

# Investigation of an innovative process for biogas up-grading – pilot plant preliminary results

*Lidia Lombardi<sup>a</sup>, Renato Baciocchi<sup>b</sup>, Ennio Carnevale<sup>a</sup>, Andrea Corti<sup>c</sup>,  
Giulia Costa<sup>b</sup>, Tommaso Olivieri<sup>a</sup>, Alessandro Paradisi<sup>a</sup> and Daniela Zingaretti<sup>b</sup>*

<sup>a</sup>*Dipartimento di Energetica, Università degli Studi di Firenze - Firenze, Italy, lidia.lombardi@unifi.it*

<sup>b</sup>*Dipartimento di Ingegneria Civile – University of Roma Tor Vergata - Roma, Italy,  
baciocchi@ing.uniroma2.it*

<sup>c</sup>*Dipartimento di Ingegneria dell'Informazione, Università degli Studi di Siena - Siena, Italy,  
corti@dii.unisi.it*

## Abstract:

Biogas up-grading treatments aimed at producing biomethane to fuel vehicles or to inject into the gas grid, are applications that are gaining increasing interest throughout Europe. Several different commercial methods are available for separating carbon dioxide from biogas. In this work an innovative carbon dioxide removal method that, differently from the currently employed commercial techniques, allows also to capture and store the separated CO<sub>2</sub> is investigated. This process, named Alkali absorption with Regeneration (AwR), consists in a first step in which CO<sub>2</sub> is separated from the biogas by chemical absorption with an alkali aqueous solution followed by a second step in which the spent absorption solution is regenerated for reuse in the first step of the up-grading process and the captured CO<sub>2</sub> is stored in a solid and thermodynamically stable form. The latter process is carried out contacting the spent absorption solution, rich in carbonate and bicarbonate ions, with a waste material characterized by a high content of calcium hydroxide and leads to the precipitation of calcium carbonate and to the regeneration of the alkali hydroxide content of the solution. The proposed processes were first investigated by preliminary laboratory and simulation analysis. On the basis of the results of these tests, air pollution control (APC) residues from Waste-to-Energy plants were selected as the waste material to use for the regeneration step and a pilot-scale regeneration plant to place downstream of an existing absorption column installed at a landfill site was designed and built. In this paper the layout of the plants, their operating conditions and the results obtained by preliminary pilot-plant tests are reported. This study was conducted in the framework of the UPGAS-LOWCO<sub>2</sub> (LIFE08/ENV/IT/000429) Life+ project.

## Keywords:

Biogas up-grading, carbon dioxide capture, accelerated carbonation, air pollution control residues, alkali absorption.

## 1. Introduction

Among renewable energy sources, the biogas industry is growing in the EU, reaching about 8,3 Mtoe in 2009 with more than 6.000 biogas plants. The main source is agriculture (52%), then landfills (36%) and sewage plants (12%) [1].

Biogas produced in AD-plants – fed with a variety of bio-materials such as waste or energy crops - or landfill sites is primarily composed of methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) with smaller amounts of hydrogen sulphide (H<sub>2</sub>S) and ammonia (NH<sub>3</sub>). Trace amounts of hydrogen (H<sub>2</sub>), nitrogen (N<sub>2</sub>), saturated or halogenated carbohydrates and oxygen (O<sub>2</sub>) are also occasionally present in biogas. Usually, the gas is saturated with water vapour and may contain dust particles and organic silicon compounds (e.g.: siloxanes). The heating value of biogas is determined mainly by the methane content of the gas.

There are four basic ways of biogas utilization: heat and steam production, electricity production and/or co-generation, use as vehicle fuel and production of chemicals. Biogas utilisation strategies may vary depending on National factors such as taxation, subsidies, availability of gas and heat grids. Worldwide, biogas is mainly used for electricity production whereas in Sweden and in Switzerland a growing amount of biogas is used in the transport sector. The major driver defining

the way for biogas utilisation is the compensation of the energy, i.e. electricity or (upgraded) biogas. Most of the European countries have increased feed-in tariffs for electricity. However, using biogas as vehicle fuel or injecting the gas into the gas grid are applications that are gaining more and more interest. After proper upgrading - i.e. removal of carbon dioxide and tracecontaminants - biogas can be fed into the natural gas distribution grid. The deregulation of the natural gas market in Europe has opened the possibility to find new customers for upgraded biogas via the gas grid. There is no international technical standard for biogas injection but some countries have developed national standards and procedures for biogas injection into the natural gas grid, such as Sweden, Switzerland, Germany and France [2]. The standards have been set to avoid contamination of the gas grid or at end use. In the standards requirements on Wobbe index values and limits on the concentration of certain components such as sulphur, oxygen, dust and the water dew point, as well as a minimum methane concentration of 96% are reported. These demands are in most cases achievable applying existing upgrading processes. In some cases landfill gas can be difficult to upgrade to sufficient quality due to high nitrogen contents.

There are several different commercial methods for reducing the carbon dioxide content of biogas [3]. The most common are High Pressure Water Scrubbing (HPWS), amine scrubbing, and Pressure Swing Adsorption (PSA) on activated carbon. New technologies are, for example, cryogenic upgrading, molecular sieves and separation membranes. When removing carbon dioxide from the biogas stream small amounts of methane are also removed. It is important to keep these methane losses low for economical and environmental reasons and to maximize the gas energy content.

The commercial technologies available for biogas upgrading have the common feature of removing carbon dioxide from biogas without focusing on the fate of the separated carbon dioxide, which is usually re-emitted into the atmosphere during the system regeneration phase. For example, when CO<sub>2</sub> removal is achieved by means of absorption with a liquid solution, the load solution containing the absorbed CO<sub>2</sub> is regenerated emitting CO<sub>2</sub> to the atmosphere. The same happens during the regeneration of activated carbon when PSA is applied. In the cases in which absorption takes place using water without regeneration, CO<sub>2</sub> is discharged with the spent solution and released to the atmosphere. It should be anyhow pointed out that these CO<sub>2</sub> emissions are of biogenic origin and should hence not be accounted for as an effective contribution to greenhouse gas emissions.

As a matter of fact, the innovative aspect proposed in this work, developed in the framework of the European Life+ project UPgrading of landfill GAS for LOWering CO<sub>2</sub> emissions (UGAS-LOWCO<sub>2</sub>), is to develop a biogas upgrading process that can not only capture but also definitely store the separated CO<sub>2</sub> in a solid form [4]. The subtraction of carbon dioxide of biogenic origin from the atmosphere can contribute as a negative emission (sink) to the overall greenhouse gases balance. In addition, the proposed method may allow to achieve also other specific environmental benefits that will be highlighted in the following paragraphs.

## 2. Alkali absorption with regeneration process concept

This method – named Alkali absorption with Regeneration (AwR) - is based on CO<sub>2</sub> chemical absorption by means of an alkali aqueous solution followed by regeneration of the spent solution using Air Pollution Control (APC) residues.

CO<sub>2</sub> is first physically absorbed in the liquid solution and here it reacts with the alkaline compound producing carbonate (CO<sub>3</sub><sup>2-</sup>) and bicarbonate ions (HCO<sub>3</sub><sup>-</sup>) (chemical absorption) [5][6][7]. The alkaline reactants that can be used in the absorption process are potassium hydroxide (KOH) or sodium hydroxide (NaOH). The reactions that take place during the absorption step are the following:



or



The load solution – i.e. the solution containing the carbonate/bicarbonate ions – can be chemically regenerated by contacting it with calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) in solid form. In this step, poorly soluble calcium carbonate ( $\text{CaCO}_3$ ) precipitation takes place (carbonation reaction), thus the  $\text{CO}_2$  separated from the biogas can be permanently stored in a chemically inert and thermodynamically stable form, whereas  $\text{KOH}$  or  $\text{NaOH}$  is recovered for the first step of the upgrading process. The basic reactions that take place during the regeneration phase are the following:



or



Since the use of calcium hydroxide for such a process would not make sense from a carbon dioxide mitigation perspective, as it is manufactured by calcination of limestone releasing carbon dioxide into the atmosphere, in order to obtain a net reduction of carbon dioxide emissions, in this project industrial waste residues were chosen as alternative alkalinity sources. Several studies have in fact shown the feasibility of using different types of industrial residues, characterized by a high content of calcium hydroxide phases, such as bottom ash and air pollution control (APC) residues from waste incineration or steel slag, to sequester  $\text{CO}_2$ . Such a capture process is known as accelerated carbonation of natural minerals or industrial residues [8][9][10]. In case of using industrial residues, the accelerated carbonation allows also improving the leaching behaviour of the residues [11][12][13].

From preliminary investigations, APC residues, which are the product of incineration flue gas treatment with calcium-based products, were selected for the regeneration process owing to their chemical, physical and mineralogical composition [14]. Figure 1 shows the schematic layout of the AwR process.

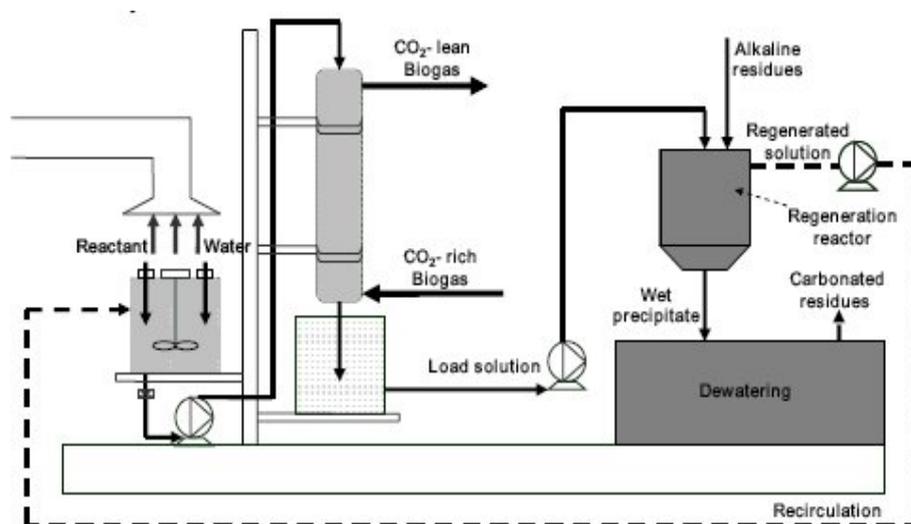


Fig. 1. Conceptual layout of the AwR process.

### 3. Results of the preliminary investigation phase

At a preliminary level the two steps of the AwR process were studied separately. In particular, the absorption step was first investigated by means of computer simulations and carrying out some absorption tests on the pilot plant – which was already available from a previous research

projectand is described in the following[]. The regeneration step was instead investigated by laboratory testing [][].

One of the main outcomesof the preliminary analysis concerned the definition of the maximum concentrations of the alkali compounds to use in the absorption process. In fact, for increasing initial concentrations of KOH or NaOH in the absorption solution and hence of K<sub>2</sub>CO<sub>3</sub> or Na<sub>2</sub>CO<sub>3</sub> in the solution resulting from the absorption treatment, the yield of the regeneration process showed to decrease owing to the combination of two negative effects: a decrease in KOH or NaOH regeneration efficiency and an increase in solution losses during the solid separation process after regeneration []. So it was concluded that a maximum of 4 eq/l of carbonate ions could be acceptable in the solution to be regenerated in order to allow for high regeneration yields during the second stage of the process[]. Hence, assuming a complete conversion of KOH or NaOH during the absorption step, the above mentioned condition would correspond to an absorption solution with a 18-20 % wt. concentration of KOH or NaOH. As a matter of fact, such concentration values are definitely lower than those used in previous pilot-scale absorption experiments aimed at treating 20 Nm<sup>3</sup>/h of landfill gas in which mass concentrations of over 50%wt. of KOH were adopted[] []. Under those conditions with a liquid flow rate of 60 l/h characterized by a KOH concentration of 48-53% wt, CO<sub>2</sub> removal efficiencies of 83-97% were achieved[] []. At least 97% CO<sub>2</sub> removal efficiency is required to obtain an acceptable upgraded biogas quality (CH<sub>4</sub>> 98%) starting from 50% in vol. CH<sub>4</sub> and 50% in vol. CO<sub>2</sub>. Consequently - keeping the same landfill gas and solution flow rates as those defined in the original design of the pilot plant - the achievable CO<sub>2</sub> removal efficiency obtained using alkali concentration values of 12-25% would be far lower than the target value, as is evident in Table 1, where the results obtained by both the simulations and the pilot plant tests are compared. In this case the simplified simulations of the absorption process were carried out using Aspen Plus[25]. The layout of the simulation was based on one absorption column, modeled using a radfrac unit, with two entering streams (biogas and absorbing solution) and two exiting streams (CH<sub>4</sub> enriched biogas and load solution).

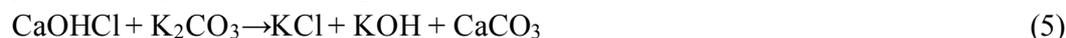
Then the simulation layout was modified, considering more than one absorption column, with the aim of evaluating the number of consecutive absorption stages, required to reach the biomethane quality in output, according to the German standards [2]. From these simulations, it was estimated that to reach the required removal efficiency, three absorption stages, with an entering solution flow rate of 60 l/h and KOH or NaOH concentrations of 12-14% wt. would be required to process 20 Nm<sup>3</sup>/h of landfill gas.

The existing pilot absorption column represents the first absorption stage of the three stage process. For this reason, the results of the pilot tests that will be reported in the following paragraphs are to be considered representative, for the moment, only of the first of the three absorption stages.

*Table 1. CO<sub>2</sub> removal efficiency obtained from simulations and pilot plant tests, considering 20 Nm<sup>3</sup>/h entering landfill gas with 50% CH<sub>4</sub> and 50% CO<sub>2</sub> in vol.; absorption solution flow rate 60 l/h.*

| Mass concentration | CO <sub>2</sub> removal efficiency % - Simulation | CO <sub>2</sub> removal efficiency % - Pilot plant test |
|--------------------|---|---|
| KOH                |   |   |
| 11,9               | 35,8  | 29,7±1,45   |
| 17,0               | 51,9  | 41,8±3,5  |
| 25,5               | 78,5  | 60,5±4,9  |
| NaOH               |   |   |
| 11,0               | 35,7  | 32,9±1,1  |
| 20,0               | 59,4  | 56,0±3,7  |

Concerning the regeneration step, specific laboratory experiments were preliminarily carried out to characterize the APC residues and to investigate their capability of regenerating the spent absorption solution rich in carbonate/bicarbonate ions. The amount of calcium phases available for the regeneration reaction was estimated as the difference between the total Ca and the Ca as CaCO<sub>3</sub> content of the ash, and consisted mainly of Ca(OH)<sub>2</sub> and CaClOH. The quite high chloride content (around 22% by weight) of the ash, mainly as calcium hydroxychloride proved to hinder the regeneration reaction. As a matter of fact, for every mole of CaOHCl, as shown in Eq. (5), only 1 mol of KOH can be produced, differently from calcium hydroxide that allows to regenerate 2 mol of potassium hydroxide (see Eq. (3)):



Since CaOHCl is more soluble than Ca(OH)<sub>2</sub>, it is more readily available for reacting with potassium carbonate than Ca(OH)<sub>2</sub>; hence an increase in the amount of ashes added to the solution produced a reduction of the efficiency of the regeneration reaction. To improve the alkali regeneration yield, a washing pretreatment of the APC residues was hence tested in order to remove most of the phases responsible of decreasing the total buffering capacity of the solution.

Furthermore, in order to improve the overall leaching behavior of the solid material so to comply with the disposal criteria for non hazardous waste landfilling, the effects of a second washing treatment applied to the residues after the regeneration step were investigated. In this case, due to the removal of part of the KOH contained in the ash, the pH of the residues decreased, but remained still well above values indicating solubility control by calcite. The mobility of most of the tested compounds (Zn, Pb, Sb, Cr and SO<sub>4</sub><sup>2-</sup>) appeared anyhow to decrease after this latter treatment, resulting lower than the limit values for non hazardous waste disposal.

The appropriate operating conditions able to maximize KOH or NaOH regeneration were defined, including pre- and post-washing of the residues, as reported in Table 2. The APC residues were added to the solution to be regenerated on the basis of their calcium content as Ca(OH)<sub>2</sub>, applying a 1,2 ratio with respect to the carbonate ions content of the solution. In this way it was possible to reach a 90% efficiency of the reaction in terms of KOH or NaOH regeneration. In addition, the solid product showed to be mainly made up by calcite and a CO<sub>2</sub> storage capacity of above 300 g/kg solid product was obtained. It should be noted however, that after the regeneration reaction the liquid solution must be separated from the solid product and that disregarding the type of method used a complete recovery of the solution is not possible and therefore a lower overall final recovery of KOH or NaOH should be anticipated.

Table 2. Operating conditions selected for the regeneration step.

| Pre-treatment                          |         |  |
|--|---------|--|
| Type                                   | Washing |  |
| L/S                                    | 5       | l/kg                                     |
| Time                                   | 15      | min                                      |
| Regeneration                           |         |  |
| Ca/CO <sub>3</sub> <sup>2-</sup> ratio | 1,2     | mol Ca/mol CO <sub>3</sub> <sup>2-</sup> |
| Temperature                            | 55      | °C                                       |
| Time                                   | 60      | min                                      |
| Post-treatment                         |         |  |
| Type                                   | Washing |  |
| L/S                                    | 5       | l/kg                                     |
| Time                                   | 15      | min                                      |

## 4. Pilot plant tests

In order to demonstrate the technical feasibility of the proposed process, an integrated pilot plant for CO<sub>2</sub> absorption and regeneration of the spent solution with CO<sub>2</sub> storage was designed and built. The pilot plant is located at the research laboratory of the University of Florence hosted at the landfill site managed by one of the partners of the UPGAS-LOWCO<sub>2</sub> project.

### 4.1. Absorption pilot plant

The absorption pilot plant (Figure 2 (i)) consists of a packed column where an aqueous solution of KOH or NaOH reacts with the carbon dioxide contained in the landfill gas, which is directly extracted from the landfill [1][2][3].

The alkali compound aqueous solution is fed to the column top, while the landfill gas is fed to the bottom of the column. The landfill gas is extracted from a collection station in the landfill and flows into the column by means of a side channel blower. The column filling consists of Sulzer laboratory DX packing, with a diameter of 80 mm and overall height of 990 cm, in stainless steel. The column was originally designed to process about 20-25 Nm<sup>3</sup>/h of landfill gas and 40-60 l/h of absorbing solution.

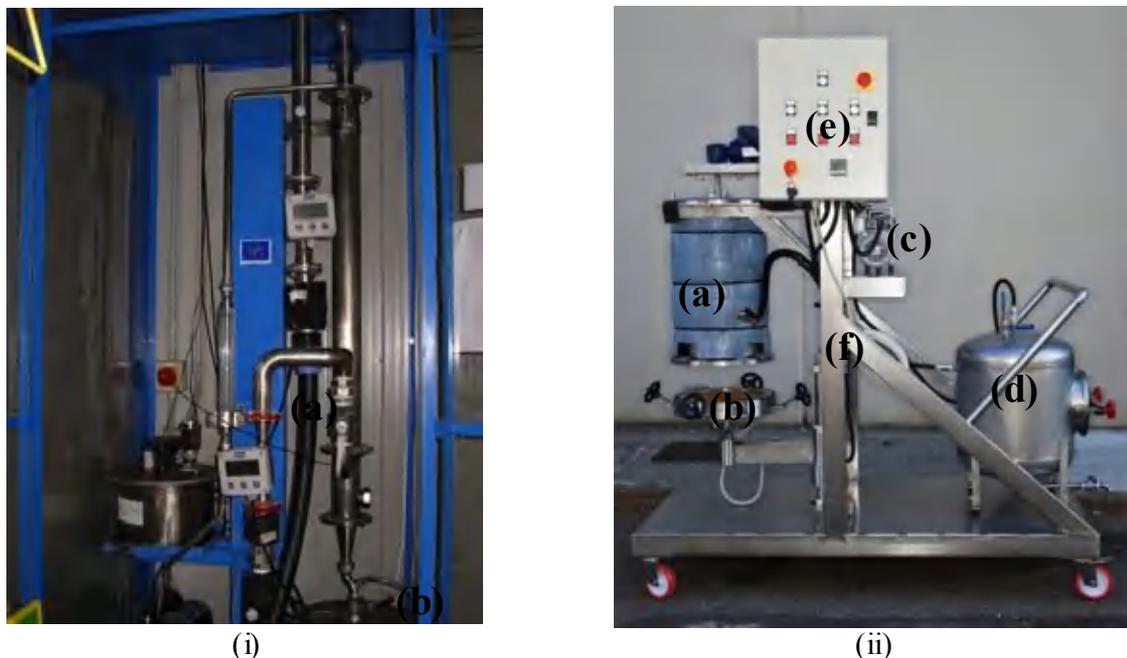


Fig. 2. Pictures of the pilot plant: i) absorption column; ii) regeneration reactor and its main components: a) regeneration reactor with mixer and heating jacket, b) bottom section of the reactor with filter tensioning system, c) vacuum filtration pump, d) liquid collection tank, e) control panel and f) steel frame.

#### 4.1.1. Monitoring equipment

Input and output gas flow rates are measured by means of a volumetric flow meter (Fluidwell – F110) able to work in the range from 2,5 to 35 m<sup>3</sup>/h. Input and output volumetric gas composition is measured too by means of a portable gas analyzer (input with Geotechnical Instruments - GA 94- and output with Geotechnical Instruments-GA2000) which measures CH<sub>4</sub> and CO<sub>2</sub> by infra-red absorption and O<sub>2</sub> by internal electro-chemical cells. Input and output differential pressure is measured by a diaphragm pressure transducer (Delta Ohm-HD 408T 100MBG) able to work in the range from -100 to +100 mbar relative to the atmospheric pressure. Atmospheric pressure is measured by means of a barometric pressure transducer (Delta Ohm HD 9908 BARO) able to work

in the range from 700 to 1100 mbar. Input and output gas temperature is measured by means of K-type thermocouples. Gas flow rate, pressure and temperature are measured and registered in a quasi-continuous manner (every 10 seconds). The measurement instruments are controlled by a programmable automation controller (Compact Field Point – National Instrument) composed by rugged I/O modules and intelligent communication interfaces. The composition is measured every 60 seconds and is directly registered by the gas analyzers.

## 4.2. Regeneration pilot plant

The regeneration pilot plant was designed and built with the aim of using the same reactor to perform in batch mode the pre-washing treatment of the residues, the regeneration/carbonation reaction and the post-washing treatment, as well as the liquid/solid separation step after each of the three operations. For the separation step it was decided to apply vacuum filtration, the same method adopted for the lab-scale experiments. As shown in Figure 2 (ii), the plant is made up by: the regeneration reactor, which includes a paddle type mixer and an external heating jacket; the filter medium, which is fitted on the bottom of the reactor in a custom made tensioning system; the vacuum filtration system, made up by the pump and filtered liquid collection tank; the control panel with switches for activating all equipment (mixer, heating system and vacuum pump) and a display for setting the heating temperature; a stainless steel support system on wheels on which all units and equipment are placed and manoeuvred.

The APC residues and the liquid medium (distilled water for the pre- and post-washing treatments and the spent solution exiting from the absorption step for the carbonation process) are mixed in the regeneration reactor tank. In the first step of pre-washing, distilled water and APC residues are mixed and kept in the tank for the required time; then filtration starts and at the end of this process a solid cake remains at the bottom of the reactor, while the filtered water is collected in the liquid collection tank and, from there, discharged. In the second step, the solution coming from the absorber is added to the cake previously formed at the bottom of the reactor. The slurry is mixed and after the required reaction time the filtration starts again. The liquid phase which accumulates in the collection tank is the regenerated solution, which is reused – after proper make up addition – in the absorption column. The carbonated cake remaining at the bottom of the reactor after the second filtration step is washed with distilled water and after a third filtration step, the final solid product is extracted from the bottom of the reactor while the filtration liquid is removed from the collection tank and disposed of.

## 4.3. AwR operation test: procedure and preliminary results

In this paragraph the procedure adopted and the results obtained from the preliminary operational tests carried out on the pilot-scale AwR plant are described. The operating conditions selected for these tests are reported in Table 3.

Table 3. Operating conditions selected for the preliminary AwR pilot plant tests.

|  |       |
|--|-------|
| Alkali compound  | KOH   |
| Absorbing solution flow rate [l/h]   | 60    |
| Absorption operation time [min]  | 10    |
| Volume of load solution to be regenerated <sup>1</sup> [l]                                     | 8     |
| Alkali mass concentration [%]  | 11,9% |
| Alkali normality [eq/l]  | 2,35  |
| Reactive Ca to CO <sub>3</sub> <sup>2-</sup> ratio [Ca mol /CO <sub>3</sub> <sup>2-</sup> mol] | 1,2   |

<sup>1</sup>The volume of liquid produced by the column during a 10 minutes absorption operation, discarding the solution generated during the first 2 minutes, in order to consider steady functioning.

Concerning the absorption reaction, after the preparation of the absorbing solution – obtained mixing the appropriate amount of KOH and water - the experiment was started. Temperature, pressure, flow rate and composition were continuously measured and recorded for the inflow and outflow gas. The average flow rate of entering landfill gas was 18,03 Nm<sup>3</sup>/h, while the average exiting flow was 15,07 Nm<sup>3</sup>/h. Entering average concentration in vol. of CH<sub>4</sub> was 50,66% while CO<sub>2</sub> was 37,48% in vol. In the exiting gas the average CH<sub>4</sub> concentration was 60,61%, while the average CO<sub>2</sub> content was 28,76%. The calculated CO<sub>2</sub> removal efficiency was about 35,86%.

The spent solution was collected at the outlet of the column in a bucket after the first two minutes of the reaction. After ten minutes the absorption experiment was stopped.

The spent solution sample was titrated, showing a complete conversion of KOH to K<sub>2</sub>CO<sub>3</sub> with a total concentration of 2,35 eq./l (Figure 3 (ii)).

Before the testing phase, the properties of the APC residues to use for the test were assessed by laboratory analysis. Basically this characterisation was necessary to determine the amount of APC residues to be used for the regeneration experiments. Specifically the total Ca(OH)<sub>2</sub> content of the washed ash was estimated as 55,5% wt, while the weight loss of the material measured upon the washing pre-treatment (mainly due to NaCl and CaClOH dissolution) was of 43,2 % by weight.

Based on the above mentioned characteristics and the conditions reported in Table 3, the required amount of washed APC residues for the regeneration test was calculated to be equal to 1,5 kg; hence considering the weight loss of the material consequent to the washing pre-treatment, it was estimated that 2,64 kg of untreated APC ash would be necessary for the complete regeneration test. Based on this, the amount of distilled water required for the washing pre-treatment with a L/S ratio of 5 l/kg was calculated (13,23 l).

Prior to the beginning of the experiment the reactor was washed and dried and the filtering material was substituted. The valve at the bottom of the reactor was closed and the required amounts of APC residues and of distilled water were weighed and fed into the reactor.

After the introduction of the residues and distilled water into the reactor, the mixer was activated. The mixing was maintained for 15 minutes at ambient temperature (internal temperature 24,3 °C), then the vacuum pump was turned on and connected to the liquid collection tank and the valve at the bottom of the reactor was opened. During the liquid separation phase the mixing of the solution was continued in order to help the filtration process. After about 100 minutes the mixer was stopped since the liquid separation appeared to be complete. The filtered washing solution was collected from the tank, which was then cleaned and dried and samples of the washing solution were taken.

The absorption spent solution (8 l) was then poured into the reactor and mixed with the washed APC residues cake. After 1 hour of reaction time at 55°C, the vacuum pump was turned on and connected to the liquid collection tank and the valve at the bottom of the reactor was opened. Also during this liquid separation phase the mixing of the solution was continued in order to help the filtration process. This separation step proved faster than the previous one and after 45 minutes the filtration appeared to be complete (Figure 3 (i)). Samples of the solid product of the regeneration process were taken and right after that the final washing treatment was performed. At the same time the regenerated solution was emptied from the collection tank and a sample of it was directly titrated. Around 1 eq./l of KOH were regenerated out of a total buffering capacity of 1,6<sup>2</sup> eq/l, hence the regeneration yield (ability of the reaction to obtain again the initial compound) was about 62,5%. This value was quite lower than the one measured in the lab scale tests (78-92%)<sup>2</sup>. Through a preliminary mass balance it is possible to estimate the overall regeneration efficiency (mass of recovered KOH with respect to the initial amount of KOH entering in the absorption column) which resulted of about 41%. This overall regeneration efficiency is quite low and needs to be increased in

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<sup>2</sup> Due to dilution with the humidity of the washed cake, the total buffering capacity of the regenerated solution was lower than the spent solution one (1,6 vs. 2,35 eq./l) as shown in Figure 3 (ii).

order to increase the competitiveness of this method compared to other upgrading processes from an environmental and economical point of view[11].

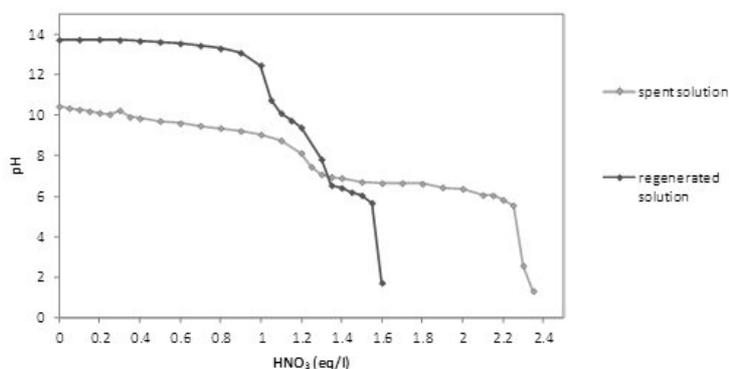
The amount of distilled water necessary for the final washing treatment was estimated assuming that the product of the regeneration phase had a humidity of 50% wt. and a weight increase of 40% compared to the washed residues characterized by a density of 0,99 kg/l (data determined in the lab-scale tests). On the basis of these assumptions, the amount of water required to set the L/S ratio to 5 l/kg was calculated to be 8,42 kg. The distilled water was poured into the reactor and the mixer was switched on. After 15 minutes the vacuum pump was turned on and connected to the liquid collection tank and the valve at the bottom of the reactor was opened. During the liquid separation phase the mixing of the solution was continued in order to help the filtration process. The liquid/solid separation appeared to be complete after 45 minutes. The bottom of the reactor was then opened and the solid cake was collected: roughly 2,64 kg of solid humid product were recovered.

In conclusion, the outcome of this preliminary pilot-scale test was considered satisfactory, since no great operating difficulties were encountered and all three steps of the regeneration process were carried out. The liquid/solid separation step after the first washing treatment proved to be as expected the most critical one in terms of time; in addition some ash particles were found in the liquid collection tank, hence it was decided to check if other types of filtering materials could be used to optimize this process. As for the outcome of the regeneration process, the lower regeneration yield was ascribed to the less constant temperature and especially to poor mixing at the bottom of the tank that did not allow the complete reaction of  $\text{Ca}(\text{OH})_2$ . To improve this aspect it was decided to try to verify if the shape of the mixer could be modified.

Finally, the amount of  $\text{CO}_2$  stored per unit of mass of solid product after the regeneration process was of about 220 g/kg solid material, and showed to increase after the final washing treatment owing to the dissolution of residual soluble phases.



(i)



(ii)

Fig. 3. Picture of the solid cake obtained at the end of the filtration process after the regeneration/carbonation reaction (i); titration curves of the spent and regenerated solution (ii).

## 5. Conclusions

An innovative method for removing carbon dioxide from landfill gas – with the final aim of upgrading its quality to that of natural gas– was proposed and investigated. With respect to commercial methods for biogas upgrading, the proposed process presents two additional environmental benefits: i) the carbon dioxide separated from the methane is permanently stored by accelerated carbonation of an alkaline waste material (air pollution control residues from waste incineration flue gas treatment), ii) the series of treatments applied during the regeneration process has shown to improve the leaching behaviour of the residues. This process, named Alkali absorption

with Regeneration (AwR), consists in a first step in which CO<sub>2</sub> is separated from the biogas by chemical absorption with an alkali aqueous solution followed by a second step in which the spent absorption solution is regenerated for reuse in the first step of the upgrading process and the captured CO<sub>2</sub> is stored in a solid and thermodynamically stable form. The processes were investigated first by simulations and laboratory testing and then in order to verify the feasibility of the method at a larger scale, a pilot-scale AwR plant for treating 20 Nm<sup>3</sup>/h of biogas was designed, built and installed at a landfill site. From the results of preliminary tests, the regeneration yield achieved at pilot scale appeared to be lower than the yields obtained in the laboratory, so the main efforts for the next testing phase will focus on the optimization of plant operation in order to increase the overall efficiency of KOH or NaOH recovery and possibly allow to improve the competitiveness of this process compared to traditional commercial biogas upgrading methods.

## Acknowledgments

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