,55	2	0,25	1,75	0,25	2,55	30,05	0,25
29-lug	1,5	0	1,5	0	2,55	24,05	2	0	2	0	2,55	32,05	0,25
30-lug	1,5	0,15	1,35	0,15	2,7	25,55	2	0,15	0,85	0,15	2,7	34,05	0,27
31-lug	1,5	0	1,5	0	2,7	27,05	1,9	0	1,9	0	2,7	35,95	0,27
01-ago	1,5	0,15	1,35	0,15	2,85	28,55	1,8	0,15	1,65	0,15	2,85	37,75	0,28
04-ago	1,6	0,15	1,45	0,15	3	30,15	2	0,15	1,85	0,15	3	39,75	0,30
05-ago	1,5	0	1,5	0	3	31,65	1,9	0	1,9	0	3	41,65	0,30
06-ago	1,5	0,15	1,35	0,15	3,15	33,15	1,8	0,15	1,65	0,15	3,15	43,45	0,31
07-ago	1,5	0	1,5	0	3,15	34,65	1,75	0	1,75	0	3,15	45,2	0,31
08-ago	1,5	0,25	1,25	0,25	3,4	36,15	1,75	0,25	1,5	0,25	3,4	46,95	0,34
18-ago	2	0,1	1,9	0,1	3,5	38,15	2	0,1	1,9	0,1	3,5	48,95	0,35
20-ago	2	0	2	0	3,5	40,15	2	0	2	0	3,5	50,95	0,35
25-ago	2,1	0,25	1,85	0,25	3,75	42,25	2,25	0,25	2	0,25	3,75	53,2	0,37
26-ago	2	0	2	0	3,75	44,25	2	0	2	0	3,75	55,2	0,37
27-ago	2	0	2	0	3,75	46,25	2,1	0	2,1	0	3,75	57,3	0,37
28-ago	1,9	0	1,9	0	3,75	48,15	2	0	2	0	3,75	59,3	0,37
29-ago	1,8	0	1,8	0	3,75	49,95	2	0	2	0	3,75	61,3	0,37
01-set	2	0,25	1,75	0,25	4	51,95	1,55	0,25	1,3	0,25	4	62,85	0,40
02-set	1,8	0	1,8	0	4	53,75	1,5	0	1,5	0	4	64,35	0,40
03-set	1,8	0	1,8	0	4	55,55	1,5	0	1,5	0	4	65,85	0,40
04-set	1,8	0	1,8	0	4	57,35	1,5	0	1,5	0	4	67,35	0,40
05-set	1,8	0	1,8	0	4	59,15	1,5	0	1,5	0	4	68,85	0,40
08-set	2	0,25	1,75	0,25	4,25	61,15	1,5	0,25	1,25	0,25	4,25	70,35	0,42
09-set	1,8	0	1,8	0	4,25	62,95	1,5	0	1,5	0	4,25	71,85	0,42
10-set	1,8	0	1,8	0	4,25	64,75	1,5	0	1,5	0	4,25	73,35	0,42
11-set	1,8	0	1,8	0	4,25	66,55	1,5	0	1,5	0	4,25	74,85	0,42
12-set	1,8	0	1,8	0	4,25	68,35	1,5	0	1,5	0	4,25	76,35	0,42
15-set	2	0,25	1,75	0,25	4,5	70,35	1,6	0,25	1,35	0,25	4,5	77,95	0,44
16-set	1,9	0	1,9	0	4,5	72,25	1,5	0	1,5	0	4,5	79,45	0,44
17-set	1,9	0	1,9	0	4,5	74,15	1,5	0	1,5	0	4,5	80,95	0,44
18-set	1,9	0	1,9	0	4,5	76,05	1,5	0	1,5	0	4,5	82,45	0,44
19-set	1,9	0	1,9	0	4,5	77,95	1,5	0	1,5	0	4,5	83,95	0,44
22-set	2	0,25	1,75	0,25	4,75	79,95	1,5	0,25	1,25	0,25	4,75	85,45	0,47

Table 3.9: Leachate volume extracted, recirculated and measured for columns AN5 and AN6 for the entire duration of the test

Data	column AN5						column AN6						L/S out cum (l/Kg_TS)
	W out (l)	W analisi	W ric (l)	W in_new	W Cum (l)	W out cum	W out (l)	W analisi	W ricirc (l)	W in_new	W cum (l)	W out cum	
03-lug	0	0	0	3	0	0	0	0	0	5	0	0	0,00
04-lug	1	0	1	2	0	1	1,5	0	1,5	1	0	1,5	0,00
04-lug	0,5	0,5	0	0,5	0,5	1,5	0,5	0,5	0	0,5	0,5	2	0,05
07-lug	1,25	0	1,25	0	0,5	2,75	1,75	0	1,75	0	0,5	3,75	0,05
07-lug	0,1	0,1	0	0,1	0,6	2,85	0,1	0,1	0	0,1	0,6	3,85	0,06
08-lug	1	0	1	0	0,6	3,85	1	0	1	0	0,6	4,85	0,06
09-lug	0,5	0	0,5	0	0,6	4,35	1	0	1	0	0,6	5,85	0,06
09-lug	0,1	0,1	0	0,1	0,7	4,45	0,1	0,1	0	0,1	0,7	5,95	0,07
10-lug	1,2	0	1,2	0	0,7	5,65	1,3	0	1,3	0	0,7	7,25	0,07
10-lug	0,15	0,15	0,15	0	0,7	5,8	0,15	0,15	0,15	0	0,7	7,4	0,07
11-lug	1	0	1	0	0,7	6,8	1,15	0	1,15	0	0,7	8,55	0,07
11-lug	0,1	0,1	0	0,1	0,8	6,9	0,1	0,1	0	0,1	0,8	8,65	0,08
14-lug	1,25	0,25	1	0,25	1,05	8,15	1,5	0,25	1,25	0,25	1,05	10,15	0,10
15-lug	1	0	1	1	1,05	9,15	1,1	0	1,1	1	1,05	11,25	0,10
16-lug	1,75	0,25	1,5	0,25	1,3	10,9	2	0,25	1,75	0,25	1,3	13,25	0,13
17-lug	1,45	0	1,45	0	1,3	12,35	1,6	0	1,6	0	1,3	14,85	0,13
18-lug	1,6	0,25	1,35	0,25	1,55	13,95	1,9	0,25	1,65	0,25	1,55	16,75	0,15
21-lug	1,8	0,25	1,55	0,25	1,8	15,75	2	0,25	1,75	0,25	1,8	18,75	0,18
22-lug	1,6	0	1,6	0	1,8	17,35	1,9	0	1,9	0	1,8	20,65	0,18
23-lug	1,45	0,25	1,2	0,25	2,05	18,8	1,8	0,25	1,55	0,25	2,05	22,45	0,20
24-lug	1,45	0	1,45	0	2,05	20,25	1,6	0	1,6	0	2,05	24,05	0,20
25-lug	1,5	0,25	1,25	0,25	2,3	21,75	1,8	0,25	1,55	0,25	2,3	25,85	0,23
28-lug	1,6	0,25	1,35	0,25	2,55	23,35	2	0,25	1,75	0,25	2,55	27,85	0,25
29-lug	1,5	0	1,5	0	2,55	24,85	1,9	0	1,9	0	2,55	29,75	0,25
30-lug	1,5	0,15	1,35	0,15	2,7	26,35	2	0,15	1,85	0,15	2,7	31,75	0,27
31-lug	1,5	0	1,5	0	2,7	27,85	2	0	2	0	2,7	33,75	0,27
01-ago	1,5	0,15	1,35	0,15	2,85	29,35	2	0,15	1,85	0,15	2,85	35,75	0,28
04-ago	1,5	0,15	1,45	0,15	3	30,95	2,1	0,15	1,95	0,15	3	37,85	0,30
05-ago	1,5	0	1,5	0	3	32,45	2	0	2	0	3	39,85	0,30
06-ago	1,5	0,15	1,35	0,15	3,15	33,95	2	0,15	1,85	0,15	3,15	41,85	0,31
07-ago	1,5	0	1,5	0	3,15	35,45	2	0	2	0	3,15	43,85	0,31
08-ago	1,5	0,25	1,25	0,25	3,4	36,95	2	0,25	1,75	0,25	3,4	45,85	0,34
18-ago	1,9	0,1	1,8	0,1	3,5	38,85	2,4	0,1	2,3	0,1	3,5	48,25	0,35
20-ago	1,75	0	1,75	0	3,5	40,6	2,4	0	2,4	0	3,5	50,65	0,35
25-ago	1,9	0,25	1,65	0,25	3,75	42,5	2,5	0,25	2,25	0,25	3,75	53,15	0,37
26-ago	1,75	0	1,75	0	3,75	44,25	2	0	2	0	3,75	55,15	0,37
27-ago	1,7	0	1,7	0	3,75	45,95	2,3	0	2,3	0	3,75	57,45	0,37
28-ago	1,6	0	1,6	0	3,75	47,55	2,4	0	2,4	0	3,75	59,85	0,37
29-ago	1,7	0	1,7	0	3,75	49,25	2,4	0	2,4	0	3,75	62,25	0,37
01-set	2,3	0,25	2,05	0,25	4	51,55	2,5	0,25	2,25	0,25	4	64,75	0,40
02-set	2,1	0	2,1	0	4	53,65	2,4	0	2,4	0	4	67,15	0,40
03-set	2,1	0	2,1	0	4	55,75	2,4	0	2,4	0	4	69,55	0,40
04-set	2,2	0	2,2	0	4	57,95	2,4	0	2,4	0	4	71,95	0,40
05-set	2,1	0	2,1	0	4	60,05	2,4	0	2,4	0	4	74,35	0,40
08-set	2,3	0,25	2,05	0,25	4,25	62,35	2,5	0,25	2,25	0,25	4,25	76,85	0,42
09-set	2,2	0	2,2	0	4,25	64,55	2,25	0	2,25	0	4,25	79,1	0,42
10-set	2,1	0	2,1	0	4,25	66,65	2,3	0	2,3	0	4,25	81,4	0,42
11-set	2,2	0	2,2	0	4,25	68,85	2,2	0	2,2	0	4,25	83,6	0,42
12-set	2,1	0	2,1	0	4,25	70,95	2,2	0	2,2	0	4,25	85,8	0,42
15-set	2,3	0,25	2,05	0,25	4,5	73,25	2,5	0,25	2,25	0,25	4,5	88,3	0,44
16-set	2	0	2	0	4,5	75,25	2,25	0	2,25	0	4,5	90,55	0,44
17-set	2,1	0	2,1	0	4,5	77,35	2,25	0	2,25	0	4,5	92,8	0,44
18-set	2,1	0	2,1	0	4,5	79,45	2,3	0	2,3	0	4,5	95,1	0,44
19-set	2,1	0	2,1	0	4,5	81,55	2,4	0	2,4	0	4,5	97,5	0,44
22-set	2,25	0,25	2	0,25	4,75	83,8	2,5	0,25	2,25	0,25	4,75	100	0,47

Table 3.10 : biogas characterization of column S1

Data	hours	Fase	Quantity	O2 [%]	CO2 [%]	CH4 [%]	Vol cum [l]	C out (g)	gC/CH4	liter CH4	liter CH4/kg	liter (CO2+CH4)/kg
						columns S1						
03-lug	17:20	1	11	1,6	33,3	0,04	11	0,54	0,00	0,00	0,00	0,20
04-lug	11:20	1	9	1,8	50	0,13	20	1,20	0,01	0,0	0,00	0,44
04-lug	15:37	1	21	3,5	39,6	0,13	41	2,43	0,02	0,0	0,00	0,90
05-lug	10:50	1	0	3,5	39,6	0,13	41	2,43	0,02	0,0	0,00	0,90
07-lug	11:00	1	13	2,3	75,1	0,21	54	3,87	0,03	0,1	0,00	1,43
07-lug	17:15	1	12	4,6	69,5	0,13	66	5,09	0,03	0,1	0,00	1,88
08-lug	11,13	1	8	4,5	55,2	0,05	74	5,74	0,04	0,1	0,00	2,12
08-lug	13:40	1	17	3,5	33,7	0,09	91	6,58	0,04	0,1	0,01	2,44
09-lug	11:00	1	1,5	8,7	30,1	0,05	92,5	6,65	0,04	0,1	0,01	2,46
10-lug	10:45	1	1,6	7,6	43,6	0,05	94,1	6,75	0,04	0,1	0,01	2,50
10-lug	13:45	1	5,83	5,7	44,8	0,05	99,93	7,14	0,04	0,1	0,01	2,64
11-lug	10:04	1	16,67	4,1	39	0,09	116,6	8,09	0,05	0,1	0,01	3,00
14-lug	10:30	1	18	2,5	42	0,05	134,6	9,20	0,05	0,1	0,01	3,41
14-lug	18:20	1	25	3,7	38,8	0,09	159,6	10,63	0,06	0,2	0,01	3,94
15-lug	09:30	1	1,3	3,6	30	0,05	160,9	10,69	0,06	0,2	0,01	3,96
15-lug	18:00	1	22	3,4	29,3	0,01	182,9	11,63	0,06	0,2	0,01	4,31
16-lug	09:20	1	0,5	3,1	26,5	0,05	183,4	11,65	0,06	0,2	0,01	4,31
16-lug	18:00	1	33,8	4,1	22	0,05	217,2	12,74	0,07	0,2	0,01	4,72
17-lug	09:30	1	1,16	3,2	24,5	0,05	218,36	12,79	0,07	0,2	0,01	4,73
17-lug	16:47	1	26,8	2,8	26,5	0,05	245,16	13,83	0,08	0,2	0,01	5,12
18-lug	09:24	1	12,7	3	18,9	0,01	257,86	14,18	0,08	0,2	0,01	5,25
18-lug	16:25	1	23,3	1,3	23,9	0,01	281,16	15,00	0,08	0,2	0,01	5,55
19-lug	11:30	1	4	2,5	18,9	0,01	285,16	15,11	0,08	0,2	0,01	5,60
21-lug	10:00	1	12,94	1,4	23,3	0,09	298,1	15,55	0,08	0,2	0,01	5,76
21-lug	16:15	1	33,8	2,3	23	0,09	331,9	16,70	0,10	0,2	0,01	6,18
22-lug	09:10	1	30	1,6	18,1	0,09	361,9	17,51	0,11	0,3	0,01	6,48
22-lug	15:30	1	36,17	1,4	22,1	0,05	398,07	18,68	0,11	0,3	0,02	6,92
23-lug	09:30	1	0	1,4	22,1	0,05	398,07	18,68	0,11	0,3	0,02	6,92
23-lug	16:50	1	16,6	1,6	23,7	0,2	414,67	19,27	0,13	0,3	0,02	7,13
24-lug	09:20	1	14,16	0,9	19,7	0,13	428,83	19,69	0,13	0,3	0,02	7,28
25-lug	09:40	1	0	0,9	19,7	0,13	428,83	19,69	0,13	0,3	0,02	7,28
25-lug	16:15	1	11,55	4,4	18,1	0,29	440,38	20,01	0,15	0,4	0,02	7,40
28-lug	09:30	1	7,22	4,8	21,3	0,84	447,6	20,26	0,17	0,4	0,02	7,49
28-lug	19:35	1	9,4	4,8	23,3	0,88	457	20,61	0,20	0,5	0,03	7,61
29-lug	09:10	1	5	2,6	18,9	0,56	462	20,76	0,22	0,5	0,03	7,66
30-lug	09:30	1	13,3	2,5	18,1	0,68	475,3	21,15	0,25	0,6	0,03	7,80
31-lug	09:10	1	20	2,6	18,1	0,88	495,3	21,75	0,32	0,8	0,04	8,01
01-ago	09:00	1	44,2	2,4	19,3	1,12	539,5	23,19	0,52	1,3	0,07	8,50
01-ago	16:30	1	0	2,4	19,3	1,12	539,5	23,19	0,52	1,3	0,07	8,50
04-ago	09:00	1	58,3	3,4	17,7	1,26	597,8	25,00	0,82	2,0	0,11	9,10
04-ago	18:46	1	58,3	4,2	19,7	2,27	656,1	27,21	1,35	3,4	0,18	9,79
05-ago	09:25	1	14,38	2,9	17,3	1,5	670,48	27,66	1,44	3,6	0,19	9,94
05-ago	17:12	1	37,94	2,9	19,7	2,35	708,42	29,11	1,79	4,5	0,24	10,39
06-ago	09:10	1	5	9,2	12,1	1,63	713,42	29,23	1,83	4,5	0,25	10,43
07-ago	09:00	1	28	3,8	19,3	2,8	741,42	30,34	2,14	5,3	0,29	10,77
07-ago	18:00	1	12,5	3,5	18,1	0,29	753,92	30,68	2,16	5,4	0,29	10,89
08-ago	09:12	1	20,5	3,3	18,5	1,84	774,42	31,39	2,31	5,7	0,31	11,12
8/ago	13:00	1	17,2	5	19,7	3,2	791,62	32,11	2,53	6,3	0,34	11,33
18-ago	13:00	2	1,94	6,9	36,5	29,5	793,56	32,44	2,76	6,9	0,37	11,40
20-ago	10:30	2	2	4,8	45,2	37	795,56	32,87	3,06	7,6	0,41	11,49
25-ago	09:00	2	3,8	5	42,8	38,3	799,36	33,69	3,64	9,1	0,49	11,66
26-ago	09:00	2	4,72	4,1	44,4	31,8	804,08	34,60	4,24	10,6	0,57	11,86
27-ago	09:00	2	5	4,7	40,8	31,4	809,08	35,53	4,87	12,1	0,66	12,05
27-ago	18:40	1	15,55	6,4	26,1	14	824,63	37,00	5,75	14,3	0,78	12,39
28-ago	09:00	1	22,5	2,9	18,1	4,37	847,13	37,99	6,14	15,3	0,83	12,67
28-ago	15:15	1	25	3,1	22,1	7,2	872,13	39,52	6,87	17,1	0,93	13,06
29-ago	09:00	1	24,5	4,8	14,5	3,35	896,63	40,37	7,20	17,9	0,97	13,30
29-ago	15:20	1	27,1	2,2	20,5	7,15	923,73	41,96	7,98	19,9	1,08	13,71
29-ago	18:00	1	12,22	4,4	14,9	3,1	935,95	42,38	8,13	20,2	1,10	13,83
01-set	09:00	1	14,61	6,4	13,3	3,06	950,56	42,84	8,31	20,7	1,12	13,96
01-set	17:30	1	38	4,3	15,7	3,82	988,56	44,30	8,89	22,1	1,20	14,36

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02-set	09:00	1	13,33	3,6	15,3	3,6	1001,89	44,79	9,08	22,6	1,23	14,50
02-set	17:10	1	27,66	3,1	18,5	6,3	1029,55	46,24	9,78	24,4	1,32	14,87
03-set	09:00	1	20	4	16,5	5,22	1049,55	47,14	10,20	25,4	1,38	15,11
03-set	18:30	1	36,66	3	18,9	7,31	1086,21	49,23	11,28	28,1	1,53	15,63
04-set	09:00	1	14,44	2,2	18,3	6,8	1100,65	50,01	11,67	29,1	1,58	15,83
04-set	19:00	1	38,67	2,8	19,3	8,58	1139,32	52,44	13,01	32,4	1,76	16,41
05-set	09:00	1	15,66	3,7	16,9	7	1154,98	53,26	13,45	33,5	1,82	16,62
05-set	16:20	1	32,77	3,9	19,7	10	1187,75	55,53	14,76	36,7	2,00	17,14
08-set	09:00	1	56,11	3,8	19,3	10,4	1243,86	59,45	17,11	42,6	2,31	18,05
08-set	17:30	1	33,1	2,5	21,7	12,4	1276,96	62,15	18,76	46,7	2,54	18,66
09-set	09:00	1	27,74	4,3	17,3	9,6	1304,7	63,93	19,83	49,4	2,68	19,07
09-set	13:15	1	23,33	4,2	21,3	15,1	1328,03	66,07	21,24	52,9	2,87	19,53
10-set	09:00	1	36,66	4	17,7	9,6	1364,69	68,43	22,66	56,4	3,06	20,07
11-set	09:00	1	20	3,5	28,8	33,8	1384,69	71,99	25,37	63,2	3,43	20,75
12-set	12:30	1	1,5	2,8	35,7	47,7	1386,19	72,35	25,66	63,9	3,47	20,82
12-set	18:00	1	1,15	0,6	40,8	51	1387,34	72,66	25,90	64,5	3,50	20,88
15-set	09:00	1	22	0,09	42,4	60,8	1409,34	79,40	31,27	77,8	4,23	22,11
16-set	09:30	1	18,8	2,9	38,4	53,3	1428,14	84,48	35,30	87,9	4,77	23,05
16-set	18:00	2	10	3,3	35,7	51,3	1438,14	87,06	37,36	93,0	5,05	23,52
17-set	09:15	2	11,11	2,7	36,9	55,3	1449,25	90,13	39,83	99,1	5,39	24,08
17-set	18:30	2	10,33	3,3	35,7	51,3	1459,58	92,80	41,96	104,4	5,68	24,57
18-set	09:30	2	12,3	2	38	60	1471,88	96,45	44,92	111,8	6,08	25,22
18-set	18:30	2	9,33	3,7	34,1	50,5	1481,21	98,81	46,81	116,5	6,33	25,65
19-set	09:00	2	10,27	3	35,5	57	1491,48	101,69	49,17	122,4	6,65	26,17
19-set	17:20	2	10	3,1	36,5	54,5	1501,48	104,41	51,36	127,8	6,95	26,66
22-set	09:15	2	25	3,3	30,5	55,6	1526,48	111,11	56,94	141,7	7,70	27,83
22-set	17:00	2	9,27	3,3	37,3	53,3	1535,75	113,61	58,93	146,7	7,97	28,29
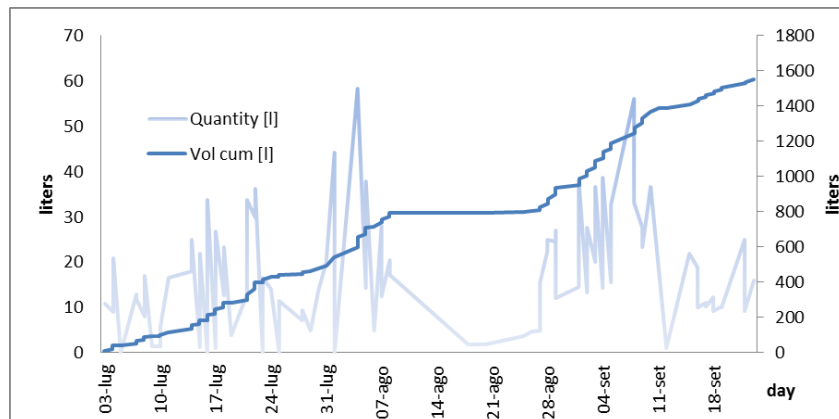
Figure 3.3: Cumulative volume and daily production of biogas measured in output from the column S1.

Figure 3.4: Gas volumetric percentage composition (O2, CO2, CH4) analyzed in output from the reactors S1.

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Table 3.11: biogas characterization of column S2.

Data	hours	Fase	Quantity	O2 [%]	CO2 [%]	CH4 [%]	Vol cum [	C out (g)	gC/CH4	liter CH4	liter CH4/kg	liter (CO2+CH4)/kg
03-lug	17:20	1	3	2,7	36,9	0,05	3	0,16	0,00	0,00	0,00	0,06
04-lug	11:20	1	6	1,8	45,2	0,05	9	0,56	0,00	0,00	0,00	0,21
04-lug	15:37	1	4	4,2	44,1	0,05	13	0,82	0,00	0,01	0,00	0,30
05-lug	10:50	1	0	4,2	44,1	0,05	13	0,82	0,00	0,01	0,00	0,30
07-lug	11:00	1	70	1,5	70,1	0,17	83	8,04	0,05	0,13	0,01	2,98
07-lug	17:15	1	22,2	6,1	56,8	0,13	105,2	9,90	0,06	0,15	0,01	3,66
08-lug	11,13	1	7	4,5	69,1	0,01	112,2	10,61	0,06	0,16	0,01	3,93
08-lug	13:40	1	8	3,6	69,5	0,05	120,2	11,42	0,06	0,16	0,01	4,23
09-lug	11:00	1	8	4	68	0,05	128,2	12,22	0,07	0,16	0,01	4,53
10-lug	10:45	1	9,6	3,3	62,8	0,05	137,8	13,10	0,07	0,17	0,01	4,85
10-lug	13:45	1	0	3,3	62,8	0,05	141,6	13,43	0,07	0,17	0,01	4,85
11-lug	10:04	1	3,8	3,7	58,8	0,05	157,1	14,75	0,07	0,17	0,01	4,97
14-lug	10:30	1	15,5	2,1	58	0,05	161,1	15,04	0,07	0,18	0,01	5,46
14-lug	18:20	1	4	3,2	50	0,09	167,9	15,49	0,07	0,18	0,01	5,57
15-lug	09:30	1	6,8	4,5	44,5	0,05	172,3	15,77	0,07	0,18	0,01	5,74
15-lug	18:00	1	4,4	3,3	44,4	0,05	176,7	16,09	0,08	0,19	0,01	5,84
16-lug	09:20	1	5,4	2,1	40,4	0,05	182,1	16,28	0,08	0,19	0,01	5,96
16-lug	18:00	1	2,94	2,4	43,4	0,05	185,04	16,47	0,08	0,19	0,01	6,03
17-lug	09:30	1	2,27	4,1	28,5	0,05	187,31	16,56	0,08	0,19	0,01	6,07
17-lug	16:47	1	5,55	3,4	27,3	0,09	192,86	16,79	0,08	0,20	0,01	6,15
18-lug	09:24	1	1,11	3,2	23,3	0,01	193,97	16,82	0,08	0,20	0,01	6,16
18-lug	16:25	1	6,11	6,2	18,9	0,01	200,08	16,99	0,08	0,20	0,01	6,23
19-lug	11:30	1	14,4	1,9	22,5	0,01	214,48	17,47	0,08	0,20	0,01	6,40
21-lug	10:00	1	0,83	14,4	7,7	0,05	215,31	17,48	0,08	0,20	0,01	6,41
21-lug	16:15	1	4,16	3,8	30,1	0,09	219,47	17,66	0,08	0,20	0,01	6,47
22-lug	09:10	1	14	0,3	26,9	0,09	233,47	18,22	0,09	0,22	0,01	6,68
22-lug	15:30	1	7,61	2,4	22,5	0,09	241,08	18,47	0,09	0,22	0,01	6,77
23-lug	09:30	1	9,17	0,8	22,9	0,09	250,25	18,78	0,09	0,23	0,01	6,89
23-lug	16:50	1	8,72	2,6	21,3	0,21	258,97	19,06	0,10	0,25	0,01	6,99
24-lug	09:20	1	5	0,7	22,5	0,13	263,97	19,23	0,10	0,26	0,01	7,05
25-lug	09:40	1	16	1,3	22,1	0,11	279,97	19,75	0,11	0,27	0,01	7,24
25-lug	16:15	1	4,72	4,5	18,1	0,09	284,69	19,88	0,11	0,28	0,02	7,29
28-lug	09:30	1	22,6	0,8	21,7	0,17	307,29	20,61	0,13	0,32	0,02	7,56
28-lug	19:35	1	9,4	2,1	21	0,09	316,69	20,90	0,13	0,32	0,02	7,67
29-lug	09:10	1	13	1,4	20,9	0,17	329,69	21,31	0,14	0,35	0,02	7,82
30-lug	09:30	1	19,16	1,8	20,5	0,25	348,85	21,90	0,16	0,39	0,02	8,03
31-lug	09:10	1	24,4	1,6	20,9	0,25	373,25	22,67	0,18	0,46	0,02	8,31
01-ago	09:00	1	20,7	1,7	20,5	0,29	393,95	23,32	0,21	0,52	0,03	8,55
01-ago	16:30	1	5,94	4,2	17,7	0,11	399,89	23,47	0,21	0,52	0,03	8,60
04-ago	09:00	1	20,5	1,9	20	0,17	420,39	24,09	0,22	0,56	0,03	8,83
04-ago	18:46	1	12,67	3,4	18,1	0,21	433,06	24,43	0,23	0,58	0,03	8,95
05-ago	09:25	1	20	2	19,3	0,25	453,06	25,02	0,25	0,63	0,03	9,17
05-ago	17:12	1	11,3	4,7	16,1	0,21	464,36	25,29	0,26	0,66	0,04	9,27
06-ago	09:10	1	20	3,4	18,1	0,25	484,36	25,84	0,28	0,71	0,04	9,47
07-ago	09:00	1	31,82	3	18,5	0,27	516,18	26,74	0,32	0,79	0,04	9,79
07-ago	18:00	1	12,5	3,5	18,1	0,29	528,68	27,08	0,33	0,83	0,05	9,92
08-ago	09:12	1	12,8	3,5	18,1	1	541,48	27,47	0,38	0,96	0,05	10,05
8/ago	13:00	1	10,55	5,1	18,5	1,8	552,03	27,84	0,46	1,15	0,06	10,17
18-ago	13:00	2	4,66	10	27,7	3,14	556,69	28,08	0,52	1,29	0,07	10,24
20-ago	10:30	2	4	8,3	33,3	10	560,69	28,44	0,68	1,69	0,09	10,34
25-ago	09:00	2	4,7	10,1	29,3	14,3	565,39	28,91	0,95	2,37	0,13	10,45
26-ago	09:00	2	6,1	6,2	34,2	22	571,49	29,75	1,49	3,71	0,20	10,64
27-ago	09:00	2	5,44	6,6	36,5	22,3	576,93	30,53	1,98	4,92	0,27	10,81
27-ago	18:40	1	15,27	5,4	37,7	10,4	592,2	32,01	2,62	6,51	0,35	11,21
28-ago	09:00	1	12,5	3	33,7	4,1	604,7	32,83	2,82	7,02	0,38	11,47
28-ago	15:15	1	6,94	5,8	20,9	1,59	611,64	33,09	2,87	7,13	0,39	11,55
29-ago	09:00	1	10,16	3,9	18,9	1	621,8	33,41	2,91	7,23	0,39	11,66
29-ago	18:00	1	10,61	4,1	16,5	0,56	632,41	33,69	2,93	7,29	0,40	11,76
01-set	09:00	1	19,27	3,9	14,5	1,67	651,68	34,23	3,06	7,61	0,41	11,93
01-set	17:30	1	9,77	4,3	14,5	0,13	661,45	34,44	3,06	7,63	0,41	12,01

| 02-set	09:00	1	13,33	2,9	15,7	0,13	674,78	34,76	3,07	7,64	0,42	12,12
02-set	17:10	1	10,55	3	16,1	0,13	685,33	35,01	3,08	7,66	0,42	12,21
03-set	09:00	1	13,33	2,5	16,1	0,17	698,66	35,33	3,09	7,68	0,42	12,33
03-set	18:30	1	8,88	3,4	16,1	0,17	707,54	35,55	3,09	7,70	0,42	12,41
04-set	09:00	1	10	3,4	16,5	0,25	717,54	35,80	3,10	7,72	0,42	12,50
04-set	19:00	1	15,67	3,1	16,9	0,29	733,21	36,21	3,12	7,77	0,42	12,65
05-set	09:00	1	9,72	3,2	16,4	0,33	742,93	36,45	3,13	7,80	0,42	12,74
05-set	16:20	1	8,66	4,2	15,7	0,45	751,59	36,67	3,15	7,84	0,43	12,81
08-set	09:00	1	5,5	5,3	16,9	1,4	748,43	36,62	3,18	7,91	0,43	12,87
08-set	17:30	1	5,72	4,6	21,3	2,6	754,15	36,86	3,24	8,06	0,44	12,94
09-set	09:00	1	7,33	5,5	16,9	1,7	761,48	37,09	3,29	8,19	0,45	13,01
10-set	09:00	1	10	4,3	16,5	1,35	771,48	37,38	3,34	8,32	0,45	13,11
11-set	09:00	1	8,88	4,2	15,7	1,2	780,36	37,63	3,39	8,43	0,46	13,19
12-set	09:15	1	14,44	3,4	16,1	1,2	794,8	38,04	3,46	8,60	0,47	13,33
12-set	12:30	1	4,6	5,2	14,5	6	799,4	38,25	3,57	8,88	0,48	13,38
15-set	09:00	1	15	1	17	1	814,4	38,68	3,63	9,03	0,49	13,53
16-set	09:30	1	20,27	3,3	15,7	1	834,67	39,23	3,71	9,23	0,50	13,71
16-set	18:00	1	10,83	4,3	15	0,96	845,5	39,51	3,75	9,34	0,51	13,80
17-set	09:15	1	14,38	3,6	15,7	1,2	859,88	39,91	3,82	9,51	0,52	13,94
17-set	18:30	1	14,44	4,1	16,1	1,2	874,32	40,32	3,89	9,68	0,53	14,07
18-set	09:30	1	13,11	4	15,7	1,4	887,43	40,69	3,96	9,86	0,54	14,19
18-set	18:30	1	11,33	3,8	16,1	1,4	898,76	41,02	4,03	10,02	0,54	14,30
19-set	09:00	1	14,94	3,7	16,5	1,5	913,7	41,47	4,12	10,25	0,56	14,45
19-set	17:20	1	10	4,7	15,3	1,47	923,7	41,75	4,18	10,39	0,56	14,54
22-set	09:00	1	13,33	4,4	15,3	1,75	937,03	42,15	4,27	10,63	0,58	14,66
22-set	17:00	1	10	4,8	14,9	1,67	947,03	42,43	4,34	10,79	0,59	14,75

Figure 3.5:Cumulative volume and daily production of biogas measured in output from the column S2.
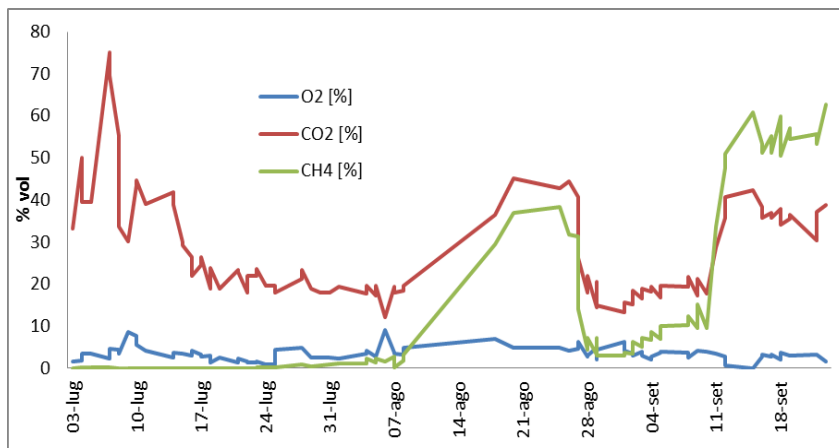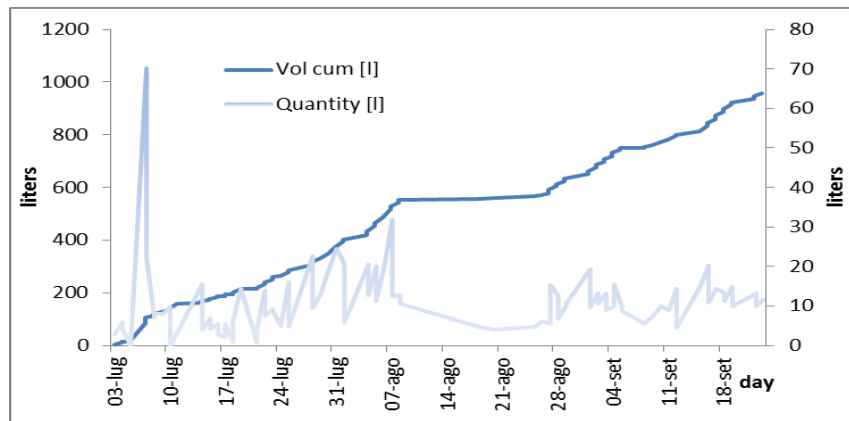

Figure 3.6: Gas volumetric percentage composition (O2, CO2, CH4) analyzed in output from the reactors S2.

Table 3.12: biogas characterization of column S3.

Data	hours	Fase	Quantity	O2 [%]	CO2 [%]	CH4 [%]	Vol cum [	C out (g)	gC/CH4	liter CH4	liter CH4/kg	liter (CO2+CH4)/kg
						column S3						
03-lug	17:20	1	5	2,1	38,3	0,09	5	0,28	0,00	0,00	0,00	0,10
04-lug	11:20	1	3	1,5	60	0,09	8	0,55	0,00	0,01	0,00	0,20
04-lug	15:37	1	14	2,5	43,6	0,09	22	1,44	0,01	0,02	0,00	0,53
05-lug	10:50	1	13	1,3	50,4	0,01	35	2,40	0,01	0,02	0,00	0,89
07-lug	11:00	1	16	1,8	73,7	0,17	51	4,14	0,02	0,05	0,00	1,53
07-lug	17:15	1	16,6	2,6	78,3	0,17	67,6	6,05	0,03	0,08	0,00	2,24
08-lug	11,13	1	13	2,9	63	0,01	80,6	7,25	0,03	0,08	0,00	2,69
08-lug	13:40	1	22	1,9	41,6	0,05	102,6	8,59	0,04	0,09	0,00	3,18
09-lug	11:00	1	4	3,5	37	0,01	106,6	8,81	0,04	0,09	0,00	3,26
10-lug	10:45	1	1,5	4,5	43,6	0,01	108,1	8,90	0,04	0,09	0,00	3,30
10-lug	13:45	1	13,94	3,1	49	0,09	122,04	9,91	0,04	0,10	0,01	3,67
11-lug	10:04	1	25	5,8	21,7	0,05	147,04	10,71	0,05	0,11	0,01	3,97
14-lug	10:30	1	2	5,4	37	0,05	149,04	10,82	0,05	0,12	0,01	4,01
14-lug	18:20	1	22	2,5	40	0,05	171,04	12,11	0,05	0,13	0,01	4,49
15-lug	09:30	1	0,8	8,3	17,3	0,01	171,84	12,13	0,05	0,13	0,01	4,49
15-lug	18:00	1	23,3	1,6	28,9	0,05	195,14	13,12	0,06	0,14	0,01	4,86
16-lug	09:20	1	0,88	1,9	29	0,05	196,02	13,15	0,06	0,14	0,01	4,87
16-lug	18:00	1	22,67	4,4	22,9	0,05	218,69	13,92	0,06	0,15	0,01	5,16
17-lug	09:30	1	0	4,4	22,9	0,05	218,69	13,92	0,06	0,15	0,01	5,16
17-lug	16:47	1	25,44	1,7	25,3	0,09	244,13	14,87	0,07	0,17	0,01	5,51
18-lug	09:24	1	19,11	3,5	17,3	0,01	263,24	15,35	0,07	0,17	0,01	5,69
18-lug	16:25	1	24,4	1,2	23,3	0,01	287,64	16,18	0,07	0,18	0,01	6,00
19-lug	11:30	1	10,38	2,7	17,7	0,05	298,02	16,46	0,07	0,18	0,01	6,10
21-lug	10:00	1	10	5,2	16,9	0,09	308,02	16,71	0,08	0,19	0,01	6,19
21-lug	16:15	1	13,4	1,8	23,3	0,09	321,42	17,17	0,08	0,20	0,01	6,36
22-lug	09:10	1	26	0,9	17,7	0,09	347,42	17,85	0,09	0,23	0,01	6,61
22-lug	15:30	1	23,3	0,8	22,5	0,05	370,72	18,62	0,10	0,24	0,01	6,90
23-lug	09:30	1	29,5	0,4	18,5	0,09	400,22	19,43	0,11	0,27	0,01	7,20
23-lug	16:50	1	29,33	2,9	18,5	0,2	429,55	20,25	0,13	0,32	0,02	7,49
24-lug	09:20	1	15,5	3,6	15,3	0,09	445,05	20,60	0,14	0,34	0,02	7,62
25-lug	09:40	1	22,5	1,2	18,9	0,09	467,55	21,23	0,14	0,36	0,02	7,86
25-lug	16:15	1	13,33	1,4	21,7	0,21	480,88	21,66	0,16	0,39	0,02	8,01
28-lug	09:30	1	0	1,4	21,7	0,21	480,88	21,66	0,16	0,39	0,02	8,01
28-lug	19:35	1	29,1	2,3	22,9	0,4	509,98	22,69	0,20	0,50	0,03	8,38
29-lug	09:10	1	5	2,7	16,9	0,33	514,98	22,82	0,21	0,52	0,03	8,43
30-lug	09:30	1	11,67	2,5	16,9	0,3	526,65	23,12	0,22	0,55	0,03	8,54
31-lug	09:10	1	55	1,1	19,3	0,48	581,65	24,78	0,33	0,82	0,04	9,13
01-ago	09:00	1	47,6	1,3	19,7	0,52	629,25	26,25	0,43	1,07	0,06	9,65
01-ago	16:30	1	32,83	1,8	24,9	0,88	662,08	27,56	0,54	1,35	0,07	10,11
04-ago	09:00	1	63	1,8	16,9	0,37	725,08	29,21	0,64	1,59	0,09	10,70
04-ago	18:46	1	12,11	4,5	25,3	2,5	737,19	29,78	0,76	1,89	0,10	10,89
05-ago	09:25	1	33,8	5,4	16,5	1	770,99	30,73	0,90	2,23	0,12	11,21
05-ago	17:12	1	82,1	4,2	17,7	0,68	853,09	33,08	1,12	2,79	0,15	12,03
06-ago	09:10	1	62,6	6,2	12,6	0,36	915,69	34,33	1,21	3,01	0,16	12,47
07-ago	09:00	1	37,7	3,2	19,3	1,47	953,39	35,61	1,43	3,57	0,19	12,90
07-ago	18:00	1	29,6	2,4	21,3	1,44	982,99	36,71	1,60	3,99	0,22	13,26
08-ago	09:12	1	22,7	3,4	16,9	1,3	1005,69	37,38	1,72	4,29	0,23	13,49
8/ago	13:00	1	10,27	2,7	24,9	3	1015,96	37,88	1,85	4,60	0,25	13,64
18-ago	13:00	2	2	7,5	37,7	29,8	1017,96	38,23	2,09	5,19	0,28	13,71
20-ago	10:30	2	4	7,7	35,1	26,6	1021,96	38,87	2,51	6,26	0,34	13,85
25-ago	09:00	2	13,88	7,1	35	32	1035,84	41,36	4,30	10,70	0,58	14,35
26-ago	09:00	2	2,77	4,7	40,8	33	1038,61	41,89	4,67	11,61	0,63	14,47
27-ago	09:00	2	2,77	5,2	39,2	30,6	1041,38	42,39	5,01	12,46	0,68	14,57
27-ago	18:40	2	7,33	6,8	22	11,6	1048,71	42,97	5,35	13,31	0,72	14,70
28-ago	09:00	2	1,2	5,2	35,2	34,2	1049,91	43,20	5,51	13,72	0,75	14,75
29-ago	09:00	2	4,44	3,7	38,1	48,1	1054,35	44,30	6,37	15,85	0,86	14,96
29-ago	18:00	2	6,44	2,3	35,1	42,1	1060,79	45,72	7,46	18,57	1,01	15,23
01-set	09:00	2	18,8	3,9	21,3	19,5	1079,59	47,78	8,93	22,23	1,21	15,64

02-set	09:00	2	6,66	3,1	36,8	52,1	1086,25	49,53	10,33	25,70	1,40	15,97
03-set	09:00	2	7,22	3,4	34,1	50,5	1093,47	51,36	11,79	29,35	1,60	16,30
04-set	09:00	2	8,88	2,8	34,9	55,6	1102,35	53,79	13,78	34,29	1,86	16,73
05-set	09:00	2	9,88	3,3	34,1	53,7	1112,23	56,42	15,91	39,59	2,15	17,21
05-set	16:20	2	5,66	4,7	31,4	48,1	1117,89	57,77	17,00	42,31	2,30	17,45
08-set	09:00	2	8	2,8	35,3	59,2	1125,89	60,09	18,90	47,05	2,56	17,86
09-set	09:00	2	12,5	3,4	36	54,8	1138,39	63,50	21,66	53,90	2,93	18,48
10-set	09:00	2	10,55	3,5	33,7	52,9	1148,94	66,26	23,90	59,48	3,23	18,98
11-set	09:00	2	9,72	2,7	35,7	57,2	1158,66	69,00	26,13	65,04	3,53	19,47
12-set	09:15	2	9,11	2,9	35,2	56,4	1167,77	71,54	28,20	70,18	3,81	19,92
12-set	12:30	2	5,55	5,6	28,8	44,9	1173,32	72,77	29,20	72,67	3,95	20,14
15-set	09:00	2	16,5	0,11	39,6	63,2	1189,82	77,92	33,39	83,10	4,52	21,06
16-set	09:30	2	12,4	3,6	35,4	54,5	1202,22	81,27	36,10	89,86	4,88	21,67
16-set	18:00	2	9,11	3,4	34,9	56	1211,33	83,79	38,15	94,96	5,16	22,12
17-set	09:15	2	8,16	3,4	34,1	56,5	1219,49	86,05	40,01	99,57	5,41	22,52
17-set	18:30	2	9,83	4,1	34,1	52,5	1229,32	88,61	42,08	104,73	5,69	22,98
18-set	09:30	2	10,44	3,4	34,1	58	1239,76	91,57	44,51	110,78	6,02	23,51
18-set	18:30	2	9,27	3,6	34,9	54,1	1249,03	94,05	46,53	115,80	6,29	23,95
19-set	09:00	2	10	2,5	35,2	59,8	1259,03	96,97	48,93	121,78	6,62	24,47
19-set	17:20	2	10	3,6	35,3	54,5	1269,03	99,68	51,12	127,23	6,91	24,96
22-set	09:15	2	16,66	3,6	33,3	55,4	1285,69	104,20	54,83	136,46	7,42	25,76
22-set	17:00	2	8,67	3,5	36,9	53,3	1294,36	106,52	56,68	141,08	7,67	26,19
23-set	09:00	2	12	2,2	36,9	60	1306,36	110,06	59,58	148,28	8,06	26,82

Figure 3.7: Cumulative volume and daily production of biogas measured in output from the column S3
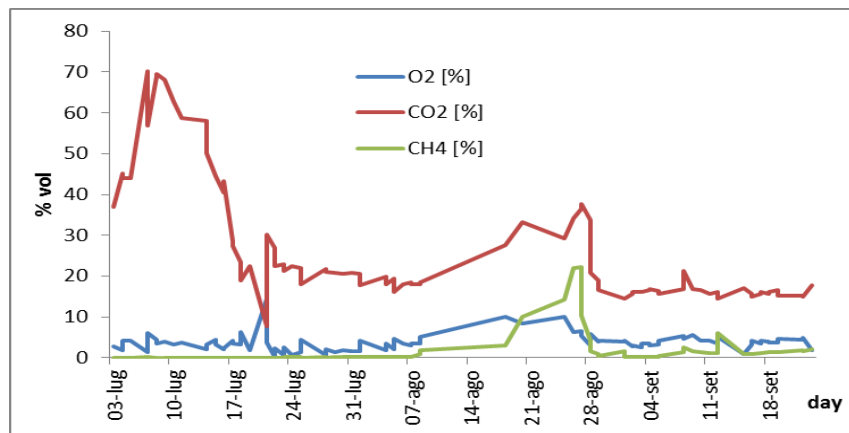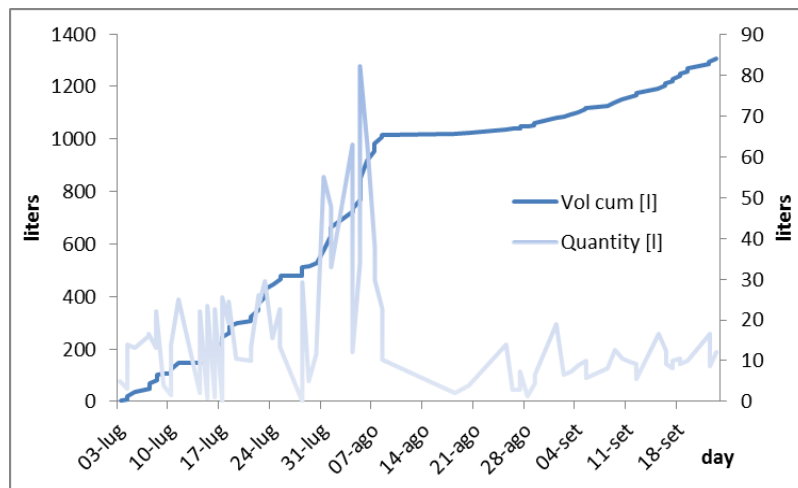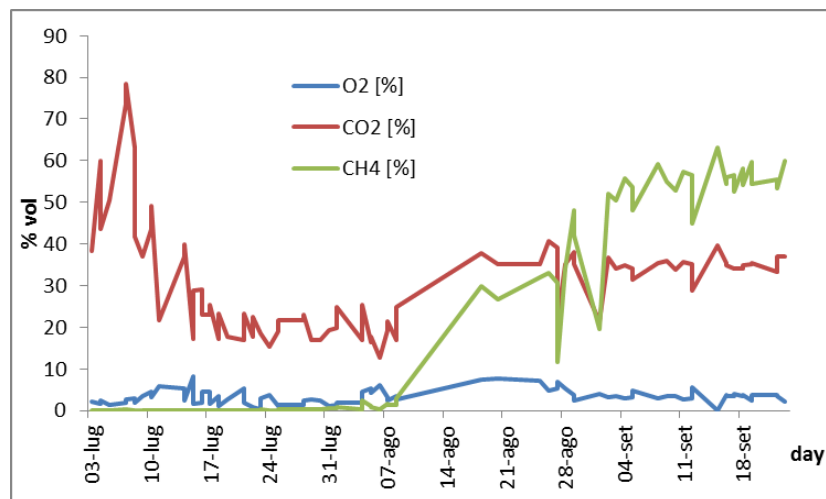

Figure 3.8: Gas volumetric percentage composition (O2, CO2, CH4) analyzed in output from the reactors S3

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Table 3.13: biogas characterization of column S4

Data	Ora	Fase	Quantità	O2 [%]	CO2 [%]	CH4 [%]	Vol cum [	C out (g)	gC/CH4	litri CH4	litri/kg	litri (CO2+Ch4)/kg
03-lug	17:20	1	2	2,2	44,8	0,09	2	0,13	0,00	0,00	0,00	0,049
04-lug	11:20	1	11	1,1	56,8	0,05	13	1,05	0,00	0,01	0,00	0,389
04-lug	15:37	1	4	5	44,4	0,05	17	1,31	0,00	0,01	0,00	0,485
05-lug	10:50	1	30	2	50	0,01	47	3,50	0,00	0,01	0,00	1,301
07-lug	11:00	1	28	2,6	50	0,09	75	5,56	0,02	0,04	0,00	2,063
07-lug	17:15	1	9	2,8	54	0,13	84	6,28	0,02	0,05	0,00	2,328
08-lug	11,13	1	4	2,8	57,2	0,01	88	6,61	0,02	0,05	0,00	2,452
08-lug	13:40	1	6	2,4	58,8	0,01	94	7,13	0,02	0,05	0,00	2,644
09-lug	11:00	1	10	2,7	55,2	0,01	104	7,94	0,02	0,05	0,00	2,944
10-lug	10:45	1	13	2,3	45	0,01	117	8,79	0,02	0,05	0,00	3,262
10-lug	13:45	1	0	2,3	45	0,01	128	9,51	0,02	0,05	0,00	3,262
11-lug	10:04	1	11	2	44,4	0,01	136,5	10,01	0,02	0,05	0,00	3,527
14-lug	10:30	1	8,5	1,9	40,8	0,01	145	10,32	0,02	0,05	0,00	3,716
14-lug	18:20	1	5,9	3	34,9	0,07	150,9	10,55	0,02	0,06	0,00	3,828
15-lug	09:30	1	5,3	4,4	30,5	0,01	156,2	10,91	0,02	0,06	0,00	3,916
15-lug	18:00	1	7,1	1,8	34	0,01	163,3	11,49	0,02	0,06	0,00	4,047
16-lug	09:20	1	13,67	2,2	28,9	0,05	176,97	11,88	0,03	0,07	0,00	4,262
16-lug	18:00	1	10,5	2,6	25,6	0,05	187,47	12,28	0,03	0,07	0,00	4,409
17-lug	09:30	1	15	1,4	26,5	0,01	202,47	12,86	0,03	0,07	0,00	4,625
17-lug	16:47	1	14,44	3,2	22,5	0,05	216,91	13,34	0,03	0,08	0,00	4,802
18-lug	09:24	1	21,94	2,5	21,3	0,05	238,85	14,03	0,04	0,09	0,00	5,056
18-lug	16:25	1	12,7	2,7	21,3	0,01	251,55	14,42	0,04	0,09	0,01	5,203
19-lug	11:30	1	20,4	1,8	20,9	0,05	271,95	15,05	0,04	0,10	0,01	5,436
21-lug	10:00	1	1,6	2,8	19,7	0,05	273,55	15,10	0,04	0,10	0,01	5,453
21-lug	16:15	1	1,38	2,9	31,3	0,13	274,93	15,16	0,04	0,11	0,01	5,476
22-lug	09:10	1	18,8	0,2	26,9	0,05	293,73	15,90	0,05	0,12	0,01	5,752
22-lug	15:30	1	0	0,2	26,9	0,05	293,73	15,90	0,05	0,12	0,01	5,752
23-lug	09:30	1	22,1	0,8	22,4	0,09	315,83	16,63	0,05	0,13	0,01	6,022
23-lug	16:50	1	12,22	3,1	19,7	0,21	328,05	17,00	0,06	0,16	0,01	6,154
24-lug	09:20	1	23,3	1,4	20,5	0,09	351,35	17,70	0,07	0,18	0,01	6,415
25-lug	09:40	1	17	1,3	21,7	0,05	368,35	18,25	0,08	0,19	0,01	6,616
25-lug	16:15	1	11,66	2,1	20,5	0,09	380,01	18,60	0,08	0,20	0,01	6,746
28-lug	09:30	1	9,55	3,5	17,3	0,13	389,56	18,85	0,09	0,21	0,01	6,837
28-lug	19:35	1	16,66	1,7	21	0,05	406,22	19,36	0,09	0,22	0,01	7,027
29-lug	09:10	1	19,61	1,3	20,1	0,13	425,83	19,95	0,10	0,25	0,01	7,243
30-lug	09:30	1	13,16	2,5	18,9	0,13	438,99	20,32	0,11	0,26	0,01	7,379
31-lug	09:10	1	25	1,3	20,9	0,25	463,99	21,11	0,13	0,33	0,02	7,666
01-ago	09:00	1	39,7	1,7	19,5	0,23	503,69	22,28	0,17	0,42	0,02	8,092
01-ago	16:30	1	8,72	3,6	19,3	0,21	512,41	22,53	0,18	0,44	0,02	8,185
04-ago	09:00	1	24,4	1,7	20,5	0,25	536,81	23,29	0,20	0,50	0,03	8,460
04-ago	18:46	1	19	2,3	18,9	0,33	555,81	23,84	0,22	0,56	0,03	8,658
05-ago	09:25	1	25	3,8	16,5	0,3	580,81	24,47	0,25	0,63	0,03	8,887
05-ago	17:12	1	18,22	2,7	20,1	0,23	599,03	25,02	0,27	0,68	0,04	9,088
06-ago	09:10	1	24,4	2,7	17,7	0,37	623,43	25,69	0,31	0,77	0,04	9,327
07-ago	09:00	1	40,83	2	18,1	0,45	664,26	26,85	0,38	0,95	0,05	9,739
07-ago	18:00	1	16,7	3,8	16,5	0,48	680,96	27,28	0,41	1,03	0,06	9,893
08-ago	09:12	1	13,33	3,2	17,7	0,61	694,29	27,66	0,45	1,11	0,06	10,026
8/ago	13:00	1	9,7	3,6	18,5	1,08	703,99	27,96	0,49	1,22	0,07	10,129
18-ago	13:00	2	2,61	11,4	16,5	5,1	706,6	28,08	0,54	1,35	0,07	10,160
20-ago	10:30	2	8	7	34,5	16,3	714,6	29,01	1,07	2,65	0,14	10,381
25-ago	09:00	2	1,6	6,7	43	19	716,2	29,23	1,19	2,96	0,16	10,434
26-ago	09:00	2	3,2	6,8	40	17,9	719,4	29,65	1,42	3,53	0,19	10,535
27-ago	09:00	2	3,72	7,2	36,4	16,7	723,12	30,10	1,67	4,15	0,23	10,643
27-ago	18:40	2	9,4	5,4	29,3	14	732,52	31,03	2,20	5,47	0,30	10,864
28-ago	09:00	2	0	5,4	29,3	14	732,52	31,03	2,20	5,47	0,30	10,864
29-ago	09:00	2	2,77	5,5	40,8	22,3	735,29	31,44	2,45	6,09	0,33	10,959
29-ago	18:00	2	4,61	4,6	26,1	11,6	739,9	31,83	2,66	6,62	0,36	11,053
1/set	09:00	2	20,5	4,6	18,1	7,7	760,4	33,01	3,29	8,20	0,45	11,341

|												
02-set	09:00	2	4,55	4,9	37,7	27,8	764,95	33,77	3,80	9,46	0,51	11,503
03-set	09:00	2	3,72	6,1	33,3	26,5	768,67	34,34	4,20	10,45	0,57	11,623
04-set	09:00	2	3,66	5,4	33,7	29	772,33	34,95	4,62	11,51	0,63	11,748
05-set	09:00	2	3,83	6	31,3	29	776,16	35,57	5,07	12,62	0,69	11,874
08-set	09:00	2	8,11	4,8	34,5	34,6	784,27	37,11	6,20	15,43	0,84	12,178
09-set	09:00	2	0	4,8	34,5	34,6	784,27	37,11	6,20	15,43	0,84	12,178
10-set	09:00	2	2,05	6,9	30,1	30,2	786,32	37,45	6,45	16,05	0,87	12,245
11-set	09:00	2	2	6,1	29,6	31	788,32	37,78	6,70	16,67	0,91	12,311
12-set	09:15	2	2,22	4,9	32,5	33	790,54	38,18	6,99	17,40	0,95	12,390
12-set	12:30	2	1,44	4,3	33,7	33,8	791,98	38,45	7,19	17,89	0,97	12,443
15-set	09:00	2	1,7	8,3	22,3	25,1	793,68	38,68	7,36	18,31	1,00	12,487
16-set	09:30	2	0	8,3	22,3	25,1	793,68	38,68	7,36	18,31	1,00	12,487
17-set	09:15	2	0	8,3	22,3	25,1	793,68	38,68	7,36	18,31	1,00	12,487
18-set	09:30	2	0	8,3	22,3	25,1	793,68	38,68	7,36	18,31	1,00	12,487
19-set	09:00	2	0	8,3	22,3	25,1	793,68	38,68	7,36	18,31	1,00	12,487
22-set	09:00	2	0	8,3	22,3	25,1	793,68	38,68	7,36	18,31	1,00	12,487
22-set	17:00	2	0	8,3	22,3	25,1	793,68	38,68	7,36	18,31	1,00	12,487
23-set	09:00	2	0	8,3	22,3	25,1	793,68	38,68	7,36	18,31	1,00	12,487
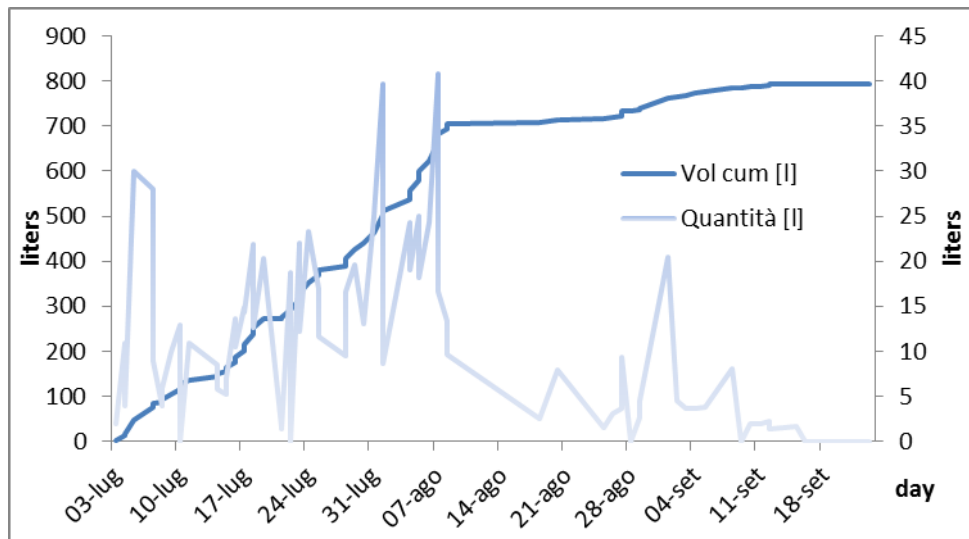
Figure 3.9: Cumulative volume and daily production of biogas measured in output from the column S4.
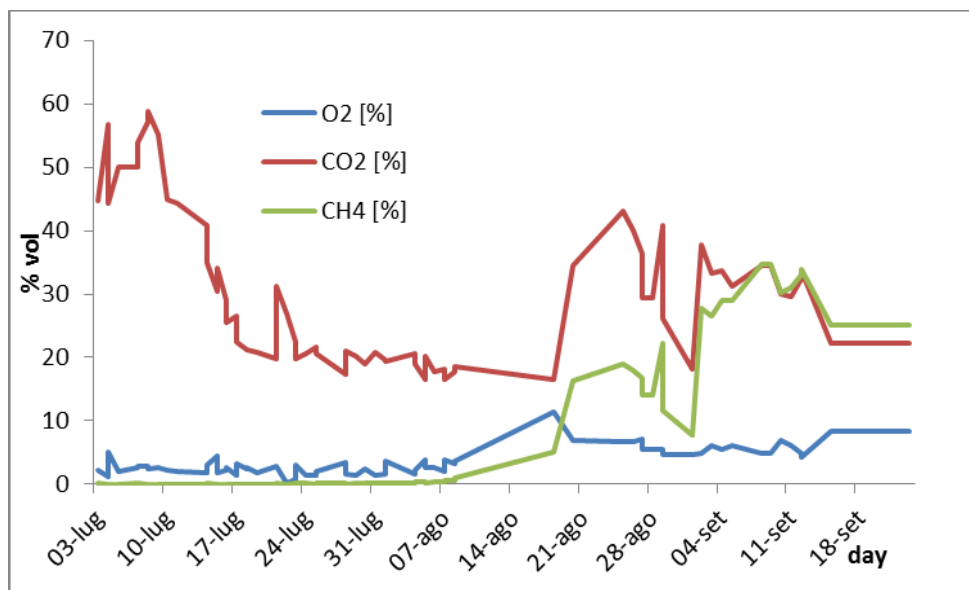

Figure 3.10: Gas volumetric percentage composition (O2, CO2, CH4) analyzed in output from the reactors S4.

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Table 3.14: biogas characterization of column AN5

Data	Ora	Fase	Quantità	O2 [%]	CO2 [%]	CH4 [%]	Vol cum [	C out (g)	gC/CH4	litri CH4	litri/kg	litri (CO2+Ch4)/kg
							column AN5					
03-lug	17:20	1	2	2,7	29,3	0,13	2	0,09	0,00	0,00	0,00	0,03
04-lug	11:20	1	2	1,3	42,8	0,13	4	0,21	0,00	0,01	0,00	0,08
04-lug	15:37	1	0	1,3	42,8	0,13	4	0,21	0,00	0,01	0,00	0,08
05-lug	10:50	1	0	1,3	42,8	0,13	4	0,21	0,00	0,01	0,00	0,08
07-lug	11:00	1	1	4	72,7	0,13	5	0,32	0,00	0,01	0,00	0,12
07-lug	17:15	1	3,5	2,4	91,5	0,17	8,5	0,79	0,01	0,01	0,00	0,29
08-lug	11,13	1	0,5	2,6	85,1	0,05	9	0,85	0,01	0,01	0,00	0,32
08-lug	13:40	1	0	2,6	85,1	0,05	9	0,85	0,01	0,01	0,00	0,32
09-lug	11:00	1	3	2,2	95	0,05	12	1,27	0,01	0,01	0,00	0,47
10-lug	10:45	1	6,3	2,4	95	0,01	18,3	2,15	0,01	0,01	0,00	0,80
10-lug	13:45	1	0	2,4	95	0,01	21	2,54	0,01	0,01	0,00	0,80
11-lug	10:04	1	2,7	2,1	99	0,05	21	2,54	0,01	0,02	0,00	0,94
14-lug	10:30	1	0	2,1	99	0,05	21	2,54	0,01	0,02	0,00	0,94
14-lug	18:20	1	1	6,1	78,3	0,05	22	2,65	0,01	0,02	0,00	0,98
15-lug	09:30	1	0	6,1	78,3	0,05	22	2,65	0,01	0,02	0,00	0,98
15-lug	18:00	1	0	6,1	78,3	0,05	22	2,65	0,01	0,02	0,00	0,98
16-lug	09:20	1	0	6,1	78,3	0,05	22	2,65	0,01	0,02	0,00	0,98
16-lug	18:00	1	0	6,1	78,3	0,05	22	2,65	0,01	0,02	0,00	0,98
17-lug	09:30	1	0	6,1	78,3	0,05	22	2,65	0,01	0,02	0,00	0,98
17-lug	16:47	1	0	6,1	78,3	0,05	22	2,65	0,01	0,02	0,00	0,98
18-lug	09:24	1	0	6,1	78,3	0,05	22	2,65	0,01	0,02	0,00	0,98
18-lug	16:25	1	0	6,1	78,3	0,05	22	2,65	0,01	0,02	0,00	0,98
19-lug	11:30	1	0	6,1	78,3	0,05	22	2,65	0,01	0,02	0,00	0,98
21-lug	10:00	1	0	6,1	78,3	0,05	22	2,65	0,01	0,02	0,00	0,98
21-lug	16:15	1	0	6,1	78,3	0,05	22	2,65	0,01	0,02	0,00	0,98
21-lug	16:35	1	10	9	54,3	0,09	32	3,45	0,01	0,03	0,00	1,28
21-lug	17:00	1	27	17	16,5	0,09	59	4,11	0,02	0,05	0,00	1,52
21-lug	17:30	1	20	19,6	5,44	0,09	79	4,28	0,03	0,07	0,00	1,58
22-lug	09:30	1	0	6,1	78,3	0,05	79	4,28	0,03	0,07	0,00	1,58
22-lug	15:30	1	0	6,1	78,3	0,05	79	4,28	0,03	0,07	0,00	1,58
23-lug	09:30	1	0	6,1	78,3	0,05	79	4,28	0,03	0,07	0,00	1,58
23-lug	16:50	1	0	6,1	78,3	0,05	79	4,28	0,03	0,07	0,00	1,58
24-lug	09:20	1	0	6,1	78,3	0,05	79	4,28	0,03	0,07	0,00	1,58
25-lug	09:40	1	0	6,1	78,3	0,05	79	4,28	0,03	0,07	0,00	1,58
25-lug	16:15	1	0	6,1	78,3	0,05	79	4,28	0,03	0,07	0,00	1,58
28-lug	09:30	1	0	6,1	78,3	0,05	79	4,28	0,03	0,07	0,00	1,58
28-lug	19:35	1	0	6,1	78,3	0,05	79	4,28	0,03	0,07	0,00	1,58
29-lug	09:10	1	0	6,1	78,3	0,05	79	4,28	0,03	0,07	0,00	1,58
29-lug	13:10	1	26	11,7	20,5	0,13	105	5,07	0,04	0,10	0,01	1,87
30-lug	09:30	1	0	6,1	78,3	0,05	105	5,07	0,04	0,10	0,01	1,87
31-lug	09:10	1	0	6,1	78,3	0,05	105	5,07	0,04	0,10	0,01	1,87
01-ago	09:00	1	0	6,1	78,3	0,05	105	5,07	0,04	0,10	0,01	1,87
01-ago	16:30	1	17,7	7,3	28,8	0,13	122,7	5,83	0,05	0,12	0,01	2,15
04-ago	09:00	1	0	7,3	28,8	0,13	122,7	5,83	0,05	0,12	0,01	2,15
04-ago	18:46	1	0	7,3	28,8	0,13	122,7	5,83	0,05	0,12	0,01	2,15
05-ago	09:25	1	0	7,3	28,8	0,13	122,7	5,83	0,05	0,12	0,01	2,15
05-ago	17:12	1	0	7,3	28,8	0,13	122,7	5,83	0,05	0,12	0,01	2,15
06-ago	09:10	1	0	7,3	28,8	0,13	122,7	5,83	0,05	0,12	0,01	2,15
07-ago	09:00	1	0	7,3	28,8	0,13	122,7	5,83	0,05	0,12	0,01	2,15
07-ago	18:00	1	0	7,3	28,8	0,13	122,7	5,83	0,05	0,12	0,01	2,15
08-ago	13:00	1	7,22	3,8	20,1	1,44	129,92	6,08	0,09	0,23	0,01	2,24
18-ago	13:00	2	0	3,8	20,1	1,44	129,92	6,08	0,09	0,23	0,01	2,24
20-ago	10:30	2	1,5	6,7	30,5	7,8	131,42	6,19	0,14	0,35	0,02	2,27
25-ago	09:00	2	4,44	4,5	39,2	6	135,86	6,55	0,25	0,61	0,03	2,38
26-ago	09:00	2	3,8	6	39,6	17,9	139,66	7,05	0,52	1,29	0,07	2,50
27-ago	09:00	2	4,16	4,3	40,8	23,1	143,82	7,68	0,91	2,25	0,12	2,64
27-ago	18:40	2	4,16	5,9	26	14	147,98	8,07	1,14	2,84	0,15	2,73
28-ago	09:00	2	0	5,9	26	14	147,98	8,07	1,14	2,84	0,15	2,73
29-ago	09:00	2	0	5,9	26	14	147,98	8,07	1,14	2,84	0,15	2,73
29-ago	18:00	2	0	5,9	26	14	147,98	8,07	1,14	2,84	0,15	2,73
01-set	09:00	2	14,8	3,9	21,3	3,81	162,78	8,76	1,37	3,40	0,18	2,93

|												
02-set	09:00	2	2,22	3,3	38,1	6	165	8,94	1,42	3,53	0,19	2,99
03-set	09:00	2	2,22	3,5	36,1	6,58	167,22	9,12	1,48	3,68	0,20	3,04
04-set	09:00	2	1,67	3,5	36,1	6,95	168,89	9,25	1,52	3,79	0,21	3,08
05-set	09:00	2	1,67	3,9	34,9	6,87	170,56	9,38	1,57	3,91	0,21	3,12
08-set	09:00	2	2,77	4,1	34,1	6,9	173,33	9,60	1,65	4,10	0,22	3,18
09-set	09:00	2	2,11	3,8	36	7,4	175,44	9,77	1,71	4,26	0,23	3,23
10-set	09:00	2	1,83	4,5	32,5	6,56	177,27	9,91	1,76	4,38	0,24	3,27
11-set	09:00	2	2,05	3,8	33,7	6,72	179,32	10,06	1,81	4,51	0,25	3,31
12-set	09:15	2	2,05	2,9	35,2	6,75	181,37	10,22	1,87	4,65	0,25	3,36
12-set	12:30	2	1,22	5,5	30,9	5,82	182,59	10,31	1,90	4,72	0,26	3,38
15-set	09:00	2	0	5,5	30,9	5,82	182,59	10,31	1,90	4,72	0,26	3,38
16-set	09:30	2	0	5,5	30,9	5,82	182,59	10,31	1,90	4,72	0,26	3,38
17-set	09:15	2	0	5,5	30,9	5,82	182,59	10,31	1,90	4,72	0,26	3,38
18-set	09:30	2	0	5,5	30,9	5,82	182,59	10,31	1,90	4,72	0,26	3,38
19-set	09:00	2	0	5,5	30,9	5,82	182,59	10,31	1,90	4,72	0,26	3,38
22-set	09:00	2	0	5,5	30,9	5,82	182,59	10,31	1,90	4,72	0,26	3,38
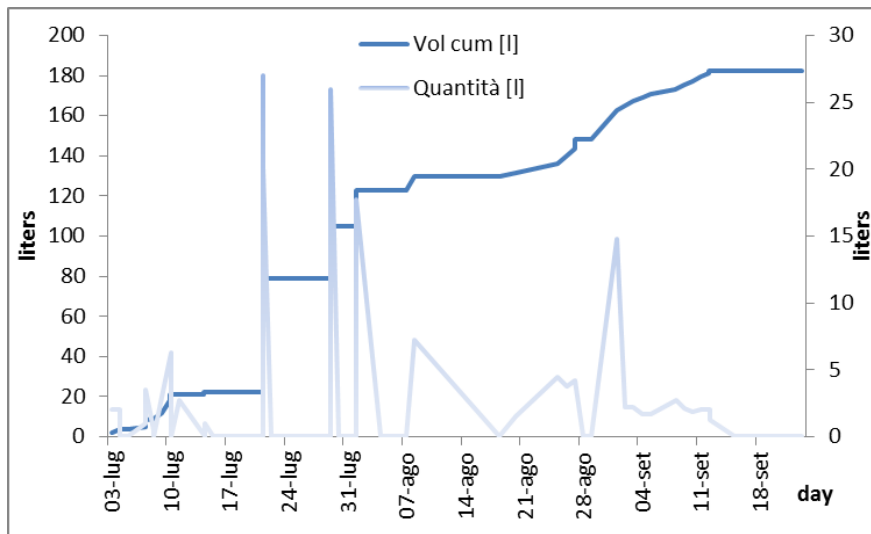
Figure 3.11: Cumulative volume and daily production of biogas measured in output from the column AN5.
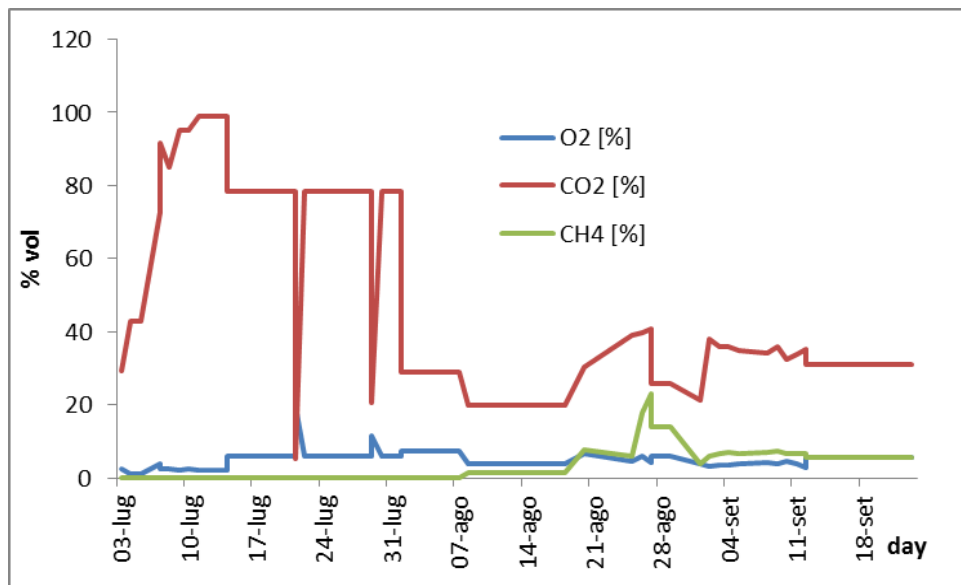

Figure 3.12: Gas volumetric percentage composition (O2, CO2, CH4) analyzed in output from the reactors AN5.

Table 3.15: biogas characterization of column AN6

Data	Ora	Fase	Quantità	O2 [%]	CO2 [%]	CH4 [%]	Vol cum [	C out (g)	gC/CH4	litri CH4	litri/kg	litri (CO2+Ch4)/kg
						column AN6						
03-lug	17:20	1	13	1,7	34,5	0,09	13	0,66	0,00	0,0117	0,00	0,24
04-lug	11:20	1	10	2	52	0,09	23	1,42	0,01	0,02	0,00	0,53
04-lug	15:37	1	4	2,3	56,4	0,09	27	1,76	0,01	0,02	0,00	0,65
05-lug	10:50	1	9	2,6	70	0,05	36	2,68	0,01	0,03	0,00	0,99
07-lug	11:00	1	10	2	94,7	0,17	46	4,07	0,02	0,05	0,00	1,51
07-lug	17:15	1	5	2,5	96,6	0,09	51	4,78	0,02	0,05	0,00	1,77
08-lug	11,13	1	4	2,8	93,9	0,05	55	5,33	0,02	0,05	0,00	1,98
08-lug	13:40	1	0	2,8	93,9	0,05	55	5,33	0,02	0,05	0,00	1,98
09-lug	11:00	1	1,2	2,9	95	0,05	56,2	5,50	0,02	0,05	0,00	2,04
10-lug	10:45	1	1	6	78	0,05	57,2	5,61	0,02	0,05	0,00	2,08
10-lug	13:45	1	0	6	78	0,05	59,1	5,88	0,02	0,05	0,00	2,08
11-lug	10:04	1	1,9	2,4	95,8	0,05	59,1	5,88	0,02	0,05	0,00	2,18
14-lug	10:30	1	0	2,4	95,8	0,05	59,1	5,97	0,02	0,05	0,00	2,18
14-lug	18:20	1	1	8	64,1	0,05	60,1	5,97	0,02	0,05	0,00	2,21
15-lug	09:30	1	0	8	64,1	0,05	60,1	5,97	0,02	0,05	0,00	2,21
15-lug	18:00	1	0	8	64,1	0,05	60,1	5,97	0,02	0,05	0,00	2,21
16-lug	09:20	1	0	8	64,1	0,05	60,1	5,97	0,02	0,05	0,00	2,21
16-lug	18:00	1	0	8	64,1	0,05	60,1	5,97	0,02	0,05	0,00	2,21
17-lug	09:30	1	0	8	64,1	0,05	60,1	5,97	0,02	0,05	0,00	2,21
17-lug	16:47	1	0	8	64,1	0,05	60,1	6,18	0,02	0,05	0,00	2,21
18-lug	09:24	1	2	6,1	70,6	0,05	62,1	6,18	0,02	0,06	0,00	2,29
18-lug	16:25	1	0	6,1	70,6	0,05	62,1	6,18	0,02	0,06	0,00	2,29
19-lug	11:30	1	0	6,1	70,6	0,05	62,1	6,18	0,02	0,06	0,00	2,29
21-lug	10:00	1	0	6,1	70,6	0,05	62,1	6,18	0,02	0,06	0,00	2,29
21-lug	16:15	1	0	6,1	70,6	0,05	62,1	6,18	0,02	0,06	0,00	2,29
21-lug	16:35	1	0	6,1	70,6	0,05	62,1	7,59	0,02	0,06	0,00	2,29
21-lug	17:00	1	23,3	11,5	41,2	0,13	85,4	7,96	0,03	0,09	0,00	2,81
21-lug	17:30	1	23	18,3	10,4	0,13	108,4	7,96	0,05	0,12	0,01	2,95
22-lug	09:30	1	0	6,1	70,6	0,05	108,4	7,96	0,05	0,12	0,01	2,95
22-lug	15:30	1	0	6,1	70,6	0,05	108,4	7,96	0,05	0,12	0,01	2,95
23-lug	09:30	1	0	6,1	70,6	0,05	108,4	7,96	0,05	0,12	0,01	2,95
23-lug	16:50	1	0	6,1	70,6	0,05	108,4	7,96	0,05	0,12	0,01	2,95
24-lug	09:20	1	0	6,1	70,6	0,05	108,4	7,96	0,05	0,12	0,01	2,95
25-lug	09:40	1	0	6,1	70,6	0,05	108,4	9,08	0,05	0,12	0,01	2,95
25-lug	16:15	1	24,61	11	31	0,09	133,01	9,08	0,06	0,14	0,01	3,36
28-lug	09:30	1	0	6,1	70,6	0,05	133,01	9,08	0,06	0,14	0,01	3,36
28-lug	19:35	1	0	6,1	70,6	0,05	133,01	9,08	0,06	0,14	0,01	3,36
29-lug	09:10	1	0	6,1	70,6	0,05	133,01	9,92	0,06	0,14	0,01	3,36
29-lug	13:10	1	26	12,5	21,7	0,13	159,01	9,92	0,07	0,17	0,01	3,67
30-lug	09:30	1	0	6,1	70,6	0,05	159,01	10,01	0,07	0,17	0,01	3,67
31-lug	09:10	1	3,5	9,7	18,1	0,13	162,51	10,10	0,07	0,18	0,01	3,70
01-ago	09:00	1	2,5	9,1	22,1	0,13	165,01	10,10	0,07	0,18	0,01	3,73
01-ago	16:30	1	0	9,1	22,1	0,13	165,01	10,10	0,07	0,18	0,01	3,73
04-ago	09:00	1	0	7,3	28,8	0,13	165,01	10,10	0,07	0,18	0,01	3,73
04-ago	18:46	1	0	7,3	28,8	0,13	165,01	10,10	0,07	0,18	0,01	3,73
05-ago	09:25	1	0	7,3	28,8	0,13	165,01	10,10	0,07	0,18	0,01	3,73
05-ago	17:12	1	0	7,3	28,8	0,13	165,01	10,10	0,07	0,18	0,01	3,73
06-ago	09:10	1	0	7,3	28,8	0,13	165,01	10,10	0,07	0,18	0,01	3,73
07-ago	09:00	1	0	7,3	28,8	0,13	165,01	10,10	0,07	0,18	0,01	3,73
07-ago	18:00	1	0	7,3	28,8	0,13	165,01	10,43	0,07	0,18	0,01	3,73
08-ago	13.00	1	9,6	3,9	20,1	1,28	174,61	10,43	0,12	0,30	0,02	3,85
18-ago	13:00	2	0	3,9	20,1	1,28	174,61	10,58	0,12	0,30	0,02	3,85
20-ago	10:30	2	2	8,5	30,1	8,34	176,61	10,88	0,19	0,47	0,03	3,89
25-ago	09:00	2	3,4	8,4	31,7	10	180,01	11,03	0,33	0,81	0,04	3,97
26-ago	09:00	2	1,6	8,2	30,9	12,8	181,61	11,33	0,41	1,01	0,06	4,00
27-ago	09:00	2	2,55	6,9	37,7	15,5	184,16	11,65	0,57	1,41	0,08	4,08
27-ago	18:40	2	3,66	5,4	30,9	10,4	187,82	11,73	0,72	1,79	0,10	4,16
28-ago	09:00	2	1,05	5,6	46,4	3,34	188,87	11,89	0,73	1,83	0,10	4,19
29-ago	09:00	2	2	5	45,2	2,86	190,87	12,00	0,76	1,88	0,10	4,24
29-ago	18:00	2	1,6	4,9	40,8	2,5	192,47	12,59	0,77	1,92	0,10	4,28
01-set	09:00	2	16,22	4,8	14,9	3,54	208,69	12,74	1,00	2,50	0,14	4,44

|											
02-set	09:00	2	2,44	6,1	36,1	2,4	211,13	12,74	1,03	2,56	0,14	4,49
03-set	09:00	2	0	6,1	36,1	2,4	211,13	12,83	1,03	2,56	0,14	4,49
04-set	09:00	2	1,38	5,5	38,4	2,23	212,51	12,91	1,04	2,59	0,14	4,52
05-set	09:00	2	1,44	6,7	34,5	1,95	213,95	12,96	1,05	2,61	0,14	4,55
08-set	09:00	2	1,55	13,4	17,7	0,96	215,5	13,07	1,06	2,63	0,14	4,57
09-set	09:00	2	2	7,8	31,3	2,39	217,5	13,07	1,08	2,68	0,15	4,60
10-set	09:00	2	0	7,8	31,3	2,39	217,5	13,23	1,08	2,68	0,15	4,60
11-set	09:00	2	3,22	9,2	26,4	2,55	220,72	13,23	1,11	2,76	0,15	4,65
12-set	12:30	2	0	9,2	26,4	2,55	220,72	13,23	1,11	2,76	0,15	4,65
15-set	09:00	2	0	9,2	26,4	2,55	220,72	13,23	1,11	2,76	0,15	4,65
16-set	09:30	2	0	9,2	26,4	2,55	220,72	13,23	1,11	2,76	0,15	4,65
17-set	09:15	2	0	9,2	26,4	2,55	220,72	13,23	1,11	2,76	0,15	4,65
18-set	09:30	2	0	9,2	26,4	2,55	220,72	13,23	1,11	2,76	0,15	4,65
19-set	09:00	2	0	9,2	26,4	2,55	220,72	13,23	1,11	2,76	0,15	4,65
22-set	09:00	2	0	9,2	26,4	2,55	220,72	13,23	1,11	2,76	0,15	4,65
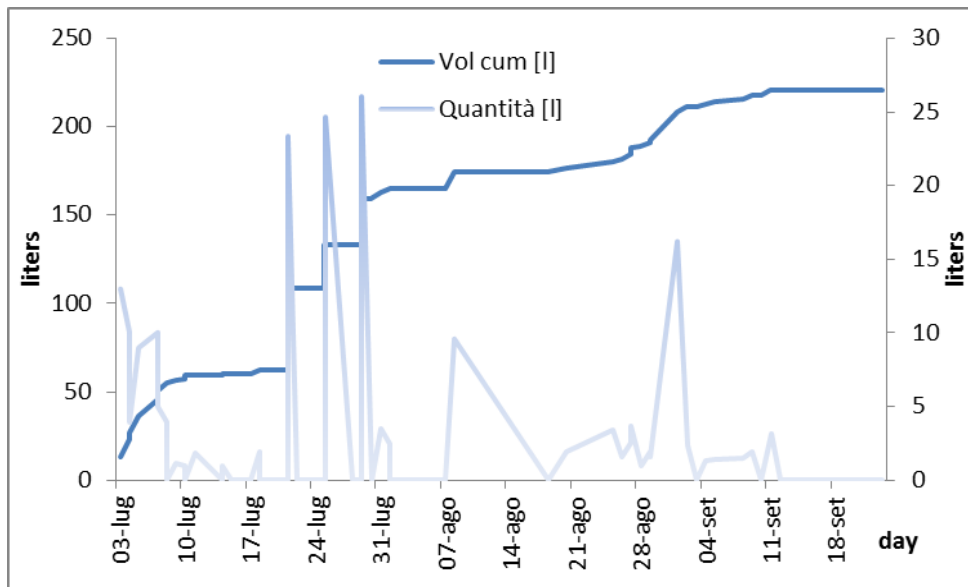
Figure 3.13: Cumulative volume and daily production of biogas measured in output from the column AN6.
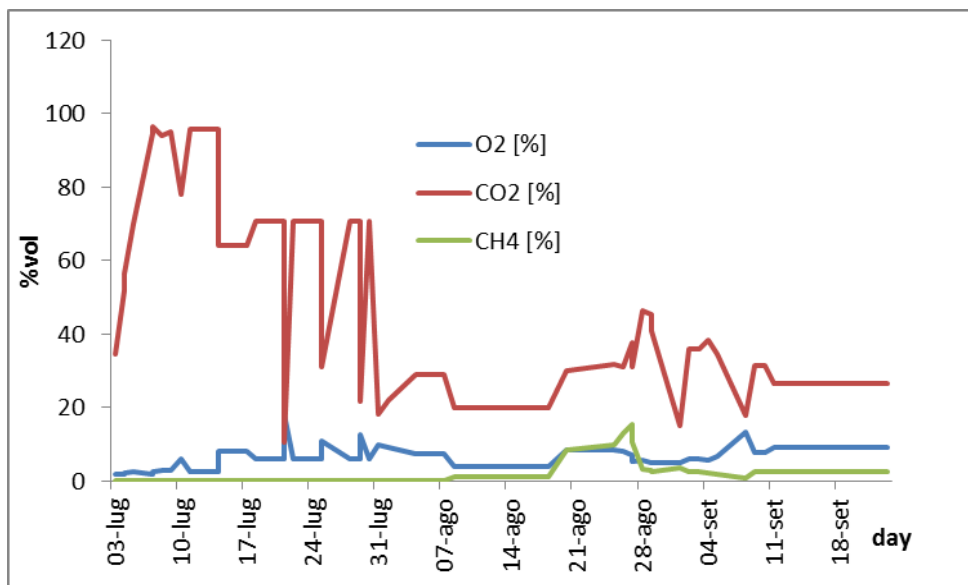

Figure 3.14: Gas volumetric percentage composition (O2, CO2, CH4) analyzed in output from the reactors AN6.

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Annex 2 : Data elaboration

The elaboration of the data started from the results of the analyses performed in the laboratory, on the collected samples from the reactors: concentration of TOC, TKN and NH4+, COD, FOS/TAC, Cl, SO_4^{2-} for all the six reactors. Also pH was a parameter analyzed in laboratory. The values of the concentration can be plotted in a graph with respect to the value of the L/S ratio. This value is calculated dividing the progressive total amount of fresh water coming in contact with the waste to the weight of the dry matter of the waste inside the reactor. The equations used are the following:

$$\frac{L}{S}\left(\frac{l_{H_2O}}{kg_{DM}}\right) = \frac{Total\ FW_{in}(l)}{M_{DM}\ (kg_{DM})}$$

$$Total\ FW_{in}(l)_{(i)_{th}\ week} = Total\ FW_{in}(l)_{(i-1)_{th}\ week} + FW_{in}(l)_{(i)_{th}week}$$

where the term on the left is the total amount of distilled water injected in the system from the beginning of the experimental study, until the considered ith week, calculated as the sum of the quantity of water inserted until the week before, the (i-1)th, and , the water inserted the ith week. The values of concentrations resulted from the analyses of the first samples, were used as the values representing the initial concentrations,

The mass of the contaminant extracted in every sample was calculated multiplying its concentration with the volume of the leachate extracted with the collection during the week, through the equation:

$$M_i(mg) = C_i\left(\frac{mg}{l}\right) * V_{out}(l)$$

The mass was then calculated with respect to the dry matter of the waste present in the columns (mg/KgTS) dividing the value of mass of contaminant by the Kg of TS. In this way it was possible to calculate the total mass of the compound of interest removed with the leachate from all the process, and calculate the percentages of removal of them with respect to the first analyses on the solid sample. In order to obtain the concentrations of samples on which the analyzes were not carried out, but that increse the L / S ratio a linear interpolation was use :

$$y* = y_a + \frac{y_b - y_a}{x_b - x_a}(x* - x_a)$$

y*= unknown value y$_a$= previous concentration y$_b$=final concentration x$_a$ = initial L/S value
       x*= intermediate L/S value   x$_b$ =final L/S value

In order to achieve a carbon mass balance in the gas phase, the ideal gases law has been used:

$$P \cdot V = n \cdot R \cdot T$$

The mass in grams of carbon was found with the following formula (*)

$$m_C = n_{CO_2} \cdot PM_{CO_2} \cdot f_{C/CO_2} + n_{CH_4} \cdot PM_{CH_4} \cdot f_{C/CH_4} \quad (*)$$

Where f_{C/CO_2} e f_{C/CH_4} are percentages by mass of that element in the CO2 and CH4 molecules measured in the outflows, respectively 0,279 e 0,7487. The molecular weight of the molecule of the gas-th is indicated with PMi, while, ni indicates the molar fraction of the i-th gas.

For a given temperature and pressure, the molar volume is the same for all ideal gases and is known to the same precision as the gas constant $R = 8.314\,4621$ J mol^{-1} K^{-1}. The molar volume of an ideal gas at 1 atmosphere of pressure is 22.414 L/mol at 0 °C.

For the ideal gas, Amagat law states that "... for a mixture of ideal gases, the mole fraction coincides with the volume fraction ...", then it:

$$x_i = \frac{V_i}{V} = \frac{n_i}{n} \qquad n_i = x_i \cdot n$$

Knowing the volume fraction of CO_2 and CH_4 we can calculate ni, which is the number of moles or mole fraction of the i-th gas. Based on the formula (*) the mass of carbon gasified in columns aerated during the test was calculated. For the quantification of carbon gasified in columns anaerobic calculation was the same. In any case the volume of gas output from the columns was measured through the use of 10 l gas bags.

Annex 3 : Analytical Methodology

3.1. Analysis on Liquids

For all the leachate analysis are necessary 250 ml of liquid, 100 ml more or less for analytical tests and 150 as stock; the samples are stored in fridge for all time. The bottle is made of plastic and it has the same capacity of the liquid taken, to avoid air presence in headspace. Italian and European law certifies all the analytical procedures used.

pH: IRSA-CNR 29/2003, Vol1, n.2060. The test is carried on immediately after the sampling because requires environment temperature to be precise and because can be performed very fast. It consist in a probe input that gives immediately the pH measure.

Total Organic Carbon (TOC): IRSA-CNR 29/2003, Vol2, n.5040. TOC is measured with the "TOC-V CSN" analytical equipment that gives directly the concentration value.

Ammonia (NH3, titration): IRSA-CNR 29/2003, Vol2, n.4030 C. Ammonia concentration is evaluated distilling a note volume of sample with NaOH addition. The condensation liquid is collected with boric acid and titrate with sulphuric acid. The concentration can be evaluate with a stoichiometric formula, starting from the sulphuric acid consumption.

Total Kjeldahl Nitrogen (TKN): IRSA-CNR 29/2003, Vol2, n.5030. The procedure is the same as for ammonia except that, before distillation, a digestion in acid environment is necessary, with the addition on kjeldahl tabs.

Nitrates (NO3-) IRSA-CNR 29/2003, Vol2, n.4040 A1. The procedure starts with the addition of Na salicylate to the sample and with the drying in stove of the sample. After that, the sample is recover with acid, a base solution is added and the nitrates value is read on a spectrophotometer.

Biological Oxygen Demand (BOD5): IRSA-CNR 29/2003, Vol2, n.5120 B2. The test is a batch reactor test long for five days after which the oxygen consumption is read.

Chemical Oxygen Demand (COD): IRSA-CNR 29/2003, Vol2, n.5130. COD test consist in an acid digestion (150°C for 120 minutes) with great quantities of sulphuric acid and potassium dichromate. After that the solution is titrate with Mohr salt that gives the chemical consumption of oxygen.

Sulphates (SO4--): IRSA-CNR 29/2003, Vol2, n.4140 B. The test is made with a turbidity reading of spectrophotometer. The problem of the procedure can be the sample turbidity before reagents addition that can false the results.

Chlorine (Cl-): IRSA-CNR 29/2003, Vol2, n.4090 A1. Test is a titration with argent nitrate 0,1 molar.

Metals: IRSA-CNR 29/2003, Vol1, n.3010 mod.+3020.

3.2. Analysis on Solids

Solids samples are stored in fringe, in large glass containers, before the milling procedure. After that they are transfer in smaller plastic bottles to avoid air in headspace. The quantity sampled is one kilo more or less, with a volume of 2 liters.

Total Solids (TS) IRSA-CNR Q. 64/84, Vol2, n.2. A fix quantity of milled sample is weighted and dried in hoven for 12 hours. This procedure avoids the presence of water and allows the evaluation of the Total Solids in percentage respect to initial mass.

Total Volatile Solids (TVS) IRSA-CNR Q. 64/84, Vol2, n.2. The same sample coming out form TS analysis can be used. The procedure requires the burning in Moffola at the temperature of 550 °C for 3 hours. The effect is the consumption of everything organic is present in the sample. The residues are weighted and the TVS are the difference between initial TS and final inorganic residues remaining after the Moffola treatment.

Total Organic Carbon (TOC): UNI-EN 13137. The test is carried on with the same equipment of liquid TOC analysis: "TOC-V CSN".

Ammonia (NH_3): IRSA-CNR Q. 64/86, Vol3, n.7 mod. The procedure is the same of the liquid sample, only is necessary weight a certain quantity of sample.

Total Kjeldahl Nitrogen (TKN): IRSA-CNR Q. 64/85, Vol3, n.6 mod. The procedure is the same of the liquid sample, only is necessary weight a certain quantity of sample and be more careful about the digestion.

Respirometric Index ANPA 3/2001 n.12.1.2.3. Is made with the "SAPROMAT" equipment that is a semi-dynamic test of oxygen consumption under controlled conditions. The test is perform in 4 days and in 7 days, the oxygen consumption can be visualize even continuously.

Annex 4 : Leaching test

The leaching test is a tool for analyze how much compounds are extractable from a solid sample, increasing the L/S ratio with a controlled washing of a small quantity of waste. The method must be a standard certified for ensure the comparability of the results with other ones. The standard choose is the UNI EN12457-2.

In a 2 liters bottle, solid sample and distilled water for reach L/S of 10 l/Kg are injected, considering the moisture content too. The bottles are fix to a agitating machine (Figure 3.15) that turns for 20 rounds per minute for 24 hours in a room at stable temperature around 20°C. After the washing time the sample is heavily filter to obtain 500 ml of elute for each solid sample(eluate 1 and eluate 2). The analysis on this liquid are, COD, alkalinity, VFA, ammonia, chloride, sulphates, sulphides, TOC, BOD with the standards of leachate samples and are reported in table 3.16 below

Figure 3.15: Agitating machine. The equipment has 6 place, three visible and three in the opposite side, at which bottles are attached. In bottles the water and the sample are continuously turned by the machine to extract all possible compounds. The turning rate is 20 rounds per minute, for 24 hours.

Table 3.16: eluation test results. Two sample was analyzed.

Characterization of eluate1									
COD	Alkalinity	VFA	FOS/TAC	NH_3 [mg/l]	TOC [mg/l]	SO_4^{--} [mgSO$_4^{--}$/l]	BOD_5 [mgO$_2$/l]	Sulphide [mgS^{--}/l]	Chloride [mgCl$^-$/l]
14746,50	306	711,6	2,33	80,5	3760	496,25	10183	12	648,8
Characterization of eluate 2									
COD	Alkalinity	VFA	FOS/TAC	NH_3 [mg/l]	TOC [mg/l]	SO_4^{--} [mgSO$_4^{--}$/l]	BOD_5 [mgO$_2$/l]	Sulphide [mgS^{--}/l]	Chloride [mgCl$^-$/l]
14617,94	241	745,2	3,09	74,83	3520	559,67	4825	10,4	588,6

Annex 5: Sampling methodology

5.1. Leachate Samples

Leachate exits form the bottom part of the reactor and is collect in tanks with through plastic and/or rubber pipes (Figure 3.16). A system of valves allows the flux interruption for accumulate leachate inside reactor. The leachate exit is generally between 2-2,5 liters and has been collect in a 5-liter tank (figure a). Leachate sample was placed in a plastic bottle and stored in fridge. The volume of sample ranging between 100 and 250 ml according to leachate production and previous extraction. During 13 weeks of test, a total of 23 samples were extracted, for a total volume of 4.9 l of leachate. In table 3.17 are summarized the frequencies of leachate extraction and analysis. These pipes were Tygon Standard pipes, having an inner diameter of 6 mm, they are constituted of nontoxic material and have a good base, acids, inorganic substances and high temperature resistance. The recirculation flow was maintained to 6 l/d, leachate was recirculated by peristaltic pumps of Heidolph model PD 5001, (figure b) driven by an analogical timer. Peristaltic pumps are suitable for the dosage of corrosive, abrasive or aggressive solvents because the liquid comes into contact only with the pipes and not with the mechanical parts of the pumps. Pumps were calibrated before to be started.

Table 3.17 : frequencies of leachate extraction and analysis

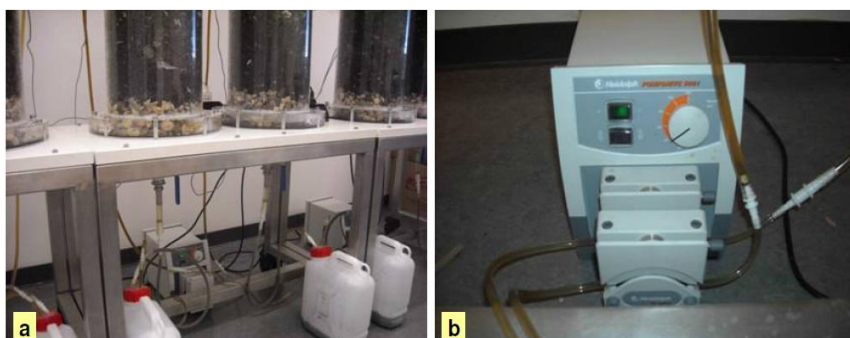| Analysis performed during first 5 week				
Daily	3 time per Week	Bi-weekly	monthly	Weekly
pH, Temperature	FOS/TAC, NH4	TKN	Metals, BOD	SO42-, Cl-, TOC, COD
Analysis performed during remaining 8 week				
Daily	3 time per Week	Bi-weekly	monthly	Weekly
pH, temperature	-	TKN	Metals, BOD	FOS/TAC, NH4, SO42-, Cl-, TOC, COD

Figure 3.16: leachate recirculation inside the reactors. (a) - Detail of the bottom of the columns with the gravel for the filtering of the leachate, the exhaust valve of the liquid, the 5 liter storage container and the recirculation pump (b) - Detail of the peristaltic pump Heidolph PD 5001.

5.2. Solid waste Samples

Solid waste samples are taken at the beginning of the test. The first sample (July 2014) is hand take form the fresh waste before inserting it in reactor and so comes from a characterization analysis. The merceological analysis was conducted on MSW unprocessed biologically and mechanically, collected from collection plant in central Italy. Grain size distribution analysis was performed on 200 kg of MSW sample using 80 mm mesh size sieves. The under-sieve, was characterized and divided considering the following categories : Garden and kitchen waste, wood, paper and cardboard, textile, composites, metal, glass, plastic and other. Around one kilogram of solid waste sample was taken and shredded whit a mill in 3 mm size piece. After that the sample was stored in the fridge in a 5 litres glass bottle (figure 3.17). All concerning analysis were carried out on solid sample in order to constituted the starting point for all the mass balances. Analyses are reported in table 3.18.

figure 3.17 : a) refuse before merceological analysis. b) solid waste sample in a 5 liter bottle.

Table 3.18: Solid waste sample analysis and resultants. Five measures were made to evaluate TOC on solid sample. Two measures ware made to evaluate ammonia nitrogen and TKN on solid sample. One for the determination on moisture content (U%), Total solids (TS, is the measure of dry matter), Volatile solids (VS).

	NH3 [mgN/l]	TKN [mgN/l]	TOC [mgC/l]	U%	VS	TS
Sample1	1137,81	9369,56	364900	45	30	55
Sample2	1165,81	10641,27	414800			
Sample3			378400			
Sample4			297600			
Sample5			383000			
Average	1151,81	10005,42	367740	45	30	55

5.3. Gas Samples

The composition of the gas produced by the columns was measured by portable analyzer (LFG20) every day (figure 3.18). The gas was collected in a 10-20 liter bag. The instrument is battery powered and is equipped with an internal pump for aspiration of the biogas; the flow is adjusted to about 200 ml / min but can be varied thanks to a potentiometer. This device allows to measure the percentage by volume (% vol) of the following gases: methane (CH_4), carbon dioxide (CO_2), oxygen (O_2). Methane and carbon dioxide are measured by infrared absorption, oxygen is measured by means of an electrolytic cell. Concentrations appear on the display which is fitted to the instrument. An hollow needle draw the air that pass through a hygroscopic filter to prevent water or other liquids, dust or dirt from getting inside the optical system of measurement. The instrument must be prepared to measure by adjusting the values that appear on the display when the air is draw. Will reset the values of methane and carbon dioxide and has the oxygen concentration of 20.9%. The adjustment is made via the knobs on the bottom of the instrument. The aspiration must take place for a period such as to allow the stabilization of the digits on the display. Inserting the needle to the biogas collection bag valve it is possible to perform the measure.

Figure 3.18: LFG20 analyzer. Gas collection bag.