Upgrading of landfill gas with household waste slag

SEYEDHANI SADATGOL

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Seyedhani Sadatgol

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KTH Chemical Engineering and Technology
SE-100 44 STOCKHOLM
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Abstract
Modern landfills produce landfill gas, LFG, on a smaller scale and with limited content of degradable organic materials in the waste. The waste deposit in the Sofielund landfill began in 2005 and the final coverage is not yet commenced. The landfill waste must contain up to 10% decomposable organic materials at most. In a previous experiment on Sofielund landfill in summer 2011, the measurements from four sample wells showed the landfill gas consisted of up to 45% Methane and about 17000 ppm of Hydrogen sulfide, and the rest was only carbon dioxide. During the earlier experiment in 2011 and during 2012 the smell of H\textsubscript{2}S got offensive periodically and apart from that, concentrations above 1000 ppm are toxic. Previous research, Bottom ash for biogas upgrading, BABIU, shows that bottom ash from municipal solid waste incinerator (MSWI) can effectively reduce CO\textsubscript{2} and H\textsubscript{2}S contents of landfill gas. Bottom ash from MSWI can be utilized in upgrading landfill gas and reduce odor problems of landfills with high H\textsubscript{2}S production. In this study, an area of 15m x 12m was covered with weathered slag from bottom ash with thickness of about 30cm, to examine how this layer can reduce the concentrations of H\textsubscript{2}S and CO\textsubscript{2}. Gas samples were taken from depths of 10cm and 15cm below the surface of bottom ash. There were also samples taken from around the slag-covered area. The surface was laid out 5 days before the first measurement was performed. The experiment was carried out for 20 days, 5, 7, 11, 13, 18 and 20 days after establishment of the surface with bottom ash. The intensity of emissions in different parts of the landfill varied from time to time, due to compacting and changing the permeability of the surface, and it shows that LFG flow in the Sofielund is near the lowest limit of it. Considering the results from the tests in 2011 in deep wells, the recent measurements done in this study showed low contents of LFGs. The highest contents of LFGs in the measurements belong to a pipe, which was found in the waste area of the landfill. Those highest contents of LFG were 15.1% methane, 12.1% carbon dioxide, 0.4% oxygen and the hydrogen sulfide did not exceed 2 ppm. This shows that in deeper depths concentrations of LFG is higher than that of the surface and 10cm below the surface. In the slag covered area CO\textsubscript{2} content increased day by day from the first day of the measurement to the last day due to carbonation of the slag and its role in CO\textsubscript{2} sequestration. According to the recent measurement, it can be suggested to cover the landfill with a layer of slag as a construction material, to minimize the LFG emissions and the bad smell from H\textsubscript{2}S. Therefore it can eliminate direct emissions of LFG to the atmosphere by diffusion through the slag layer. This diffusion allows adsorption of CO\textsubscript{2} and oxidation of H\textsubscript{2}S.
ABBREVIATION LIST

<table>
<thead>
<tr>
<th>ABBR</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>BABIU</td>
<td>Bottom ash for biogas upgrading</td>
</tr>
<tr>
<td>Ca</td>
<td>Calcium</td>
</tr>
<tr>
<td>CaO</td>
<td>Calcium oxide</td>
</tr>
<tr>
<td>Cd</td>
<td>Cadmium</td>
</tr>
<tr>
<td>CH₄</td>
<td>Methane</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>Cl₂</td>
<td>Chlorine gas</td>
</tr>
<tr>
<td>ClO⁻</td>
<td>Hypochlorite</td>
</tr>
<tr>
<td>Cr</td>
<td>Chromium</td>
</tr>
<tr>
<td>DM</td>
<td>Dry matter</td>
</tr>
<tr>
<td>DO</td>
<td>Dissolved oxygen</td>
</tr>
<tr>
<td>H₂S</td>
<td>Hydrogen sulfide</td>
</tr>
<tr>
<td>H₂O</td>
<td>Water</td>
</tr>
<tr>
<td>HPWS</td>
<td>High pressure water scrubbing</td>
</tr>
<tr>
<td>KMnO₄⁻</td>
<td>Potassium permanganate</td>
</tr>
<tr>
<td>LFG</td>
<td>Landfill gas</td>
</tr>
<tr>
<td>MSWI</td>
<td>Municipal solid waste incinerator</td>
</tr>
<tr>
<td>N₂</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>Nitrate</td>
</tr>
<tr>
<td>N₂O</td>
<td>Nitrous oxides</td>
</tr>
<tr>
<td>O₂</td>
<td>Oxygen</td>
</tr>
<tr>
<td>ORP</td>
<td>Redox potential</td>
</tr>
<tr>
<td>Pb</td>
<td>Lead</td>
</tr>
<tr>
<td>Ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>PSA</td>
<td>Pressure swing adsorption</td>
</tr>
<tr>
<td>SRV</td>
<td>SRV återvinning AB</td>
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INTRODUCTION

1.1. **Background**

Landfilling is an important disposal method of municipal solid waste. In Sweden landfilled wastes contains up to 10% decomposable organic materials. In this section the construction and design of a landfill will be described, i.e., the bottom layer and the walls, what materials is used in them, and the main focus will be on Sofielund landfill. In Landfills gaseous emissions are formed such as methane (CH$_4$) carbon dioxide (CO$_2$) and hydrogen sulfide (H$_2$S). Hydrogen sulfide has been recognized as main contributor to odors at landfills. In the landfill gas at Sofielund high concentrations of H$_2$S were detected in wells, during the earlier experiments in 2011 and during 2012 the smell of H$_2$S got offensive periodically. Apart from bad smell, concentrations above 1000 ppm are toxic.

SRV wants to estimate H$_2$S content of landfill gas (LFG) emissions in Sofielund landfill and the concentrations, which causes bad smell. They are also interested to know if the slag from bottom ash can eliminate CO$_2$ and upgrade CH$_4$ in the landfill gas.

![Figure 1: Sofielund landfill](image-url)
1.2. **Purpose and scope**

The purpose of this project is to investigate how efficiently slag from incineration from household waste can reduce H$_2$S and upgrade CH$_4$ by capturing CO$_2$ from landfill gas which is produced at Sofielund, SRV Återvinning.

1.3. **Methods**

*Literature study*

In this section information is provided on:

- Landfill design
- Landfill gas (LFG)
- Formation of CH$_4$ and H$_2$S
- Methane upgrading
- Carbonation and slag

Using previously released articles.

*Description of the site*

Dimensions of the slag covered area and locations of sampling spots

*Measurements of landfill gas on Sofielund’s landfill*

Different methods will be used to collect landfill gas for analyses (the measurements on the surface, digging deep wells and digging a trench with slag in it.)

*Results are presented*

Evaluation of technical and environmental, potentials and discuss the possibility to do it.
LITERATURE STUDY

1.4. Landfill and landfill gas

General

Today landfilling is an important disposal method of municipal solid waste. Landfilling of sorted burnable waste has been made illegal in Sweden since 2002. Also there has been made a ban on landfilling organic matter since 2005 with the goal of improving resource preservation and decreasing environmental impacts that landfill wastes must contain up to 10% decomposable organic materials at most. The movement today in Sweden is towards more separation of waste materials in the landfills. Policies in European countries are the same as described. [1][2]

Waste

Degrading of organic matter present in household wastes, construction wastes and sludges, are the major generic wastes entering municipal landfills which cause the gas emissions. The highest amounts of landfill gas are expected to be generated by the household wastes. [3] A landfill is not a homogeneous mixture of waste, thus methane formation in some parts of the landfill is higher than the other parts. [4] Compacting the wastes is essential in landfills; in order to be able to commute on top of the landfill waste, make an efficient use of landfill volume, reducing the need for cover material, reducing risk of fire and spreading of material by wind, and also reducing settlement problems after putting down the waste. Since the compaction can only be effective for layers of about 50-70 cm, for more effective compaction, the waste layers should be thin. [14]

Design

Waste materials existing in landfills emit contaminated gas and leachate. Landfills must be built hydro geologically isolated from their surroundings. It should be sited on impermeable bottom liner which requirements depends on type of the waste; If it has a high contaminating potential, the bottom barrier must be built with a low permeability. There is a drainage layer with pipes, constructed at the bottom of the landfill above the bottom liner, which transport the leachate out of the landfill and conduct it to the leachate collecting trenches around the landfill. There are also barrier constructions as top covers, bottom and side barriers, to make the landfill hydro geologically isolated from its surroundings. In a recharge area the leachate can go down and reach the groundwater, therefore the bottom liner will reduce the leachate amount going down to the ground. In discharge area the bottom liner makes a barrier and will not let the groundwater enter
the landfill; the bottom liner also collect the produced leachate, which is transported out of the landfill by a drainage layer.
Landfills are generally building up in 2-3 meters layers. The best form is to complete and cover each layer in a working day, but it is not always achieved. Landfill is covered with a low permeability soil layer when it is finished, and plants will be put on this cover. This layer helps the landfill to get adapted to its environment and control the amount of water going into the waste. Landfills remain active often about 25-30 years before they are closed, since usually they can produce methane and carbon dioxide up to 30 years. [14]

**Landfill gas**

LFG is the gas produced at anaerobic condition in landfills, containing the combination of emissions from the degradation of organic wastes, gases emitted from landfilled materials and atmospheric air, which enters the landfill. It was first used as a fuel in 1970’s and since then there has been a development of technologies for its collection and use. [14]

The main gaseous emissions that are formed in landfills are methane (from 40% to 60%), carbon dioxide (from 35% to 50%) and hydrogen sulphide (from 50 to 200 ppm). Other gas constituents in landfills are nitrogen (from 0% to 20%) and oxygen (from 0% to 1%) [5]

Landfill gas emissions have different scales of impacts. Most of the impacts belong to the local scale, in which it can contribute in damaging to vegetation and health of inhabitants; also it causes dust, odours, fire and explosion in site. At regional scale it can be offensive by its smell, and finally at global scale it has bad influence on greenhouse effect. These impacts are briefly introduced in the following picture:

![Figure 2: Different impact scales of LFG emissions](image-url)

[6]
In general, 0.001 - 0.5 m³ LFG is produced per one square meter landfill. [6]

Modern landfills have been reported to have unexpectedly high contents of hydrogen sulphide. [4]

**Production of landfill gas**

Bacterial decomposition of landfill waste is in four phases. (See Figure 3)

It might take 20 to 30 years for a landfill to be closed; therefore old wastes in one area of the landfill can be in a different phase from new wastes in other parts of the landfill.

First phase is aerobic decomposition; in this phase the main by product of the process is carbon dioxide. Nitrogen content is extremely high in this phase but decreases when the landfill grows old.

The aerobic phase will continue until the oxygen content is used up, which can take days or months depending on the amount of oxygen that was present on disposal day of the waste.

The second phase is an anaerobic process in which compounds that were produced during the aerobic phase will convert into acetic, lactic, and formic acids and alcohols like ethanol and methanol. In this phase landfill becomes greatly acidic. Acids combine with the moisture and this will cause certain nutrients dissolve and make nitrogen and phosphorus. The byproducts are CO₂ and H₂. It is possible for the landfill to return to the first phase if somehow again oxygen enters into the landfill.

The third phase is still an anaerobic process in which anaerobic bacteria use the organic acids from the second phase and form acetate which is an organic acid. At this stage landfill becomes neutral the bacteria which produce methane, establish themselves in this environment.

In the last phase decomposition is when production rates and composition of LFG stay moderately constant, and this production remains at a steady rate for almost 20 years. [7]
1.5. **Forming of CH₄ and H₂S in landfills**

*Methane*

Anaerobic decomposition of organic matter in landfills includes several steps such as hydrolysis, acidogenesis and methanogenesis. In the absence of oxygen, these three processes convert organic carbon into methane and carbon dioxide. During anaerobic degradation, the fermentative bacteria hydrolyzes the organic polymers to form monomers, these monomers are fermented to hydrogen, carbon dioxide, acetate, alcohols and longer chain organic acids. The organic acids use hydrogen and 1- and 2-carbon compounds to produce methane, carbon dioxide and water. Since methanogens only use 1- and 2-carbon compounds, acetate is an important intermediate. It takes a few months for methane generation to be started. The whole processes happen in an anaerobic condition, since oxygen will poison methanogens. [14]

Organic acids produced in acidogenic step, are converted to methane and carbon dioxide.

\[(CH_2O) + 1/2 CO_2 \rightarrow CO_2 + 1/2 CH_4\]

*Hydrogen sulfide*

Hydrogen sulfide has been recognized as main contributor to odors at landfills, it is colorless and heavier than the air. Apart from bad smell, concentrations above 1000 ppm are toxic. The landfill areas are generally vast H₂S emissions doesn’t belong to a specific spot and usually the
concentration of H$_2$S is low comparing to the flow rate of LFG, therefore this can be one of the difficulties of moderating H$_2$S emissions from a landfill. [1]

Hydrogen sulfide smells like rotten egg and its odor threshold varies in different reports. The threshold has been reported at concentrations of 0.0005ppm to 0.01 ppm and also at 0.01 ppm to 0.3 ppm. It can be found offensive when it reaches 0.05 ppm. At concentrations of 150 ppm it can paralyze the olfactory nerve so it is no longer detectable by its smell at this concentration. [6]

Hydrogen sulfide’s solubility in water in different temperatures has been reported as 5.3 g/L at 10 °C; 4.1 g/L at 20 °C; 3.2 g/L at 30 °C, which shows that solubility increases with increasing the temperature. [6]

During anaerobic conditions in landfills, decomposition of organic constituents which contain sulfur and bacterial reduction of sulfate will result in producing of hydrogen sulfide. Production of H$_2$S is in the absence of electron acceptors like H$_2$O$_2$, Cl$_2$, dissolved oxygen (DO), NO$_3^-$, ClO$^-$, Fe$^{3+}$ and KMnO$_4$. Generation of hydrogen sulphide is because of low redox potential (ORP). The optimal range of ORP for hydrogen sulphide production is between -100 to -250 mV. By increasing the redox potential with addition of electron acceptor compounds, which are thermodynamically favourable, the production of H$_2$S can be decreased. Oxidants such as O$_2$, nitrate and molybdates are of use in decreasing H$_2$S generation during waste water treatment, but adding molybdates and nitrates is an expensive method. Alternatively O$_2$ supply is an essential part in the process of aeration composting. Hence in decreasing H$_2$S production, optimizing aeration factors can be a better option. [8]

Experiments had been done on samples of red clay, compost, waste wire and sand in Liu et al.’s study to find out the adsorption properties of each to hydrogen sulphide. The maximum adsorption of selected waste materials to hydrogen sulphide in order was red clay, waste wire, compost and sand. In which the fastest rate of adsorption belonged to waste wire and the slowest was sand. The adsorption rate of compost is higher than red clay. In conclusion, due to its fast adsorption rate, low price and high adsorption capacity, waste wire should be the primary selection according to the authors. By increasing the adsorption surface of waste wire the adsorption effect will improve to a great extent. Because of relative high adsorption quantity and fast rate of adsorption, the second choice was compost. There was region limitation in use of red clay; therefore it can merely be used in a number of areas. Finally sand was the last choice in the study. [9]

### 1.6. CH$_4$ upgrading and carbonization och CO$_2$

Slags are alkaline and rich in hydroxides and oxides of calcium and are suitable for sequestration of CO$_2$. They are produced in industrial areas with low costs. The slag carbonation has a significant effect on CO$_2$ sequestration and also improves the environmental quality. [10]

Natural weathering is a way of stabilizing the slag through changing its mineralogical characteristics. Carbonation is a main step in weathering process. The main carbonation reaction is like the equation described in equ.1: [11]
In a study that Huijgen et al did, the purpose with carbonation of calcium rich slag was to make it as a CO$_2$ storing/sequestering agent. In carbonization of steel slag the reactor temperature, CO$_2$ partial pressure and reaction time will affect the speed of carbonation but particle size has the most important role in the extent of carbonation. [10]

Samples of MSWI bottom ash were investigated regarding carbonation efficiency, in order to do that they were sieved in size of 4 mm and less, in a study that Rendek et al. did. During carbonation of the samples, using pure CO$_2$, one of the important parameters of the reaction is moisture content of the ash and the most excellent option is ash humidity of 15%. If the humidity is above 15% there will be a decrease in trapped CO$_2$ volume. In their study there was also an experiment with sieved particles 4 mm and less and unsieved with unknown particle size. Both samples were under the same conditions including equal moisture content. After the complete carbonation, the samples ≤4 mm sieved absorbed 24 L/kg dry matter (DM) and the unsieved sample absorbs 12.5 L/kg DM. The sieved sample absorbs almost twice as much as the unsieved sample. There was an increase in proportion of Ca of a sieved sample of bottom ash, which improves the carbonation reaction. In accelerated carbonation there was found to have a positive effect on leaching of Cr, Pb, and Cd, which are the main heavy metals, existing in bottom ash. When the carbonation was carried out completely, the leaching of these elements decreased. According to the tests, the partial pressure of CO$_2$ (between 2 – 17 bars), can only affect on the kinetic of the reaction and not on the volume of trapped CO$_2$, if the partial pressure is higher the reaction takes place faster. [11]

Smaller particles of bottom ash contain higher contents of heavy metals than bigger ones. Small particles leach more than bigger ones, since they have bigger specific surface area. The release of heavy metals is one of the important causes of restrictions to the reuse of MSW bottom ash outside landfill areas e.g. roads. Natural weathering of a pile of slag for a period of almost 50 days can

$$Ca(OH)2(aq) + CO2 \rightarrow CaCO3(s) + H2O(l) \quad \text{Equ.1}$$
reduce the release of heavy metals for all size fractions. Therefore the bottom ash fractions which are even smaller than 4 mm can be reused, depending on the technical properties. [12]

1.7. BABIU

P.Mostbauer et al did several experiments on bottom ash from MSWI to find out about its adsorbing capacity for CO$_2$ and H$_2$S removal from landfill gas. The experiments were done on seven bottom ash samples with approximate weight of 250 kg. The sampling took place from April 2006 to January 2007, at two incineration site (S, F), and the waste was residual household waste and commercial waste from Vienna, Austria. The sample from site F includes more metal particles, because the ferrous metal separation from dry, hot bottom ash was done after quenching (fast cooling in a water bath), but on site it was separated before quenching. After sampling the samples were 20 mm sieved and particle size $\leq$ 20 mm were used. [13]

P.Mostbauer et al did several experiments on bottom ash from MSWI to find out about its adsorbing capacity for CO$_2$ and H$_2$S removal from landfill gas, in order to upgrade LFG and sequestration of CO$_2$. The common LFG upgrading technologies, which are applied today (High Pressure Water Scrubbing (HPWS), pressure swing adsorption (PSA) and chemical scrubbing), cause CH4 losses, CO2 emissions and they also consume significant electricity. Therefore P.Mostbauer et al did some tests at laboratory scale in 2007, 2008 and 2011 on the name of BABIU (Bottom Ash for Biogas Upgrading) process. In this process CO$_2$ and H$_2$S are removed by using moisturized MSW bottom ash, which was quenched in water. BABIU has some basic steps:

- Removal of coarse metals and storage and natural weathering of quenched bottom ash (or bottom ash fractions) for one to three weeks.
- Filling one or several static containers (“carbonation tanks”) with the weathered bottom ash. This tank is a gas-tight polyethylene reactor.
- Flushing with N2 to remove air/O2
- Reaction of biogas or landfill gas with the bottom ash, whereupon H2S and CO2 are fixed, CaCO3 is formed and CH4 is enriched in the product gas.
- Second flushing with N2 to increase CH4 recovery and reduce CH4 losses.
- Removal of the treated bottom ash (with lower leachability) from the carbonation tank.

The tests on laboratory scale were until December of 2011 and in each test, approximately 75 to 90 kg bottom ashes from Austria, Germany and Italy were used. In December of 2011 the experiment was done at a scale of 1 ton bottom ash. [15]

Reactions in bottom ash during weathering and carbonation

Ca-containing compounds in waste will form CaO by calcinations during combustion. Quenching of bottom ash results in a hydration reaction which forms Ca(OH)$_2$. [15]

\[
CaO + H_2O \rightarrow Ca(OH)_2, \Delta H = -65 \text{ kJ/mol} \quad \text{(Slaking)} [15]
\]
Afterwards this portlandite dissolves partially in water:

$$\text{Ca(OH)}_2 \rightarrow \text{Ca} + 2 \text{ + 2 OH} \quad [15]$$

The hydrated bottom ash takes up CO2 slowly during natural weathering. The carbonation reaction can be accelerated by adding CO2, LFG, biogas or other gases which contain CO2. Carbonation consists of two steps: [15]

1) CO2 dissolution: $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$

1) Neutralization: $\text{H}_2\text{CO}_3 + \text{Ca}^{2+} + 2 \text{OH}^- \rightarrow \text{CaCO}_3 + 2 \text{H}_2\text{O}$

A layer of Ca(OH)$_2$ was formed on the surface of CaO during slaking of lime. Impurities in lime or a layer of CaCO$_3$ which is formed by carbonation reaction, decline reaction rate of CaO hydration by creating a physical surface sealing effect. It is not known if the same effect happens in hydration of bottom ash too. Lime contains about 100% CaO but bottom ash contains about 20-40% CaO. It is recommended to store the moistened bottom ash in large piles for one to three weeks, since the laboratory results showed that the stored bottom ash uptakes up to 15% more CO2 than fresh bottom ash, and there is also a probability that even after the complete carbonation of fresh bottom ash, CaO may be present in the core of some particles. This storage will result in complete hydration of CaO and during LFG upgrading; it prevents the extreme heat and hydrogen production in carbonation tanks. Bottom ash which Aluminium was not separate d with eddy current technique can produce H2 more than standard amount. It should be considered that the enthalpy of oxidation reaction of Al is rather large and it will lead to producing extreme heat which makes the temperatures go beyond 70°C inside carbonation tanks. By this means there would be more water evaporation which has to be taken away from the upgraded gas. [15]

Alkaline oxidation of Al: $\text{Al} + 2 \text{H}_2\text{O} \rightarrow \text{AlOOH} + 1.5 \text{H}_2$

In case of excess of OH$^-$: $\text{Al} + \text{OH}^- + 3 \text{H}_2\text{O} \rightarrow \text{Al}[\text{OH}]_3^- + 1.5 \text{H}_2\text{O}, \quad \Delta H = -415.6 \text{kJ/mol}$

In the experiment the bottom ash was piled up at room temperature and different sieved sizes shown in the following table. Approximately 75 to 90 kg humid ash were used for each test. The bottom ash particles were compacted in 3 layers in the carbonation tank, then flushed with N2 and next letting synthetic gas in immediately afterwards, to react with the bottom ash. [15]

### Results from the laboratory scale experiments – bottom ash from Italy

The behavior and results from bottom ashes were similar during BABIU process. The process performance was quite good with the input flow rate of 2 to 3 m$^3$ synthetic LFG per hour and ton of bottom ash. The produced gas contained up to 99% of methane. It was estimated that in industrial scale there would be a heat loss of 21°C to 26°C. [15]
Table 1: Experimental conditions of laboratory scale experiments [15]

<table>
<thead>
<tr>
<th>Test run identifier</th>
<th>Initial temperature (°C)</th>
<th>Input gas composition</th>
<th>Specific flow rate (m³/h)</th>
<th>H₂S removal efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>#4 LLFG tests</td>
<td>depending on storage conditions: 23 to 40°C</td>
<td>synthetic LLFG a) 61.8 to 65.6 Vol% CH₄, rest CO₂</td>
<td>0.38 to 1.01</td>
<td>~ 2.3 &gt; 98 %</td>
</tr>
<tr>
<td>#4 LFG tests</td>
<td></td>
<td>synthetic LLFG a) CO₂ + N₂ + H₂S</td>
<td>1.47 / 1.60</td>
<td>~ 3.1 &gt; 98 %</td>
</tr>
<tr>
<td>#5 H₂S run 1,2,3,4</td>
<td></td>
<td>CO₂ + N₂ + H₂S</td>
<td>0.54 to 1.13</td>
<td>3.7 98.5 %</td>
</tr>
<tr>
<td>UPGAS Lab 1</td>
<td></td>
<td>CO₂ + N₂ + H₂S</td>
<td>2.5 to 7.8</td>
<td>5.5 98.4 %</td>
</tr>
<tr>
<td>UPGAS Lab 2</td>
<td></td>
<td></td>
<td>3.09 during the first two hours, then: 1.97</td>
<td>9.2 98.5 %</td>
</tr>
<tr>
<td>UPGAS Lab 3</td>
<td></td>
<td></td>
<td>1.97</td>
<td>2.4</td>
</tr>
</tbody>
</table>

a) simulated lean landfill gas = mixture of CH₄ (mostly 24.8 Vol% CH₄, ranging from 16.9% to 46.4%) and CO₂
b) input gas volume at room temperature and ambient pressure (~ 994 mbar) per hour and per ton of humid bottom ash
c) industrial scale separation of metals in the waste treatment installations
d) particles > 100 mm were separated by hand. The mass of large particles amounts to approx. 6.8% (mass%) of the total sample flow

Figure 5: Example synthetic LFG flow of 5.5 m³/h [15]

Figure 6: H₂S removal efficiency vs. input gas flow [15]

Table 1: Experimental conditions of laboratory scale experiments [15]
In BABIU process at flow rate of 9.2 Nm³/h only 0.7 m³ of ash was needed for H₂S removal in 80 m³ of landfill gas.

The main chemical reactions of bottom ash taking place in BABIU process are as following:

1) \( \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \rightarrow \text{Ca}^{2+} + 2 \text{OH}^- \) (lime hydration)

Bottom ash is alkaline with pH of more than 12, and this hydration reaction is exothermic.

2) \( \text{Al} + 3 \text{H}_2\text{O} + \text{OH}^- \rightarrow \text{3/2 H}_2(\text{g}) + \left[\text{Al(OH)}_4\right]^- \)

In this reaction hydrogen is formed and this is also a very exothermal reaction.

3) \( \text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \) (carbonation)

In this reaction the pH decreases and is also exothermic.

Ageing of bottom ash prevents excessive heat formation in the processes.

**1.8. Previous experiment on Sofielund landfill**

A test at Sofielund landfill had been done during the summer and fall of 2011, to measure levels of hydrogen sulfide emissions from Sofielund and also the amount of methane produced. There were four sample wells placed on the landfill surface to get a clear measurement of landfill gas. The wells were connected individually to a sample pump. The concentration and flow of methane were measured by a portable Dräger analyzer, and the instantaneous flow was measured by reading the Gemu rotameter.

Well 1 (PB01) was constructed with 9 meters depth; well 2 (PB02) by 12 meters depths, and well 3 (PB03) and 4 (PB04) were both 15 meters depth. While checking the depth, none of the wells had free water in them. Generally when the ground water level is high, the area in which gas can be collected will be less, thus when the ground water level is low there would be a bigger area in the landfill to collect LFG.

In all of these four wells, hydrogen sulfide content exceeded measurable levels of analytical instrument’s measurement range. [4]

The locations of the four wells are shown in the following map of Sofielund landfill:
Figure 5: Location of the four wells on the map of Sofielund [4]

PB01

During the Period mentioned in the table, concentration of Methane and Carbon dioxide in PB01, in comparison to other Swedish landfills was low. The Oxygen level changed with significant different values, this might be either for measurement error or leaking from the surface into the well, when the area around the testing well is under pressure. [4]
<table>
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</thead>
<tbody>
<tr>
<td>Average from 2011-06-22 to 2011-07-01</td>
<td>44</td>
<td>40</td>
<td>&gt;1000</td>
<td>6.9</td>
<td>4</td>
<td>15</td>
<td>36.3</td>
</tr>
<tr>
<td>Median</td>
<td>45</td>
<td>43</td>
<td>4.7</td>
<td></td>
<td></td>
<td></td>
<td>39</td>
</tr>
</tbody>
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**PB02**

The experiment in PB02 resulted in the highest Methane and Carbon dioxide concentration among all the wells. The Oxygen content was similar to the previous well which is to some extent higher than normal; it might be due to a leaky surface which can get higher when the weather is windy. [4]

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<tbody>
<tr>
<td>Average from 2011-07-04 to 2011-07-15</td>
<td>51</td>
<td>42</td>
<td>&gt;1000</td>
<td>4</td>
<td>8</td>
<td>42</td>
<td>37.8</td>
</tr>
<tr>
<td>Median</td>
<td>51.5</td>
<td>43</td>
<td>3.15</td>
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<td>38</td>
</tr>
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</table>

**PB03**

In PB03 the concentration of methane and carbon dioxide were lower than all the other wells. The average temperature was lower comparing to other wells but still in mesophilic range. [4]
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<tbody>
<tr>
<td>Average from 2011-07-19 to 2011-07-25</td>
<td>36</td>
<td>28</td>
<td>&gt;1000</td>
<td>5</td>
<td>5</td>
<td>19</td>
<td>34.2</td>
</tr>
<tr>
<td>Median</td>
<td>39</td>
<td>31</td>
<td>1.8</td>
<td></td>
<td></td>
<td></td>
<td>35</td>
</tr>
</tbody>
</table>

**PB04**

In PB04 the oxygen content in some plots was very high comparing to other wells. This might be because of both a leaky surface and windy weather. [4]

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<tbody>
<tr>
<td>Average from 2011-07-25 to 2011-07-29</td>
<td>44</td>
<td>38</td>
<td>&gt;1000</td>
<td>8</td>
<td>5</td>
<td>22</td>
<td>37.4</td>
</tr>
<tr>
<td>Median</td>
<td>43</td>
<td>38</td>
<td>7</td>
<td></td>
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<td>38</td>
</tr>
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</table>

**Long-term testing on PB02**

During the short tests mentioned before on the four wells at Sofielund, PB02 had the most interesting results in terms of methane content and the flows. Therefore the decision was made to do another test on PB02 in a longer period. The results are available in the following table.
<table>
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</thead>
<tbody>
<tr>
<td>Average from 2011-08-23 to 2011-09-20</td>
<td>48</td>
<td>38</td>
<td>&gt;1000</td>
<td>1.9</td>
<td>9</td>
<td>42</td>
<td>40.23</td>
</tr>
<tr>
<td>Median</td>
<td>51</td>
<td>40</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
<td>41</td>
</tr>
</tbody>
</table>

As can be seen Methane and Carbon dioxide were at similar values, while the Oxygen was at lower level.

![Flow vs. Energy](image)

**Figure 6: Flow vs. Energy**

With drawing the figure flow vs. energy it can be seen that the highest amount of produced energy was in flow range of 10 to 12.
METHOD & INSTRUMENT

1.9. Control of the slag

In order to characterize the slag, we need to get a sample from the slag we are going to use and send it to laboratory to find out what kind of slag is it and what it contains. Also we are going to send another sample of the slag to laboratory to see how does its leachability changes due to carbonization after upgrading and recognize what kind of slag it is now and what can we do with it. Unfortunately this laboratory work was not done.

1.10. Test site description on Sofielund landfill

Field measurement & field conditions
Several field tests are going to be done on Sofielund landfill. In these tests the gas emissions from the landfill is going to be measured with a special device. Based on previous experiments, the slag from bottom ash is used as an adsorption agent in the experiments. An area of 20 m x 20 m is chosen as the experimental area, and it is marked for that part of the landfill to be avoided from driving on the surface. This experimental area is chosen around one of the old gas wells where the highest concentration of hydrogen sulfide has been detected in previous experiments in Sofielund (PB02). The measurements are done with a device called Gemu rotameter, with an arm of about 30cm long to be able to take gas samples from different depths in the layers of bottom ash. This stick is perforated with holes on one level to take samples into the tube through the perforation at the level directly above the tip, like the figure below.
Two different types of test methods are going to be investigated:
1.10.1. Layer of slag from bottom ash

For the test on surface, an area of 15m x 12m in the middle of the experimental area is covered with the weathered slag from bottom ash with thickness of about 30 cm. The measurements on surface will be done on different spots of the mentioned area, in depths of 5cm and 15cm and it will be repeated in several days. Boundary conditions must be considered in this system, the LFG flow containing CH4, CO2 and H2S is going through the slag from inside the landfill, wind, and rain and density of the slag are other parameters.
In general, 0.001 - 0.5 m$^3$ LFG is produced per one square meter landfill per day, since the landfill is new, the flow is supposed to be more near to 0.5 m$^3$. The H2S concentration in deep wells of Sufielund was 17000 ppm. By using the ideal gas law (PV=nRT), it can be found that how much H$_2$S is emitted in grams and by knowing the adsorption capacity of the slag, it can be calculated how much time is needed for H$_2$S to be adsorbed. The measurements started one week after building up the slag area. The spots chosen in the slag covered area are called “A” spots, and all the other spots which are outside this area are called “B” spots.

1.10.2. Trench filled with slag from bottom ash

Although installation of trench did not happen, it was planned to be built before the ashes were put on the surface of experimental area. The trench was going to have dimensions of: Approximately 0.5 m wide, 0.5 m deep and about 4 m long. It was going to be filled with the slag from bottom ash with a thickness of 0.2 dm, and a drainage pipe with a diameter of 50 mm was planned to be installed, then again fill the trench with bottom ash. Finally put the bottom ash with 0.3 m thickness on top of it.
1.11. Measurements of landfill gas on Sofielund’s landfill

The measurements took place on Sofielund landfill in 6 different days from May 22 to June 7th. These measurements were done by a portable gas analyzer (GA5000), (Figure 15).

At the end of the tube from the device, a metal bar was assembled with the length of 30 cm perforated with holes on one level. The spots in which the measurements were made are presented in figure 12. “A” spots are the spots which had been chosen in the slag covered area of landfill, and “B” spots are the spots outside the slag area.

In the “A” area, samples were taken from several levels, on the surface of the slag, from 10 cm below the surface and 15 cm below the surface. In this case, for each level the metal bar was pushed vertically into the field in order to take the gas samples into the tube. In four corners of the slag area (A10, A11, A13, A14) there were just one measurement in each day, in 15 cm down from the surface, that the metal bar was pushed in again 15 cm horizontally from the side of the slag area.

In the “B” area, samples were taken from an average depth of 10 cm below the surface of the landfill.
In all the first four measurements, the landfill was relatively wet for the day before it had rained, and the temperature was between 12 c and 16 c. But in 2 last measurements, weather was sunny on days before and the temperature was about 23 c. During the measurements even on 5th and 7th of June in which the weather before and during the measurements was sunny with no rain, the bottom ash was dry on surface and naturally wet in 7cm below the surface.

1.12. Economical potential

Assessing economical potentials, such as price of the slag at the first place, upgrading costs and value of upgraded gas, etc. Also How does upgrading effect on the quality of the slag and thereby its price. SRV is allowed to use slag from bottom ash as the layer, if they pay the waste tax. Therefore they must convince environmental protection agency that slag from bottom ash is a construction material with the purpose of improving environment by reducing LFG, especially CO₂ and H₂S reaching the atmosphere.
RESULTS

With fulfilling the purpose of this study we can describe if slag from household wastes can efficiently reduce \( \text{H}_2\text{S} \) emission from the landfill sites and how it increases the \( \text{CH}_4 \). Also we will discuss what to do with the slag and how its leachability changes after \( \text{CO}_2 \) participated in slag’s carbonization. Results can be used to discuss how to optimize the upgrading method. Also it is an input to discuss if this solution can be generalized to similar slag and landfill gas problems.

1.13. Results are presented

**AREA B**

The following figures present the oxygen, carbon dioxide and methane contents in different spots of the landfill, outside the slag area and at different dates. These measurements were done in the average depth of 10cm below the surface of the waste area. They show that methane content is very low from the surface to almost 20cm depth from the surface of the landfill with average of 1% and at the highest points it is about 3-4%. Contents of \( \text{CO}_2 \) vary between a few percentages to 9%. There are some “hot spots” but the location of these spots varies between different dates. The same spot like B9 had \( \text{CO}_2 \) levels of 9.35% at 2013-05-28 and two days later it had only about 2.5%.

![Figure 13](image1.png)

![Figure 14](image2.png)

![Figure 15](image3.png)

![Figure 16](image4.png)
In the recent measurement Hydrogen emissions were higher than the expectation; also the hydrogen sulfide emissions did not exceed 2ppm in the whole measurements in different parts of the landfill. The following figures of hydrogen and hydrogen sulfide emissions present this fact. H$_2$ contents at the same spot varies between different dates.
There is also a correlation between CO$_2$ and H$_2$ which is shown in following figures.

The highest amount of CH$_4$ in the measurements of “B” area belongs to a pipe with an unknown depth. The measurements took place 90cm inside the pipe. The measurements from this pipe shows that there are higher contents of methane, carbon dioxide and hydrogen in a deeper depth of the landfill, but still hydrogen sulfide did not exceed 2ppm.

The measurements were done on 5 occasions 05/24, 05/28, 05/30, 06/05, 06/07. The results show that the content of CH$_4$ went from ~2% at 10 a.m. to 13% two hours later. On the next two occasions the pipe had the same gas content as air (05/28 and 05/30). On the last two occasions CH$_4$ content was about 14% (06/05) and between <2% to 10% (06/07).
At the same time when CH$_4$ content in the pipe went down from 10% to <2% a truck went by the site.

Figure 26

Figure 27

Figure 28

Figure 29

**AREA A**

In “A” area, The measurements show that Hydrogen content of the emissions, increases with time at a certain depth. Following are the figures concerning H$_2$ emissions in A area in depth of 10 cm and 15 cm below the surface of the slag covered area.

**Sampling points 10 cm below the surface:**
Sampling points 15 cm below the surface:
Other diagrams extracted from the measurement results, show that carbon dioxide increases with time day by day in the slag covered area both in 10 cm and 15 cm below the surface. Following figures represent this fact.

**Sampling points 10 cm below the surface:**
Sampling points 15 cm below the surface:
By comparing two specific spots in the “A” area, it is found out that CO$_2$ content increases also with depth. There were no CH$_4$ content in the same spot in different depths and CO$_2$ content did not exceed 6%. Following figures of two specific spots are an evidence for this fact.
Spot A16 in three different depths in four days of the measurement

Figure 50

A16_2013-05-28

Figure 51

A16_2013-05-30

Figure 52

A16_2013-06-05

Figure 53

A16_2013-06-07

Spot A6 in three different depths in five days of the measurement
In all the measurements, the emissions on the surface of each spot were like the contents of the air.
5. DISCUSSION

Considering the results from the test which had been made in Sofielund landfill in summer and fall of 2011 in deep wells, it was expected the landfill to have high emissions of methane, carbon dioxide and Hydrogen sulfide even at the surface. But measurements done in this study showed low contents of LFGs.

From comparing the landfill gas contents in spots which had been measured more than once in different days, it can be suggested that landfill gas finds cracks in the landfill, not the same way from day to day. This can be because of the heavy trucks traffic on the landfill which close some of the cracks and create new ones, and landfill gas finds new ways to diffuse to the surface. Therefore emissions from the same spots vary day by day. (Figure 16-21)

In the waste area of the landfill a pipe was found (figure 28), in which a higher contents of landfill gas was measured, comparing to all the other measurements. Figures 29 to 32 show high contents of methane, carbon dioxide and hydrogen, comparing to other parts of the landfill in 10cm below the surface.

In the first measurement of the pipe on 24th of May, hydrogen content of the pipe exceeded 1000ppm, and the methane content was about 15% at the most; which shows in deeper depth concentrations of LFG was higher than the contents of CH₄ and CO₂ at the surface and 10cm below the surface. On two days of the measurements (May 28 and May 30), the contents from the pipe were neglectable, but on June 5th the contents got high again, there is a possibility that the pipe was blocked for a few days, for there are trucks in traffic on the landfill every day and compacting the area. During the first measurement of the pipe on June 5th when the emissions were high (about 10% methane, 11% carbon dioxide and 540ppm hydrogen), a truck drove over a few meters away from the pip, and the emissions started to decline with a high rate. After about 5minutes the gas contents were reached to 1.4% methane, 1.7% carbon dioxide and 130ppm hydrogen. This shows that it is possible that compacting has a great effect on landfill gas diffusion. The reason can be changing the permeability of landfill surface due to daily activity on the surface. If LFG does not find areas of high permeability to go through them vertically and emit to the air, it has to move horizontally inside the landfill and find other ways out or probably build up new ones.

Considering all the measurements, the concentration of landfill gas is depth dependent.

Figures 53-61 show that in certain spots, more contents of carbon dioxide are found in deeper depth. Therefore carbon dioxide increases with the depth in “A” area. Also comparing the figures 15-20 to the figures 42-47 shows that generally in B area the contents of CO₂ are higher than that of A area at the same depth (10cm below the surface).

By comparing figure 33 to 42 (H₂ and H₂S emissions in “A” area) with figure 22 to 27 (H₂ and H₂S emissions in “B” area), it can be seen that hydrogen distributes evenly in A area. H₂S emissions were at very low levels both in slag area and waste area, therefore any results couldn't be shown due to these low levels.

Considering the results it is suggested that in future studies a trench is needed to be able to measure the slag from bottom ash’s effect on landfill emissions on the surface. Measurements in deep wells would be also important to compare with the previous measurements in 2011. Also restricting the
area of measurements from traffic of heavy vehicles; in order to keep the diffusion and permeability of surface in a constant condition.

According to the previous experiment on Sofielund, H$_2$S smell was distinct right after the wells were dug in 2011 and after a while it disappeared, this can suggest that the H$_2$S production is low.

During the interview with Ove S. who works at SRV about the old landfill they have which is closed, following information has been gathered:
- The old landfill has quite low content of H$_2$S (26 ppm)
- The old landfill was constructed with layers of bottom ash as a construction material, and generally H$_2$S content is much lower than that of new landfill where no bottom ash was used. [16]
6. CONCLUSION

Considering the results from the measurements, in the slag covered area, carbon dioxide content in the first measurement is less than that of the last day of the measurement. It increases day by day from the first day of the measurement to the last day. It is suggested that carbonation of the slag and its role in CO₂ sequestration, contribute to these results.

The highest contents of landfill gas in the measurements belong to one measurement of the pipe which was 15.1% Methane, 12.1% Carbon dioxide and 0.4% Oxygen. The sum of these contents is 27.6%, which shows the major content of this landfill gas (about 70%) is most probably Nitrogen.

In different parts of the landfill, in an average depth of 10 cm below the surface, the emissions vary from time to time. As discussed before it shows that compacting and changing the permeability of the surface has a great effect on landfill gas emissions in the mentioned depth, from this it is concluded that the landfill gas flow, which generally is between 0.001 and 0.5 m³ per one square meter on the surface of the landfill, in the Sofielund landfill is near the lowest limit.

The landfill was wet in first days of measurement due to previous day’s rain, since when the temperature goes up the solubility of H₂S in water decreases, in last two measurements when the temperature was higher than the other days, H₂S content of the emissions reached 2ppm at the most in some spots, which was higher than the other days (0 or 1ppm), but still it is low comparing to previous report. Instead the landfill is producing more hydrogen than hydrogen sulphide.

According to the measurements in this study, it can be suggested to cover the landfill with a layer of slag to minimize the LFG emissions and bad smell from H₂S. Therefore using the slag can eliminate direct emissions of LFG to the atmosphere by diffusion through the slag layer. This diffusion allows adsorption of CO₂ and oxidation of H₂S. The slag itself can be improved by less leachability.
7. FUTURE STUDY

There are some laboratory works, which can improve the results of this study:

- Measuring the effects of landfill gas on slag in laboratory scale with a completely controlled condition and compare it with the measurements in the field.
- Adsorption of CO\textsubscript{2} and H\textsubscript{2}S on the slag.
- Leaching of slag before and after the test.
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