



## Biogas – Municipal solid waste incinerator bottom ash interactions: Sulphur compounds removal

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### ARTICLE INFO

#### Article history:

Received 10 June 2008

Received in revised form

23 November 2008

Accepted 1 December 2008

Available online 7 December 2008

#### Keywords:

MSWI bottom ash reuse

Landfill gas purification

Hydrogen sulphide

Methyl mercaptan

Dimethyl sulphide

### ABSTRACT

This study focuses on a new way of reusing municipal solid waste incinerator bottom ash: landfill gas purification before energetic valorisation. A pilot plant was designed and operated on a landfill site located in France (Loire). One kilogram bottom ash is able to sequester more than 3.0 g of hydrogen sulphide, 44 mg of methyl mercaptan, and 86 mg of dimethyl sulphide. Hydrogen sulphide retention is probably due to acid–basic reactions conducting to sulphur mineralisation under the form of low solubility metal sulphides. The reaction medium is hydration water. The retention mechanism for methyl mercaptan is probably similar but dimethyl sulphide is most likely retained by physical adsorption. As methane is not retained by bottom ash, the landfill gas energetic content will not be lowered. There seems to be no appreciable difference in these results whether bottom ash is fresh or carbonated. These results are encouraging in the perspective of a field scale application of this biogas treatment process.

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### 1. Introduction

The two main municipal solid waste (MSW) management methods in most European countries are disposal in landfills and/or incineration [1]. For instance, in France, MSW management consists of a mixture of landfill (38% w/w), incineration (43%), recycling (13%), and composting (6%).

Landfills are producing significant amounts of biogas, due to anaerobic fermentation when organic waste decomposes. Landfill gas is composed primarily of methane (up to 60 vol.%) and carbon dioxide. This presents a hazard because the methane can explode and/or burn. Moreover, both methane and carbon dioxide are considered some of the most important greenhouse gases.

As methane is combustible, it is usable for energy purposes. The energy of the collected biogas can be used to run generators or water heating plants (biogas is then used as fuel in the boilers to generate steam). The produced heat can also be exploited to make a plant function as a combined power and heating plant.

But a large number of volatile organic compounds (VOCs) (such as sulphur compounds, chlorinated compounds, terpenes, alcohols, ketones, alkenes, alkanes, aromatics and silicon compounds) are

found in trace quantities in landfill gas [2–4]. Some of them contribute to the greenhouse effect and hydrogen sulphide (H<sub>2</sub>S) causes an offensive “rotten egg” odour. When landfill gas is collected to be upgraded, removal of some of these constituents (sulphur and chlorinated compounds) in the biogas before burning is necessary in order to prevent the boilers or engines from corroding. In particular, sulphur compounds have acidifying characteristics.

Among these compounds, we were interested in some reduced sulphur compounds: H<sub>2</sub>S, methyl mercaptan (CH<sub>3</sub>SH) and dimethyl sulphide ((CH<sub>3</sub>)<sub>2</sub>S), main sulphur compounds in the studied biogas. The possible technologies for removing some of these sulphur compounds in biogases from sewage treatment plant sludge digester or landfill include various adsorbents [5,6], absorbents [7] or biofilters [8].

With respect to incineration, MSW is treated in incineration plants to reduce the volume (typically by 90%), the toxicity and the reactivity of the waste. Bottom ash is the most significant by-product of municipal solid waste incineration (MSWI): around 250 kg of bottom ash per ton of MSW. The incineration of MSW results in the production of more than 3 million tons of bottom ash in France each year. After combustion, bottom ash is processed for subsequent utilisation or disposal. Due to their geotechnical properties, MSWI bottom ashes are usually used as a secondary road construction material: they can be used as an aggregate substitute in road sub-bases, road bases and embankments [9–12].

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Reuse of bottom ash is encouraged in France but strictly regulated. After processing and ageing, 70% (w/w) meet specific criteria and can be reused. During ageing on weathering platforms, mineralogical characteristics of bottom ash evolve: weathering (and especially carbonation reaction) will have some positive effects on bottom ash, as decreasing the pH and decreasing heavy metal leaching [13–19]. But bottom ash, even meeting regulation criteria, is not always reused due to a poor social acceptability. So there is a need to investigate some alternatives for bottom ash utilisation.

In some previous studies, bottom ash physico-chemical properties were investigated, and particularly purification capacities were shown to be of interest for polluted effluents treatment. The first application consisted in treating landfill leachate and was patented by France Déchets and INSA de Lyon [20]. Blanchard et al. [21] demonstrated the adsorption capacities towards several pollutants: phenol contained in some paint sludge, Congo red, landfill leachate. Then, Pascual et al. [22] demonstrated bottom ash adsorption capacities towards gaseous HCl, in the perspective of MSWI fly ash dechlorination. More recently, MSWI bottom ash was successfully used for the removal of dyes (alizarin yellow, fast green and methyl violet) from wastewater [23].

This study focuses on an innovative alternative for MSWI bottom ash utilisation, using bottom ash adsorption capacities and potential reactivity: landfill gas purification. The overall study concerned the purification capacities of bottom ash, either alone or as a part of a mixture (with coke) towards several sulphur compounds ( $\text{H}_2\text{S}$ , methyl mercaptan and dimethyl sulphide) and other potentially harmful landfill gas compounds: VOCs. This process, worldwide patented by Novergie, links the two most common solid waste disposal methods and has two advantages: on the one hand it contributes to bottom ash reuse, and on the second hand, it purifies landfill gas.

In this paper, we focus on a part of the performed work: only results concerning bottom ash alone are discussed. We evaluated and quantified bottom ash purification capacity towards three sulphur compounds: hydrogen sulphide, methyl mercaptan, and dimethyl sulphide.

The objective of this preliminary study was to assess the feasibility of a field scale implementation with bottom ash layers laid directly in landfill cells. Then, in this perspective, it seemed necessary to investigate also the effect of MSWI bottom ash on the two main compounds of landfill gas: methane and carbon dioxide.

## 2. Materials and methods

### 2.1. Landfill site and landfill gas

Experiments were performed at the Biovale Company landfill (Loire department), where landfill gas is used for energy purposes by Satrod Company located just besides. Seven gas engines use the gas as fuel and spin generators to produce electricity. With more than 6.2 electrical MW supplied to the power distribution system, this is one of the most significant operation of energy recovery from landfill gas in Europe. The modern landfill is made of watertight landfill cells in which all the landfill gas is collected. During the experiments, landfill gas production was about  $5000 \text{ Nm}^3 \text{ h}^{-1}$ .

The mean dry composition of the landfill gas was 45–49% (v/v) methane, 24–39% carbon dioxide, with small amounts of nitrogen (11–15%), and oxygen (around 2%). Landfill gas also contained trace amounts of inorganic compounds ( $97\text{--}150 \text{ mg Nm}^{-3} \text{ H}_2\text{S}$  for instance) and VOCs.

### 2.2. Pilot plant

The pilot plant (Fig. 1) was designed and instrumented at LGCIE (Laboratoire de Génie Civil et d'Ingénierie Environnementale). For

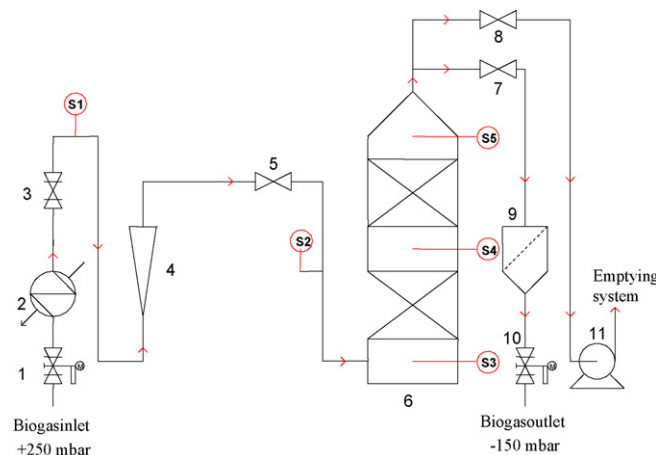


Fig. 1. Experimental apparatus: pilot plant.

the experiments, it was connected on site to the landfill gas collection system via polyethylene pipes upstream and downstream the reactor. Two stainless steel explosion-proof solenoid valves (1 and 10 in Fig. 1) allowed landfill gas circulation and reactor insulation.

Landfill gas was first cooled using a  $5^\circ\text{C}$  thermostatic bath (2), in order to condensate one part of the gas water content. The inlet flow rate, adjusted with a valve (3), was measured using a rotameter (4). Sampling for gas analysis and temperature measurement upstream the reactor could be performed via two septa (S1 and S2).

The reactor (6) was a 30-cm diameter and 170-cm height PVC column. The lower part of the reactor remained empty for a better gas distribution. Bottom ash was supported by a stainless steel grid and a layer of nonwoven fabric. It was covered by a layer of the same fabric, in order to avoid clogging and fine bottom ash particles migration. The upper part of the reactor was cone-shaped in order to avoid gas stagnation. Three sampling points were distributed along the column height (septa S3, S4 and S5). At the top of the column, landfill gas outlet was made of stainless steel pipes and allowed to separate the outlet from the emptying system.

Moreover, the treated landfill gas went through a particle filter (9), to avoid bottom ash dust transport before being reintroduced in the main collecting system, towards the engines.

### 2.3. Bottom ash

The bottom ash used in this study came from an MSWI facility in France located in the metropolitan area of Lyon. A 3 tons sample was collected in one time from the weathering areas stockpiles, after only a few days of weathering (fresh sample). Bottom ash coming from the same French facility has also been used and analysed by Kaibouchi and Germain [24] and Rendek et al. [25].

Before sampling, bottom ash was spread out on the ground in a 10-cm thickness layer and air dried for 3 days, in order to reduce its moisture content and stop phase evolution. Bottom ash moisture content was then around 8% (w/w) and leaching tests indicated a pH value of 9.8 for the leachates. This low value for the leachates pH indicated that the bottom ash had already been partially carbonated during this drying step. Then bottom ash was stored in hermetically closed buckets to slow down further physico-chemical evolutions.

Before each experiment, bottom ash moisture content was adjusted to 15% (this value corresponds to the mean moisture content value on weathering areas). Then, the reactor was filled up with the moistened bottom ash in successive layers, tamped with a rammer, using the same operating procedure each time.

**Table 1**  
Operating conditions.

Experiment	Landfill gas flow rate (NL h <sup>-1</sup> )	Bottom ash mass (kg)	Experiment duration (h)	Followed compounds
1	1710	13	69	H <sub>2</sub> S
2	879	13	134	H <sub>2</sub> S
3	895	13	404	H <sub>2</sub> S
4	914	13	93	CH <sub>3</sub> SH, (CH <sub>3</sub> ) <sub>2</sub> S
5	898	13	164	CH <sub>3</sub> SH, (CH <sub>3</sub> ) <sub>2</sub> S, CH <sub>4</sub>
6	821	13	85	CH <sub>3</sub> SH, (CH <sub>3</sub> ) <sub>2</sub> S
7	820	13	136	CH <sub>3</sub> SH, (CH <sub>3</sub> ) <sub>2</sub> S
8	897	13	47	CO <sub>2</sub>

#### 2.4. Gas analysis

The chosen compounds were analysed upstream and downstream the column by gas chromatography. Reduced sulphur compounds (H<sub>2</sub>S, methyl mercaptan and dimethyl sulphide), CO<sub>2</sub> and CH<sub>4</sub> were analysed using a VARIAN-CP 2003 gas chromatograph.

For reduced sulphur compounds and CH<sub>4</sub> analysis, the Varian chromatograph was fitted with a PORAPLOT Q capillary column (10 m × 0.25 mm i.d.). The pressure was 100 kPa at the column head and the temperature was 35 °C for H<sub>2</sub>S and 115 °C for methyl mercaptan, dimethyl sulphide and CH<sub>4</sub>.

The analysis of CO<sub>2</sub> was performed using a 10 m × 0.32 mm i.d. CP-MOLSIEVE 5A capillary column. The pressure was 80 kPa at the column head and the temperature was 50 °C.

The absolute uncertainty of the measurements is estimated to be around ±1–3 ppmV with the VARIAN-CP 2003 gas chromatograph, depending on the compounds.

### 3. Results

During some preliminary experiments, the influence of some parameters, such as pressure, temperature or gas moisture content could be observed. Thanks to those tests, an operating procedure was established and both gas flow rate and bottom ash quantity were chosen, in order to ensure moderate experiments duration (around a few hundreds of hours).

On an analytical point of view, as we had only one chromatograph, followed gas concentrations were measured in a continuous way downstream the bottom ash bed and in a discontinuous way in the entering landfill gas.

The results of eight experiments are discussed in this article. The main operating parameters for these experiments are summarised in Table 1.

#### 3.1. H<sub>2</sub>S retention

H<sub>2</sub>S is generally the most abundant sulphur compound in landfill gas. During the experiments, H<sub>2</sub>S content was measured several times and could be considered as constant, around 100 ± 10 ppmV (~140 mg H<sub>2</sub>S Nm<sup>-3</sup>).

Experiments concerning H<sub>2</sub>S were all performed with the same bottom ash quantity (13 kg) and with two landfill gas flow rates. Results will be expressed as the H<sub>2</sub>S retention factor evolution against time.

##### 3.1.1. Experiment 1: high flow rate (1710 NL h<sup>-1</sup>)

The first experiment lasted for 70 h. Results are shown in Fig. 2. H<sub>2</sub>S retention factor shows a rapid decrease: initially equal to 100%, the retention factor drops during the first 10 h and stabilises during the 60 following ones. H<sub>2</sub>S is then 50% retained during this second phase.

Due to the high landfill gas flow rate, it seems that it is not possible to completely saturate the bottom ash. As a matter of fact,

considering an estimated bottom ash bed void fraction of 0.3, a bottom ash bed volume of 8 L, the contact time between landfill gas and bottom ash is only about 12 s, which is probably not enough. In the first phase (quick decrease), the external surfaces of bottom ash particles are probably getting saturated: H<sub>2</sub>S can hardly penetrate in the bottom ash pores. It would then be an inter-granular reactivity rather than an intra-granular one.

Consequently, it was decided to reduce the landfill gas flow rate in order to increase the contact time.

##### 3.1.2. Experiments 2 and 3: at lower flow rate (879 and 895 NL h<sup>-1</sup>, respectively)

The objective of experiments 2 and 3 was, on the one hand, to confirm our hypothesis concerning the effect of the flow rate (and consequently of the contact time between landfill gas and bottom ash) on H<sub>2</sub>S retention factor (experiment 2) and, on the other hand, to try and reach bottom ash saturation, or reach a retention factor close to zero (experiment 3).

So, for these experiments, landfill gas flow rate was approximately divided by 2, but bottom ash quantity was kept constant (13 kg). The contact time between landfill gas and bottom ash was then about 23 s. Experimental results for these two experiments are shown in Fig. 3.

First, let us consider experiment 2 and the 395 first hours of experiment 3. The evolution of H<sub>2</sub>S retention factor is quite different from the previous one: bottom ash efficiency decreased slowly with time, in a relatively linear way.

It can be noticed that during the 130 first hours, the evolution of H<sub>2</sub>S retention factor is similar for the two experiments performed at the same gas flow rate. Results seem to be reproducible.

In experiment 3, the 395 first hours showed a slow decrease of H<sub>2</sub>S retention factor. After 395 h, the retention factor was about 50%. So bottom ash load was not yet completely saturated.

Unfortunately, experiment 3 had to be stopped before reaching bottom ash saturation because of very low temperatures on the experimental site for several days (winter period). This induced landfill gas water condensation, which progressively froze in the

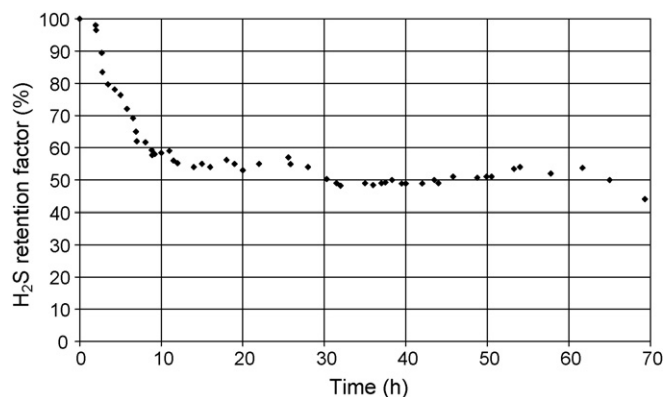


Fig. 2. H<sub>2</sub>S retention factor versus time (experiment 1).

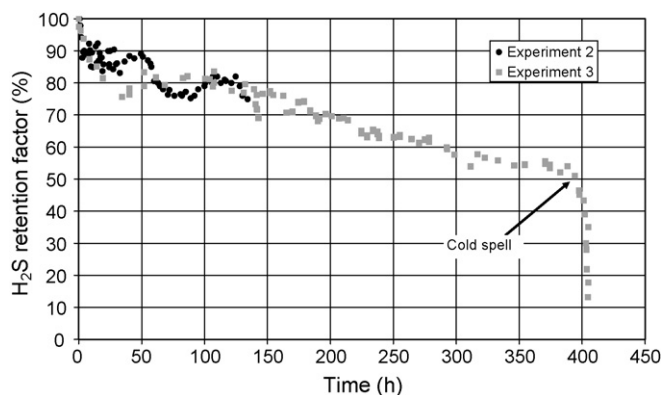


Fig. 3. H<sub>2</sub>S retention factor versus time (experiments 2 and 3).

pipes. In a first step, a dry landfill gas entered the column, then, when the pipes were totally clogged up by ice, landfill gas circulation stopped and so did the experiment.

Nevertheless, the consequences of this cold spell were interesting: as a matter of fact, a sudden decrease of bottom ash efficiency could be observed before the definitive stopping. This decrease could be explained in this manner: first, when the external temperature dropped, the cold and dry landfill gas entering the column was heated up and rehydrated by coming through the bottom ash (which temperature was a little higher). So bottom ash progressively dried, which induced the sudden decrease of H<sub>2</sub>S retention factor, as shown in Fig. 3.

This hypothesis is supported by the observation that bottom ash moisture content at the end of the experiment was nearly equal to zero. This shows the important role of interstitial water in H<sub>2</sub>S reactivity with some bottom ash constituents. This point will be discussed again in Section 4.1.1.

Considering the quasi-linear evolution of H<sub>2</sub>S retention factor versus time (Fig. 3), by extrapolating the curve for the experiment 3, the duration for complete bottom ash saturation could be estimated to be around 900–1000 h.

### 3.1.3. H<sub>2</sub>S accumulation

These results could be expressed, for the three experiments, in terms of accumulated H<sub>2</sub>S mass in bottom ash load (Fig. 4), in order to assess the total quantity of retained compound during each experiment. The accumulation curves trend also brings qualitative information concerning bottom ash saturation state.

An accumulation rate inside the bottom ash can be defined, corresponding to the slope of the accumulation curve. For experiment 3 for instance, this rate was around 0.14 g h<sup>-1</sup> (for the 13 kg sam-

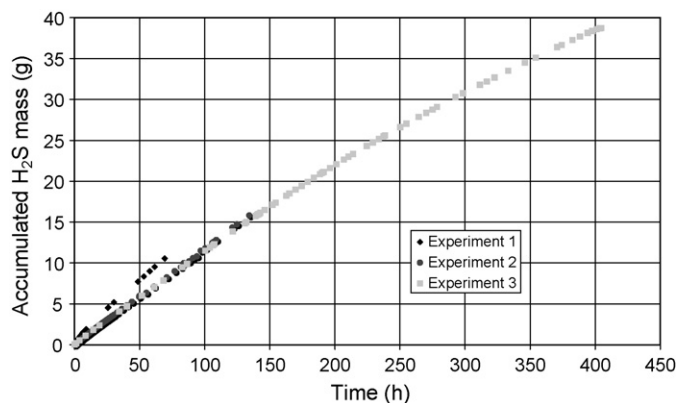


Fig. 4. Accumulated H<sub>2</sub>S mass in bottom ash versus time (experiments 1–3).

ple) at the beginning of the experiment and was only 0.07 g h<sup>-1</sup> after 395 h, just before the cold spell. It is obvious that, after 395 h experiment, bottom ash was not totally saturated.

It can be observed that the accumulation curves for experiments 2 and 3 are identical (for the 130 first hours). On the contrary, for experiment 1, performed with a twice higher landfill gas flow rate, H<sub>2</sub>S accumulation rate was a little higher (during the 69 h experiment).

The 13 kg bottom ash sequestered around 39 g H<sub>2</sub>S in 404 h (experiment 3), that is to say 3 g H<sub>2</sub>S per bottom ash kg. As the bottom ash was not saturated, we can suppose that in fact, more than 3 g H<sub>2</sub>S could be sequestered per bottom ash kg. Assuming a linear decrease of H<sub>2</sub>S retention (Fig. 3), it is estimated that 4 g H<sub>2</sub>S could be trapped by 1 kg of bottom ash.

### 3.2. Methyl mercaptan and dimethyl sulphide retention

Experiments 4–7 concerned the retention of methyl mercaptan and dimethyl sulphide. Average concentrations in untreated landfill gas were 4 ppmV (9 mg Nm<sup>-3</sup>) for methyl mercaptan and 30 ppmV (80 mg Nm<sup>-3</sup>) for dimethyl sulphide. For methyl mercaptan, the concentration is close to the detection limit, which is likely to induce high uncertainties.

As concentrations were measured at the column outlet only, it has to be noticed that any undetected change of methyl mercaptan or dimethyl sulphide content in landfill gas upstream the column induces an error in the retention factor calculation. This is especially true for methyl mercaptan, which had a low concentration (close to the detection limit).

Similar experiments were performed with these two components as for H<sub>2</sub>S (Table 1). As an example, only one experiment is presented here: results for experiment 6. It can be seen in Fig. 5 that methyl mercaptan is better retained than dimethyl sulphide. Methyl mercaptan is 100% retained at the beginning, after which the retention factor decreases. Dimethyl sulphide initial retention factor is initially close to 50% and decreases to between 0 and 10% after 60 h of experimenting.

Periodical decreases of the retention factor were observed for both components (Fig. 5). They can be partly explained by day/night cycle: low temperatures induced partial condensation of landfill gas water, and consequently partial dissolution of methyl mercaptan and dimethyl sulphide in condensed water via Henry's law. As a result, the inlet concentrations of methyl mercaptan and dimethyl sulphide could be lower than the measured ones as inlet concentrations were measured only during the day. Moreover, these two compounds have boiling temperatures under atmospheric pressure close to ambient temperature (6 °C for methyl mercaptan and 37 °C for dimethyl sulphide): it seems possible that changes in the

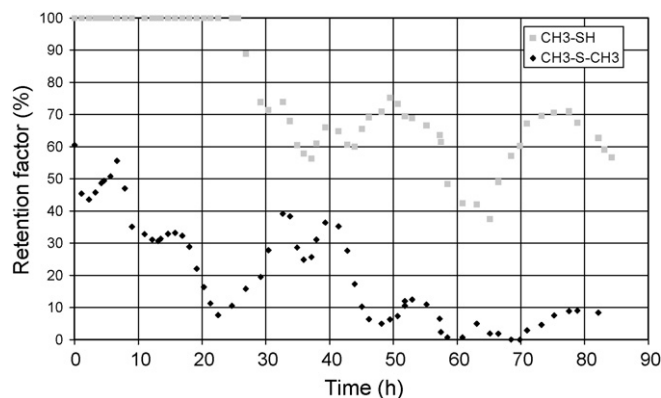


Fig. 5. CH<sub>3</sub>-SH and CH<sub>3</sub>-S-CH<sub>3</sub> retention factors versus time (experiment 6).



**Table 2**  
Sequestered mass of H<sub>2</sub>S, CH<sub>3</sub>-SH and CH<sub>3</sub>-S-CH<sub>3</sub> per bottom ash kg.

Compound	Retained g per bottom ash kg	Nm <sup>3</sup> purified landfill gas per bottom ash kg
H <sub>2</sub> S	3.0	21
CH <sub>3</sub> -SH	0.044	5
CH <sub>3</sub> -S-CH <sub>3</sub>	0.086	1

landfill gas temperature and in water partial pressure can locally make these compounds change state from gas to liquid. The fluctuations could then be partly explained by condensation/vaporisation phenomena in the outside pipes (before the column entrance). Condensation/vaporisation phenomena could be due to temperature changes at night for instance. Consequently, experimental results have to be interpreted carefully.

It has to be noted that reproducibility for these experiments was not as good as for H<sub>2</sub>S, probably due to the following reasons: condensation/vaporisation phenomena, possible undetected concentration changes in entrance, low input concentration for methyl mercaptan.

### 3.3. Comparison of results

The previous experimental results are summarised in Table 2. For each studied compound, the sequestered compound mass per bottom ash kg is given. For each compound, the chosen mass was the one obtained at the end of the longest experimentation (experimentation 3 for H<sub>2</sub>S and experimentation 5 for methyl mercaptan and dimethyl sulphide). Then, knowing the mean compound concentration in the biogas (140 mg Nm<sup>-3</sup> for H<sub>2</sub>S, 9 mg Nm<sup>-3</sup> for methyl mercaptan and 80 mg Nm<sup>-3</sup> for dimethyl sulphide), the volume of biogas that could be purified by one kg bottom ash was calculated (if each compound was 100% retained). Actually, in full-scale conditions (bottom ash layers in landfill to purify biogas), the contact time between bottom ash and biogas would be much higher.

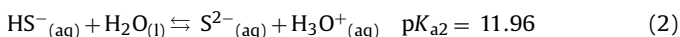
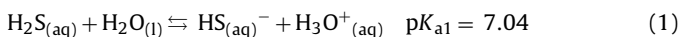
We can consider that these values are default values and that the actual bottom ash purification potential is probably superior. Bottom ash was indeed not saturated at the end of the experiments.

## 4. Discussion: hypotheses concerning retention mechanisms

### 4.1. Interactions bottom ash–hydrogen sulphide

#### 4.1.1. Retention mechanisms

Hydrogen sulphide is a diacid, dissociating in aqueous solutions according to



pK<sub>a1</sub> and pK<sub>a2</sub> are the acid dissociation constants at 18 °C.

Bottom ash pore water and interstitial water have a basic pH and even a very basic pH in the case of fresh bottom ash, corresponding to the pH of a calcium hydroxide (Ca(OH)<sub>2</sub>) saturated solution. Calcium hydroxide is formed in bottom ash as a result of calcium oxide (CaO) hydrolysis at the exit of the furnace during the water quenching step. Because of its strong basic properties, acid–basic reactions are induced. In these pH conditions, hydrogen sulphide is essentially under the ionic form (hydrosulphide ion and mainly sulphide ion). The sulphide ion (S<sup>2-</sup>) in a basic medium reacts with many metal cations in solution to produce the corresponding metal sulphides, such as iron sulphide, lead sulphide, zinc sulphide, etc. As the solubility products of metal sulphides are generally very low, these metal sulphides probably precipitate for a large part. Conse-

quently, sulphur from hydrogen sulphide is stabilised for the main part under solid form.

These hypotheses confirm the very important part of bottom ash hydration water: the aqueous phase is the necessary reaction medium for physico-chemical equilibria described before (species dissolution and chemical reactions). The rapid decrease of bottom ash retention factor during manipulation 3, when bottom ash was totally dried, is in accordance with our hypotheses.

#### 4.1.2. Transport mechanisms

As the acid–basic reactions occur in the pore and interstitial water, internal diffusion can be neglected, and the two main transport mechanisms that should be considered are external diffusion and acid–basic reactions kinetics.

Using the method proposed by Truong and Abatzoglou [6], the mass transfer coefficient for the external diffusion  $k_D$  can be calculated from:

$$k_D = \frac{Sh D_{\text{H}_2\text{S-gas}}}{d_p} \quad (3)$$

where the Sherwood number is

$$Sh = 2.0 + 1.8 Re^{1/2} Sc^{1/3} \quad (4)$$

The Reynolds number is

$$Re = \frac{u_{\text{gas}} d_p \rho_{\text{gas}}}{\mu_{\text{gas}}} \quad (5)$$

and the Schmidt number is

$$Sc = \frac{u_{\text{gas}}}{\rho_{\text{gas}} D_{\text{H}_2\text{S-gas}}} \quad (6)$$

The  $k_D$ ,  $Sh$ ,  $Re$  and  $Sc$  were calculated using the following parameters:

- $u_{\text{gas}}$  is the linear velocity of gas (m s<sup>-1</sup>),
- $d_p$  is the average diameter of the media particles and can be estimated from the results of Kaibouchi and Germain [24]:  $d_p \approx 7.8 \times 10^{-3}$  m,
- $\rho_{\text{gas}}$  is the density of the gas:  $\rho_{\text{gas}} \approx 1$  kg m<sup>-3</sup>,
- $\mu_{\text{gas}}$  is the dynamic viscosity of the gas:  $\mu_{\text{gas}} = 1.267 \times 10^{-5}$  Pa s at  $P = 1$  atm and  $T = 293$  K [6],
- $D_{\text{H}_2\text{S-gas}}$  is the diffusivity of H<sub>2</sub>S in the gas:  $D_{\text{H}_2\text{S-gas}} = 0.14131 \times 10^{-4}$  m<sup>2</sup> s<sup>-1</sup> at  $P = 1$  atm and  $T = 293$  K [6].

Results presented in Table 3 show that in the case of experiments 2 and 3, the speed of the external mass transfer ( $k_D$ ) is 2.4 times the velocity of the gas. This leads to the assumption that the external diffusion step is faster than the rate of the gas crossing the reactor; thus, the external diffusion might not be the controlling step. As acid–basic reactions are fast kinetic reactions, the reaction is not controlled by the chemical kinetics either and the linear decrease could be due to the progressive interstitial and pore water saturation.

In the case of experiment 1,  $k_D$  is 1.5 times the velocity of the gas ( $u_{\text{gas}}$ ): as  $k_D$  and  $u_{\text{gas}}$  are of the same order, the reaction could be partially controlled by the external diffusion. This could explain the rapid decrease of the retention factor in the beginning of experiment 1. In the second phase, where H<sub>2</sub>S is 50% retained, interstitial and pore water probably slowly saturate.

**Table 3**  
Comparison of  $k_D$  and  $u_{\text{gas}}$  (experiments 1–3).

Experiment	Linear velocity of gas, $u_{\text{gas}}$ (m s <sup>-1</sup> )	Mass transfer coefficient for external diffusion, $k_D$ (m s <sup>-1</sup> )
1	$6.7 \times 10^{-3}$	$10.0 \times 10^{-3}$
2 and 3	$3.5 \times 10^{-3}$	$8.2 \times 10^{-3}$

#### 4.2. Interactions bottom ash–methyl mercaptan and bottom ash–dimethyl sulphide

Even if methyl mercaptan and dimethyl sulphide belong to the same chemical family, their physical and chemical characteristics are quite different: methyl mercaptan can be ionised in some conditions. Its  $pK_a$  value is approximately 10 and, at basic pH, it is highly dissociated. Consequently, as  $H_2S$ , it can take part in acid–basic reactions when in presence of a strong base such as  $Ca(OH)_2$  that can be found in pore water. Therefore, methyl mercaptan is probably retained in bottom ash via chemical acid–basic reactions and sulphur from methyl mercaptan is probably also stabilised under solid form.

As concerns dimethyl sulphide, it is a symmetrical non-polar (or slightly polar) molecule, which cannot release a proton. Consequently, there is a weak affinity for polar water, and it is difficult to imagine any chemical interactions with bottom ash. Thus, dimethyl sulphide retention could be due to physical adsorption phenomena. This is only a hypothesis, in accordance with experimental results (Fig. 5) that showed a lower retention factor than for methyl mercaptan.

#### 5. Complementary experiments: interactions bottom ash– $CH_4$ and bottom ash– $CO_2$

The interactions between bottom ash and methane and between bottom ash and carbon dioxide were studied via two separate experiments: experiment 5 for  $CH_4$  (during experiment 5, methyl mercaptan and dimethyl sulphide were also studied) and experiment 8 for  $CO_2$  (Table 1). As methane and carbon dioxide are the main constituents of landfill gas, these two experiments can bring useful information in view of a field scale implementation of this landfill gas purification process directly in the landfill cells, and especially in the case where the treated landfill gas is used for energy purposes.

##### 5.1. Interactions bottom ash– $CH_4$

With respect to the interactions between bottom ash and methane, no figure is presented since methane concentration was the same upstream and downstream of the bottom ash bed.

So we can assert that methane is not retained by bottom ash. There will not be any lowering of landfill gas energetic content after purification with bottom ash.

Methane is a non-polar compound and its solubility in water is low. For these reasons, it is not surprising that it is not retained by bottom ash: there is no reason why it should interact with bottom ash mineral compounds.

##### 5.2. Interactions bottom ash– $CO_2$

The evolution of  $CO_2$  retention factor versus time is illustrated in Fig. 6.  $CO_2$  concentration in landfill gas upstream the column was constant and equal to 379,000 ppmV ( $\approx 38\%$  v/v).

As is shown in Fig. 6, carbon dioxide is partially trapped by bottom ash within several hours. The retention factor falls until it is equal to zero. It seems obvious that the bottom ash load is rapidly saturated. After a few hours (less than 5 h),  $CO_2$  is no longer retained.

$CO_2$  sequestration mechanism is now well known under the name of carbonation reaction: when landfill gas goes through bottom ash bed, bottom ash is subjected to an accelerated carbonation phenomenon (similar effects as natural ageing occurring during a much longer period in the presence of atmospheric  $CO_2$  on weathering areas).

Carbonation mechanism is often described as an at least two step process including a prior  $CO_2$  absorption in bottom ash pore

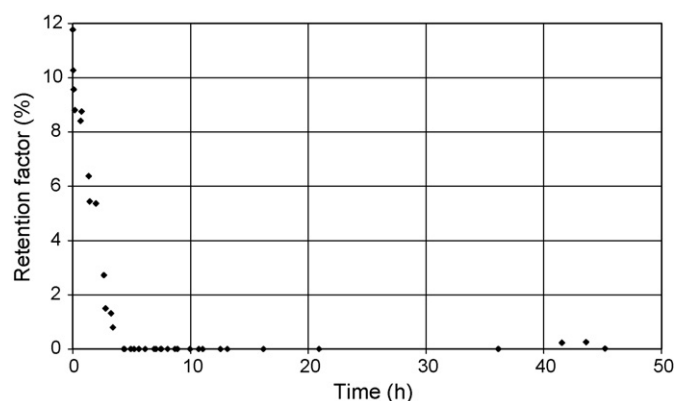
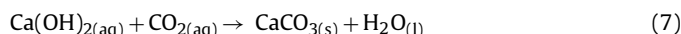


Fig. 6.  $CO_2$  retention factor versus time (experiment 8).

water, followed by the carbonation reaction in aqueous medium:  $CO_2$  reacts with some components of MSWI bottom ash (calcium or other cations) to produce carbonated species. The main reaction is known to be the portlandite ( $Ca(OH)_2$ ) carbonation, which corresponds to the following expression [1,13,17]:



In this way,  $CO_2$  is sequestered under carbonate forms. This reaction is irreversible. This leads to an important comment: Fig. 6 shows that bottom ash is totally carbonated after about 5 h. But in experiments concerning  $H_2S$ ,  $CH_3-SH$  and  $CH_3-S-CH_3$  (Figs. 3 and 5), no specific retention factor decrease could be observed during or after these 5 h. This means, in an obvious way, that the rapid and complete carbonation of bottom ash in the few contact hours with landfill gas does not modify its capacity for landfill gas purification towards  $H_2S$ ,  $CH_3-SH$  and  $CH_3-S-CH_3$ . This is an important remark from the view point of field scale implementation. As a matter of fact, it will be possible to use either fresh bottom ash or weathered (and already partly or completely carbonated) bottom ash.

The volume of trapped  $CO_2$  per bottom ash kg was calculated. We found that 6 L (11 g) of  $CO_2$  were trapped by 1 kg of bottom ash. Two studies performed at LGCIÉ concerning accelerated carbonation of bottom ash with pure  $CO_2$  [24,25] gave similar results: in very different conditions and with bottom ash coming from the same MSWI plant, the volume of trapped  $CO_2$  per bottom ash kg was in the same order of magnitude.

#### 6. Conclusion

This study links the two most commonly used management methods for municipal solid waste in Europe: landfilling and incineration. MSWI bottom ash was able to remove part of hydrogen sulphide, methyl mercaptan, and dimethyl sulphide from a real landfill gas.

Within the context of a real scale implementation of this process with bottom ash layers laid directly in landfill cells, results are satisfactory since the landfill gas energetic content will not be lowered (methane is not retained by bottom ash) and either fresh or carbonated bottom ash can be used. The quantity of retained hydrogen sulphide, methyl mercaptan and dimethyl sulphide was calculated to be 3.0, 0.044 and 0.086 g, respectively, but, as experiments were stopped before bottom ash saturation, probably more of these compounds can be trapped. Moreover, the retention factors will probably be higher since contact time will be better in a landfill cell than in the pilot plant. These results will allow us to design a full-scale landfill gas treatment process using MSWI bottom ash for the removal of hydrogen sulphide, methyl mercaptan and dimethyl sulphide.

## Acknowledgements

We wish to thank Novergie and Elyo-Cylergie for financial support and fruitful discussion. We are also grateful to Biovale and Satrod for letting us experiment on the landfill site and for technical assistance.

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