



# Design and scale-up of an oxidative scrubbing process for the selective removal of hydrogen sulfide from biogas

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## ABSTRACT

Reliable and selective removal of hydrogen sulfide ( $H_2S$ ) is an essential part of the biogas upgrading procedure in order to obtain a marketable and competitive natural gas substitute for flexible utilization. A promising biogas desulfurization technology has to ensure high separation efficiency regardless of process conditions or  $H_2S$  load without the use or production of toxic or ecologically harmful substances. Alkaline oxidative scrubbing is an interesting alternative to existing desulfurization technologies and is investigated in this work. In experiments on a stirred tank reactor and a continuous scrubbing column in laboratory-scale,  $H_2S$  was absorbed from a gas stream containing large amounts of carbon dioxide ( $CO_2$ ) into an aqueous solution prepared from sodium hydroxide ( $NaOH$ ), sodium bicarbonate ( $NaHCO_3$ ) and hydrogen peroxide ( $H_2O_2$ ). The influence of pH, redox potential and solution aging on the absorption efficiency and the consumption of chemicals was investigated. Because of the irreversible oxidation reactions of dissolved  $H_2S$  with  $H_2O_2$ , high  $H_2S$  removal efficiencies were achieved while the  $CO_2$  absorption was kept low. At an existing biogas upgrading plant an industrial-scale pilot scrubber was constructed, which efficiently desulfurizes  $180\text{ m}^3/\text{h}$  of raw biogas with an average removal efficiency of 97%, even at relatively high and strongly fluctuating  $H_2S$  contents in the crude gas.

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## 1. Introduction

Biogas is a renewable and sustainable energy source which is produced by the anaerobic fermentation of organic matter. The common technology to use this energy source is the production of combined heat and power in internal combustion engines. An alternative approach developed in recent years is biogas upgrading and its utilization as a natural gas substitute in households and industry or as a vehicle fuel [1,2]. Although in recent years several biogas-upgrading procedures have been developed, much optimization effort still has to be done in order to turn upgraded biogas into a marketable and competitive energy carrier.

This work deals with the removal of hydrogen sulfide ( $H_2S$ ), an important step in the biogas upgrading procedure.  $H_2S$  is a toxic, malodorous and sour gas, which is typically limited to a few ppm in the natural gas grids (e.g. in Austria this limit is  $5\text{ mg}/\text{m}^3_{\text{STP}}$ ). Well developed processes for  $H_2S$  removal that are applied in the processing of coke gas, gasification gas, natural gas or in the petrochemical industry often require high temperature and pressure as

well as bulky constructions that are hard to scale down. A promising technology for biogas desulfurization should, on the other hand, provide a reliable and selective removal of varying  $H_2S$  loads at moderate process conditions using cheap and ecologically harmless reagents. Also, no toxic or ecologically harmful components should be produced and the construction should be designed in a compact and simple way.

A well-known method in the biogas upgrading technology is the biological conversion of  $H_2S$  to elemental sulfur and sulfate using the species *Thiobacilli* in biological scrubbers [3,4]. This technology meets the above-mentioned criteria owing to its low operational costs and harmless reagents and products, as biological scrubbers can be operated with air as the only reactant. However, a drawback is the high sensitivity of the bacteria to changing process conditions like the change of temperature or fluctuations in the  $H_2S$  content of the crude gas. As a result, this method is not able to guarantee constant and high removal efficiencies.

Another popular biogas desulfurization method is the adsorption on metal oxides or activated carbon [5,6]. With these methods, very low  $H_2S$  contents in the sweetened gas ( $<1\text{ ppm}$ ) can be achieved. However, at higher  $H_2S$  contents in the crude gas the adsorption material has to be changed frequently due to sulfurous precipitations on its surface, which results in high operational costs.

Alternatively,  $H_2S$  can be removed by absorption into a liquid scrubbing solution (Eq. (1)).  $H_2S$  is a sour gas which dissociates in water in two steps as shown in Eqs. (2) and (3), each time releasing

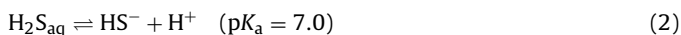
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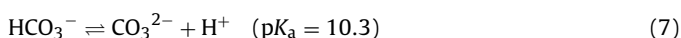
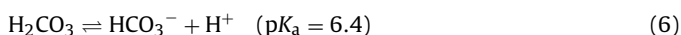
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one equivalent of protons. By adding a certain amount of base to the liquid, the produced protons can be removed. As a consequence, the equilibria are shifted to the right, resulting in an increased H<sub>2</sub>S absorption rate.



Depending on the kind of base used, one can distinguish between two technologies. The first one is the amine scrubbing process using ethanolamines (diethanolamine, methyl diethanolamine, diisopropanolamine) for alkalinity [7–9]. This method is well established and mostly applied for combined H<sub>2</sub>S and carbon dioxide (CO<sub>2</sub>) absorption in natural gas processing or in the treatment of refinery off-gases. The scrubbing solution loaded with sulfide ions needs to be regenerated in a desorption unit at elevated temperature. The desorbed gas is treated in a Claus plant where H<sub>2</sub>S is converted to elemental sulfur [10]. This configuration is rather complex and does not scale down well. As a result, it is not suitable for low-size biogas upgrading tasks because of the high specific costs. Moreover, in typical biogas plants all the energy needed to provide elevated temperatures has to be supplied externally, as there is not enough industrial waste heat to be used.

Another approach is the alkaline absorption into a solution of an inorganic base [11–17]. An issue to be considered in alkaline absorption processes used for biogas desulfurization is the concurrent absorption of CO<sub>2</sub>, which exists in biogas in much higher concentrations than H<sub>2</sub>S and shows similar acidic behavior. Absorption, hydrolysis and dissociation of CO<sub>2</sub> in water are shown in Eqs. (4)–(7). The pK<sub>a</sub> values in Eq. (6) (first dissociation step of H<sub>2</sub>CO<sub>3</sub>) and Eq. (2) (first dissociation step of H<sub>2</sub>S) are similar, thus H<sub>2</sub>S and CO<sub>2</sub> absorption proceed at similar pH values. The CO<sub>2</sub> absorption leads to a consumption of large amounts of base and, therefore, high operational costs.

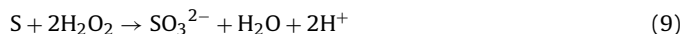
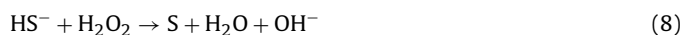


It is known that H<sub>2</sub>S absorption occurs faster than CO<sub>2</sub> absorption, as CO<sub>2</sub> undergoes a slow hydrolyzing step [10,13] that is given in Eq. (5). This fact can be used to increase the selectivity towards H<sub>2</sub>S by minimizing the contact time between gas and liquid [11,13,15]. The drawback of this method is that increasing selectivity is typically accompanied by lowered removal efficiencies of H<sub>2</sub>S.

If an oxidizing agent is added to the scrubbing solution, both H<sub>2</sub>S selectivity and removal efficiency can be improved. Since H<sub>2</sub>S is a reducing gas, its dissociation products are oxidized and selectively removed from the dissociation equilibrium by irreversible reactions. A number of oxidizing agents can be used for this application: ferric ions [18–20], sodium hypochlorite (NaOCl) [17] or hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) [16]. In this work H<sub>2</sub>O<sub>2</sub> was used, as it is a cheap and widely available chemical that is easy to handle and does not require elaborate safety measures. A stabilizer is necessary in order to inhibit H<sub>2</sub>O<sub>2</sub> decomposition [16,21–23].

During the oxidation process, the sulfur atom passes through several oxidation states. In the first step the HS<sup>-</sup> ions are oxidized to elemental sulfur consuming one equivalent of H<sub>2</sub>O<sub>2</sub>, as shown in Eq. (8). The produced elemental sulfur can react with two equivalents of H<sub>2</sub>O<sub>2</sub> to form sulfite (SO<sub>3</sub><sup>2-</sup>), which can subsequently be oxidized to sulfate (SO<sub>4</sub><sup>2-</sup>), consuming another equivalent of H<sub>2</sub>O<sub>2</sub>

(Eqs. (9) and (10)). Additionally, elemental sulfur can react with sulfite to form thiosulfate (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>), as shown in Eq. (11). According to Couvert et al. [17], elemental sulfur, sulfate and thiosulfate are stable oxidation products and can be found in the liquid phase. Sulfite cannot be found in the liquid phase, it is an unstable intermediate for the formation of sulfate and thiosulfate.



In this study an aqueous solution of sodium hydroxide (NaOH), sodium bicarbonate (NaHCO<sub>3</sub>) and H<sub>2</sub>O<sub>2</sub> was used as a scrubbing solution for the H<sub>2</sub>S absorption. In the first step, the general behavior of the absorption process was investigated in a discontinuous stirred tank reactor in laboratory-scale. After the method had proven to be efficient in terms of H<sub>2</sub>S removal, a continuous absorption column was built in laboratory-scale for further experiments and optimization. An industrial-scale pilot scrubber was constructed at an existing biogas upgrading plant, which now efficiently desulfurizes 180 m<sup>3</sup>/h of raw biogas. As only stable oxidation products (sulfur, sulfate, thiosulfate) are present in the liquid phase, it can be fed back to the fermenter and discharged together with the digestate.

## 2. Materials and methods

### 2.1. Stirred tank reactor

A gas stream containing 50% (v/v) CO<sub>2</sub> and 1040 ppmv H<sub>2</sub>S with methane (CH<sub>4</sub>) being the balance was brought in contact with the liquid (an aqueous solution of NaOH and H<sub>2</sub>O<sub>2</sub>) and circulated through the system until all H<sub>2</sub>S was absorbed. Then the system was emptied from the remnant gas and filled with a new dose of gas mixture containing H<sub>2</sub>S. Each experiment was terminated when the capacity of the scrubbing solution was reached, i.e. when there was no further absorption of H<sub>2</sub>S.

Dosage and mixing of the gases was done by mass flow controllers (type 5850S from Brooks Instruments, controlled by RS 485 digital). A mass spectrometer (type GSD 300 T2 Thermostar from Balzers Instruments) was used for gas analysis. Redox potential and pH of the liquid were measured by dual-chamber electrodes (JUMO tecLine equipped with KCl/KCl-bridge and temperature compensation by a Pt100-sensor). Signal conversion and data acquisition was done by PLC and computer software provided by GE-FANUC. Fig. 1 shows the flowsheet of the process. The operating parameters are shown in Table 1.

The aim of the experiments on the stirred tank reactor was to observe the influence of pH and redox potential on the absorption of H<sub>2</sub>S and CO<sub>2</sub>. The change of absorption behavior due to

**Table 1**

Operating parameters of the stirred tank reactor. Specifications of liquid and gas compositions are given as the initial conditions for each experiment.

System volume (without bag)	6.9 L
Bag volume	7 L
Liquid volume	1 L
CO <sub>2</sub> content (gas)	50% (v/v)
H <sub>2</sub> S content (gas)	1040 ppmv
NaHCO <sub>3</sub> concentration (liq.)	0–90 kg/m <sup>3</sup>
NaOH concentration (liq.)	0.15 kg/m <sup>3</sup>
H <sub>2</sub> O <sub>2</sub> concentration (liq.)	0.15 kg/m <sup>3</sup>
Gas–liquid contact area	0.07 m <sup>2</sup>
Operating temperature	298 K
Operating absolute pressure	≈10 <sup>5</sup> Pa

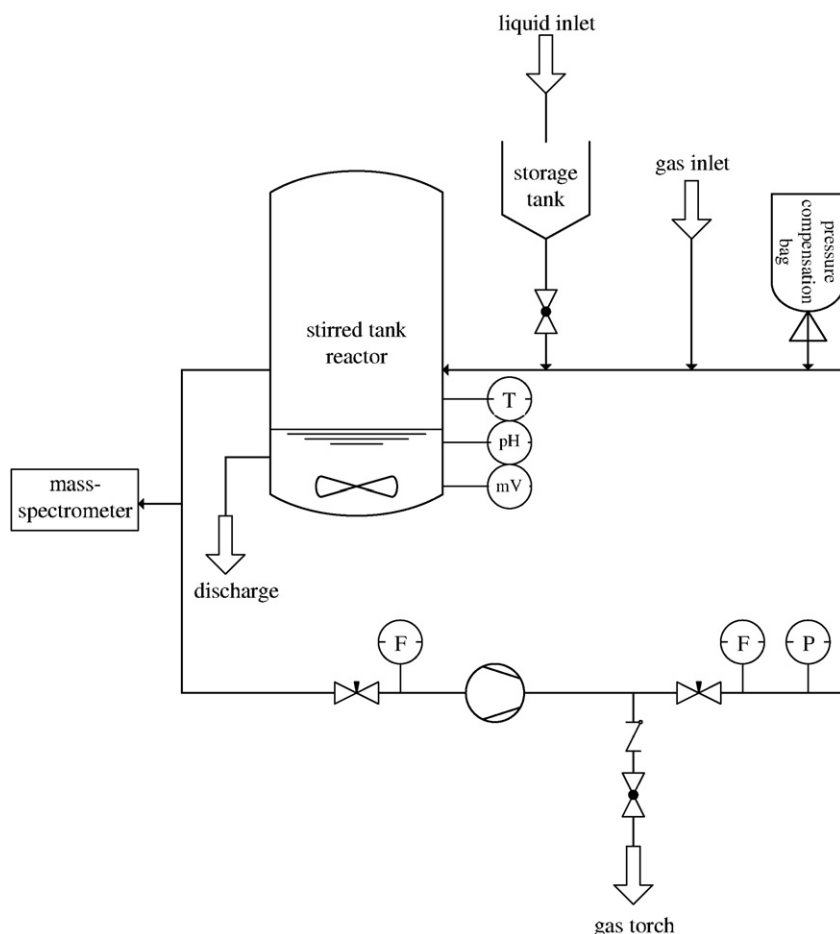


Fig. 1. Flowsheet of the stirred tank reactor.

increasing concentrations of sulfate ( $\text{SO}_4^{2-}$ ) and bicarbonate ( $\text{HCO}_3^-$ ) ions with the aging of the liquid was also investigated. Therefore, the scrubbing solution was reused for all experiments. The absorption capacity was restored after each run by adding a new amount of NaOH and  $\text{H}_2\text{O}_2$  in order to reach the respective starting condition of  $0.15 \text{ kg/m}^3$  in the scrubbing solution (see Table 1). The electrical conductivity of the solution was measured (with a GMH 3430 sensor from GREISINGER electronic) previously to each experiment, as a criterion for the total ion concentration. For some experiments, additional amounts of sodium bicarbonate ( $\text{NaHCO}_3$ ) and sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) were added in order to test the absorption at higher values of electrical conductivities (up to  $74.4 \text{ mS/cm}$ ), as they are possible to occur during a continuous process without a frequent exchange of the scrubbing solution. It could be observed that the aging of the scrubbing solution lead to a better absorption behavior due to the increasing buffer capacity with increasing concentration of  $\text{NaHCO}_3$ , which forms carbonic acid ( $\text{H}_2\text{CO}_3$ ) by taking up protons (backward reaction in Eq. (6)). This phenomenon will be further discussed in Section 3.

## 2.2. Laboratory scrubbing column

The second set of experiments was done on a continuous packed scrubbing column in laboratory-scale. In these experiments the same gas mixture was used as in the experiments on the stirred tank reactor. The gas stream passed through the column continuously and was subsequently burned in a gas torch. The scrubbing solution circulated in a closed loop through the column and the storage tank. Eventually,  $\text{H}_2\text{O}_2$  was added with a syringe, while an

equal amount of liquid was discharged. The analytic devices were the same as in the experiments on the stirred tank reactor. The mass spectrometer was used to analyze the outlet gas. Redox potential, pH and electrical conductivity were measured in the storage tank. Fig. 2 shows the flowsheet of the process. The operating parameters are shown in Table 2.

The aim of the experiments on the continuous absorber was to obtain process control parameters that can ensure an effective  $\text{H}_2\text{S}$  absorption while keeping the consumption of chemicals low. At the beginning of the experiments, the scrubbing solution had a concentration of  $80 \text{ kg/m}^3$   $\text{NaHCO}_3$  and an electrical conductivity of about  $45 \text{ mS/cm}$ . This value was chosen based on the results from the stirred tank reactor. It was assumed to be close to the values reached in a large-scale absorber at continuous operation. In order

Table 2

Operating parameters of the scrubbing column. The  $\text{NaHCO}_3$  concentration is given as the initial concentration of each experiment. The  $\text{H}_2\text{O}_2$  concentration refers to the amount periodically added to the scrubbing solution.

Gas flow rate	$0.48 \text{ m}_{\text{STP}}^3/\text{h}$
Liquid flow rate	$0.02 \text{ m}^3/\text{h}$
Column diameter	0.1 m
Active height	0.4 m
$\text{CO}_2$ content (crude gas)	50% (v/v)
$\text{H}_2\text{S}$ content (crude gas)	1040 ppmv
$\text{NaHCO}_3$ concentration (liq.)	$80 \text{ kg/m}^3$
NaOH concentration (liq.)	Not used
$\text{H}_2\text{O}_2$ concentration (liq.)	$0.1\text{--}1.4 \text{ kg/m}^3$
Specific area (packing material)	$300 \text{ m}^2/\text{m}^3$
Operating temperature	298 K
Operating absolute pressure	$\approx 10^5 \text{ Pa}$

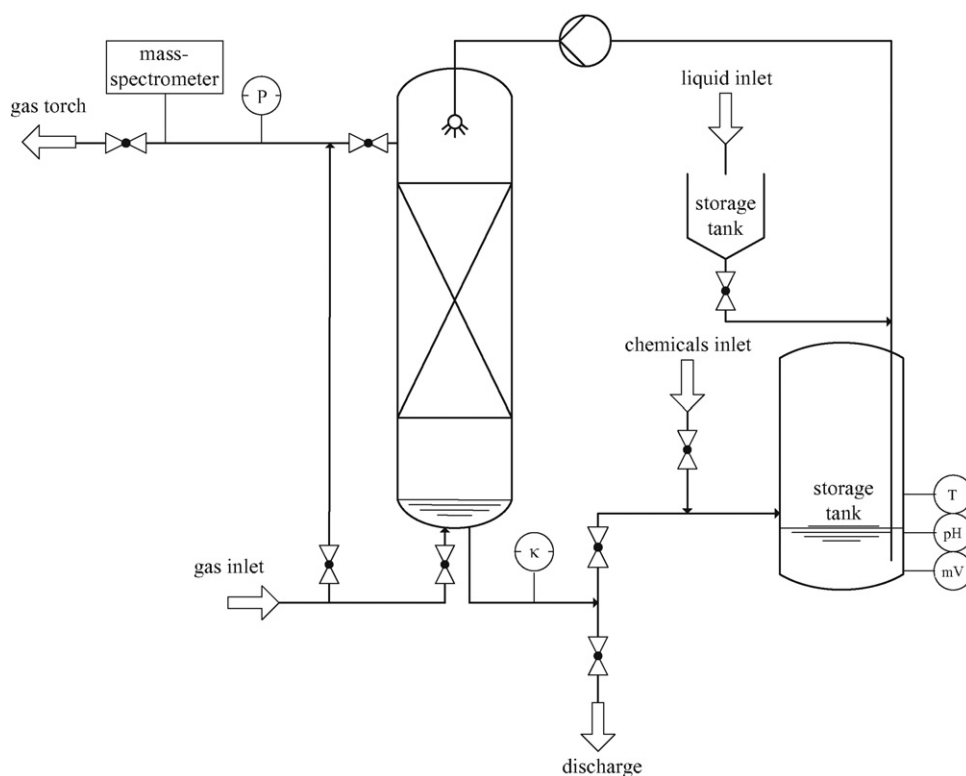


Fig. 2. Flowsheet of the laboratory plant.

to investigate the influence of the  $\text{H}_2\text{O}_2$  concentration on the  $\text{H}_2\text{S}$  absorption, different amounts of  $\text{H}_2\text{O}_2$  were added periodically by injection, whenever a complete  $\text{H}_2\text{S}$  absorption no longer occurred, i.e. the  $\text{H}_2\text{O}_2$  became depleted. There was no need to add  $\text{NaOH}$ , as the solution was strongly buffered by  $\text{NaHCO}_3$  and the pH value was constant on approximately the same level within 8 hours of experiment.

### 2.3. Pilot plant

The industrial-scale pilot plant was constructed at an existing biogas upgrading plant for the desulfurization of  $180 \text{ m}^3/\text{h}$  of raw biogas. Fig. 3 shows the flowsheet of the absorber. The operating parameters are shown in Table 3. The criteria of similarity considered during the process of scale-up were the residence time of the gas in the column, the ratio between gas and liquid flow rate, the ratio between column diameter and column height as well as the specific surface area of the packing material. The dosage of  $\text{NaOH}$  and  $\text{H}_2\text{O}_2$  is carried out through a regulation of pH and redox potential, respectively. The electrical conductivity of the scrubbing solution is controlled by a periodical discharge of scrubbing solution and replacement with fresh water through level control.

In order to obtain some data on the separation efficiency of the pilot plant, the contents of  $\text{H}_2\text{S}$  at the inlet and the outlet of the

plant were measured by the plant operators for several months. The measurements were performed using a portable gas analyzer BM2000 provided by GSI. Due to technical reasons the collection of data at the pilot plant was done irregularly. The collected values for the consumption of chemicals are hourly averages, while the  $\text{H}_2\text{S}$  content was measured at certain time instants. The separation efficiency is defined as the difference in  $\text{H}_2\text{S}$  content between the inlet and the outlet divided by the  $\text{H}_2\text{S}$  content at the inlet of the scrubber. The specific consumption of chemicals is defined as the molar amount of the consumed pure reagent divided by the molar amount of the separated  $\text{H}_2\text{S}$ .

The constructed pilot plant is used as a desulfurization step in connection with the biogas upgrading process based on membrane gas permeation technology [2]. The task of this process combination is the production of natural gas substitute and supply to a public gas grid.

## 3. Results and discussions

### 3.1. General behavior

Exemplary results obtained in an absorption process on the laboratory column are shown in Fig. 4. At the beginning of the experiment the  $\text{H}_2\text{S}$  content in the sweetened gas was zero because of an alkaline absorption into the  $\text{NaHCO}_3$  solution as shown in Eqs. (1)–(3). At the same time  $\text{CO}_2$  was absorbed into the liquid, which could be observed by the lowered  $\text{CO}_2$  content of about 49% (v/v). This led to a decrease of pH due to Eqs. (4)–(7). After about 10 minutes the equilibrium was reached and no more  $\text{H}_2\text{S}$  or  $\text{CO}_2$  could be absorbed. As a result,  $\text{H}_2\text{S}$  could be observed in the sweetened gas. The subsequent addition of  $\text{H}_2\text{O}_2$  resulted in the oxidation of  $\text{HS}^-$  ions as shown in Eqs. (8)–(10). At this point, the  $\text{H}_2\text{S}$  content in the sweetened gas began to decrease rapidly. The increased oxidation potential of the scrubbing solution was indicated by the redox signal, which peaked from approximately  $-390 \text{ mV}$  to

Table 3  
Operating parameters of the pilot plant.

Gas flow rate	$180 \text{ m}^3_{\text{STP}}/\text{h}$
Liquid flow rate	$7.9 \text{ m}^3/\text{h}$
Column diameter	0.71 m
Active height	3 m
$\text{CO}_2$ content (gas)	30–50% (v/v)
$\text{H}_2\text{S}$ content (gas)	$\leq 3000 \text{ ppmv}$
Specific area (packing material)	$300 \text{ m}^2/\text{m}^3$
Operating temperature	298–313 K
Operating absolute pressure	$\approx 10^5 \text{ Pa}$

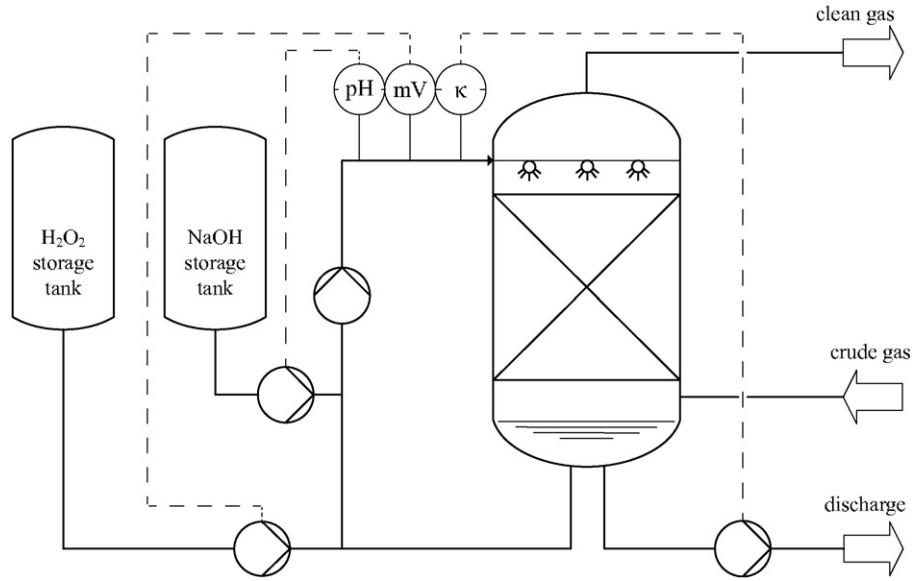


Fig. 3. Flowsheet of the pilot plant.

higher values depending on the added amount of H<sub>2</sub>O<sub>2</sub>. As the absorption proceeded, H<sub>2</sub>O<sub>2</sub> was consumed and the redox potential gradually decreased. If higher amounts of H<sub>2</sub>O<sub>2</sub> were added, the redox potential remained at the saturation value of approximately 180 mV, as in Fig. 4 at process times of 6000 s and above. The continuous absorption of H<sub>2</sub>S caused a gradual decrease of redox potential down to a value of about 90 mV, then a rapid decrease started, indicating that the H<sub>2</sub>O<sub>2</sub> became depleted. A minimum value between –370 and –390 mV was reached when there was no H<sub>2</sub>O<sub>2</sub> present in the solution. H<sub>2</sub>S absorption still occurred until the equilibrium of Eqs. (1)–(3) was reached. Then the H<sub>2</sub>S content in the sweetened gas began to increase. This behavior proves a correlation between the redox potential and H<sub>2</sub>S absorption of the solution. For a better visualization of this correlation, Fig. 5 shows the column volume specific H<sub>2</sub>S absorption rate  $r''_{H_2S}$  and the redox potential over the course of the process. The maximum rate of  $4.4 \times 10^{-5} \text{ m}^3/\text{m}^3\text{s}$  was achieved independently of the exact amount of H<sub>2</sub>O<sub>2</sub>, as long as the redox potential was above around 100 mV.

The CO<sub>2</sub> absorption, on the other hand, is not influenced by the redox potential. As one can see in Fig. 4, the CO<sub>2</sub> content in the sweetened gas levels off at 50% (v/v) in the course of the process.

HCO<sub>3</sub><sup>-</sup> ions cannot be further oxidized and are not removed from the dissociation equilibrium. Therefore, the problem of strong pH decrease and high NaOH consumption due to CO<sub>2</sub> absorption occurs only at the beginning of the experiment until the chemical equilibrium is reached. Then the decrease in pH is mainly caused by the H<sub>2</sub>S absorption, which results in a much smaller slope. This behavior provides the main advantage of the proposed method. By adjusting the pH just high enough for H<sub>2</sub>S to dissolve and by constantly removing the sulfide ions from the equilibrium with H<sub>2</sub>O<sub>2</sub>, a high selectivity can be achieved without a reduction of the absorption efficiency.

### 3.2. Influence of solution aging

The influence of solution aging on the absorption behavior was mainly studied during the experiments on the stirred tank reactor. At the start of each experiment, the same amounts of NaOH and H<sub>2</sub>O<sub>2</sub> were added to the reused scrubbing solution. The contents of Na<sub>2</sub>SO<sub>4</sub> and NaHCO<sub>3</sub> increased from run to run, the latter providing a pH buffer with increasing strength. This is shown in Fig. 6, where the change of pH during the progress of different runs

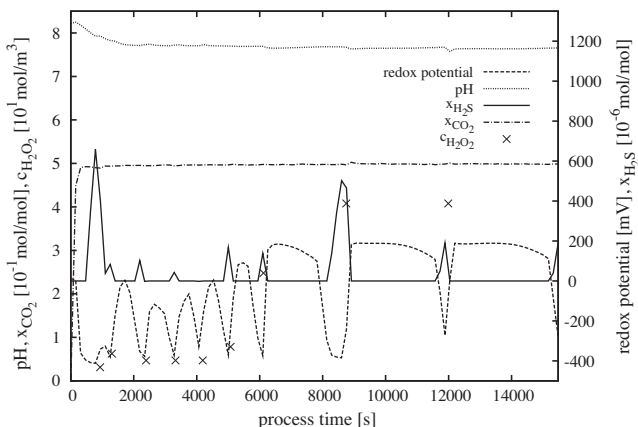


Fig. 4. Absorption behavior on the laboratory column.

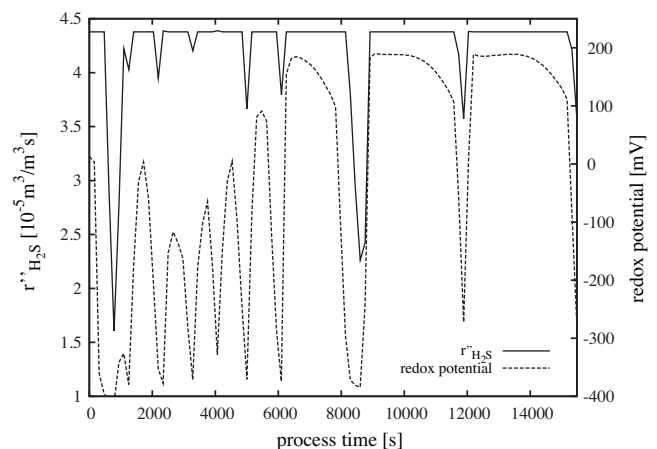


Fig. 5. Correlation between the redox potential and the H<sub>2</sub>S absorption rate.



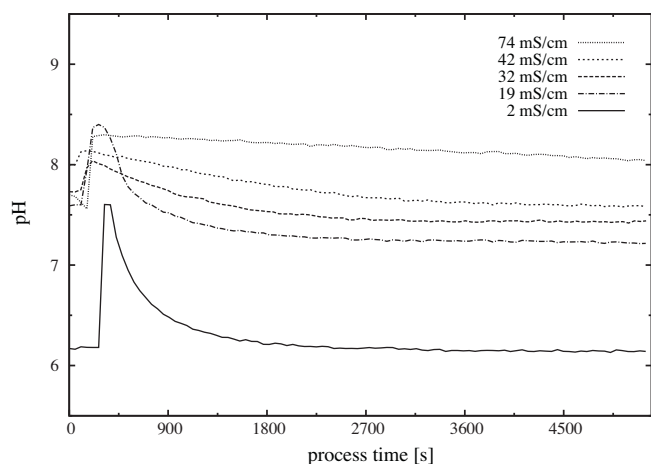


Fig. 6. Change of pH during the progress of selected experiments on the stirred tank reactor.

Table 4

H<sub>2</sub>S absorption velocities for scrubbing solutions with different electrical conductivities.

$\kappa$ [mS/cm]	pH	$r'_{\text{H}_2\text{S}}$ [ $\text{m}^3/\text{m}^2 \text{ s}$ ]
2.1	6.1	$4.0 \times 10^{-8}$
18.8	7.4	$1.0 \times 10^{-7}$
31.8	7.6	$2.0 \times 10^{-7}$
42.0	7.9	$4.4 \times 10^{-7}$
74.4	8.2	$2.5 \times 10^{-7}$

is displayed. Both the rapid increase with the addition of freshly recovered solution and the decline due to H<sub>2</sub>S and CO<sub>2</sub> absorption were damped by increasing NaHCO<sub>3</sub> concentrations (increasing electrical conductivities in Fig. 6). Also, the average operating pH increased with the electrical conductivity of the scrubbing solution, as shown in Fig. 7. This behavior illustrates the advantage of adjusting the pH with NaHCO<sub>3</sub> instead of NaOH, as NaOH is quickly consumed by reaction with CO<sub>2</sub>, while NaHCO<sub>3</sub>, as the product of CO<sub>2</sub> dissociation, shifts Eq. (6) to the left and counteracts CO<sub>2</sub> absorption.

Table 4 shows the average electrical conductivities of experiments performed with different amounts of added NaHCO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub>, the respective average pH and the respective average H<sub>2</sub>S absorption velocities based on the interfacial area  $r'_{\text{H}_2\text{S}}$ . The absorption velocities were calculated from the time needed for

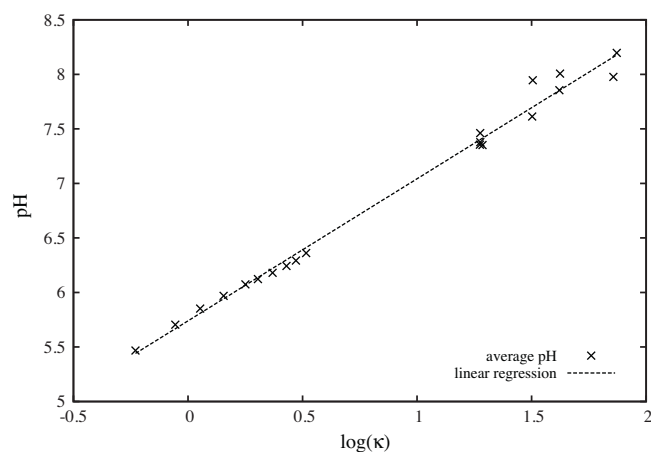


Fig. 7. Correlation between the average pH and the electrical conductivity of the scrubbing solution.

a defined volume of H<sub>2</sub>S to be absorbed into the scrubbing solution. Generally, an increase of the H<sub>2</sub>S absorption rate with increasing electrical conductivity (and, therefore, increasing average pH) could be observed. This phenomenon was to be expected, as the equilibria of Eqs. (1)–(3) are shifted to the right with increasing pH (see Section 1). However, a lower absorption rate was observed during the experiments performed at an average electrical conductivity of 74.4 mS/cm. This might be caused by a limitation in mass transfer because of the high ionic strength of the liquid. The highest absorption rates were achieved with electrical conductivities of the scrubbing solution between 40 and 45 mS/cm. Therefore, this range of electrical conductivity was chosen for the experiments on the laboratory scrubbing column.

### 3.3. Process control parameters

From the experiments on the stirred tank reactor and the laboratory column, the following conclusions considering H<sub>2</sub>S absorption could be drawn:

- Reasonable H<sub>2</sub>S absorption could be observed for all tested pH values from 6.1 to 8.2.
- Higher concentrations of NaHCO<sub>3</sub> in the solution buffer the pH, which leads to higher absorption rates and a lower consumption of base.
- As long as there is enough H<sub>2</sub>O<sub>2</sub> in the solution, the redox potential has a value of above 100 mV. When H<sub>2</sub>O<sub>2</sub> becomes depleted, the redox potential rapidly drops below zero.
- This rapid decline, which starts reproducibly around 90 mV, is always coupled with the shortage of H<sub>2</sub>O<sub>2</sub> and the termination of H<sub>2</sub>S absorption.

Therefore, the approach for the second set of experiments on the laboratory column was to ensure complete H<sub>2</sub>S absorption at any time by keeping the pH above 6.1 and the redox potential above 100 mV. The scrubbing solution used was again a NaHCO<sub>3</sub> solution with an electrical conductivity in the range of 45 mS/cm. This buffer was strong enough to keep the pH above 7.7 for the whole period of continuous absorption (more than 8 h). Different amounts of H<sub>2</sub>O<sub>2</sub> were injected, whenever the redox potential dropped down to 100 mV. With this method, virtually complete H<sub>2</sub>S absorption could, in fact, be ensured at any time. The H<sub>2</sub>S content in the sweetened gas remained below the limit of detection during the whole process, i.e. in ppb range.

### 3.4. H<sub>2</sub>O<sub>2</sub> consumption

In the experiments on the laboratory column, different amounts of H<sub>2</sub>O<sub>2</sub> were added at a time. This affected the specific H<sub>2</sub>O<sub>2</sub> consumption, i.e. the amount of H<sub>2</sub>O<sub>2</sub> consumed per amount of H<sub>2</sub>S absorbed. Fig. 8 shows the specific uptake averaged between the injection points ( $v_{\text{H}_2\text{O}_2}$ ) plotted over the initial H<sub>2</sub>O<sub>2</sub> concentration, i.e. the concentration at the time of injection. It is clearly noticeable that the specific H<sub>2</sub>O<sub>2</sub> consumption increases with the initial concentrations of H<sub>2</sub>O<sub>2</sub>.

This can be explained by the different possible oxidation states of sulfur during the oxidation of the HS<sup>-</sup> ion, as explained by means of Eqs. (8)–(11) in Section 1. Apparently, if the concentration of H<sub>2</sub>O<sub>2</sub> is very low, Eq. (8), where one equivalent of H<sub>2</sub>O<sub>2</sub> is consumed, predominates and elemental sulfur is the main oxidation product. With increasing amounts of H<sub>2</sub>O<sub>2</sub> the formations of sulfite and sulfate, that consume three or four equivalents of H<sub>2</sub>O<sub>2</sub>, respectively, become more prevalent, which leads to a higher consumption of H<sub>2</sub>O<sub>2</sub>. This issue was discussed and experimentally verified by Couvert et al. [17].

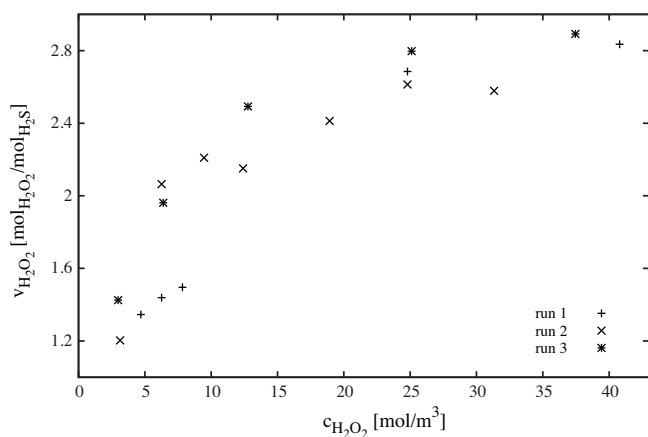


Fig. 8. Correlation between the consumption of  $\text{H}_2\text{O}_2$  and its concentration.

The lowest consumption of  $\text{H}_2\text{O}_2$  is theoretically obtained if only elemental sulfur is produced. Also, as can be seen in Eq. (8), the byproduct of sulfur formation is the hydroxide ion, which helps to stabilize the pH and, therefore, reduces the consumption of base. For the formation of sulfite and sulfate, the consumption of  $\text{H}_2\text{O}_2$  is three and four times higher, respectively. Besides, in Eq. (9) protons are produced, which leads to a higher consumption of base. On the other hand, elemental sulfur is hardly soluble in water and precipitates in pipes and on the packing material. The process time on the laboratory column was not long enough to observe problems related to these precipitations, like an increasing pressure drop due to plugging. Nevertheless, their occurrence can be expected at continuous operation of a large-scale plant and is also reported for other processes where elemental sulfur is produced [24]. The consequences are high predicted maintenance costs for emptying and cleaning pipes and packing material. Thiosulfate and sulfate have a better solubility in water. They can be discharged with the waste water and, therefore, are not likely to cause such precipitations.

It should be noted that  $\text{H}_2\text{O}_2$  decomposition, as described by Charron et al. [22] and Spalek et al. [23], can also be a possible explanation for the higher  $\text{H}_2\text{O}_2$  consumption at higher initial  $\text{H}_2\text{O}_2$  concentrations, as the use of a stabilizer cannot guarantee a complete inhibition of  $\text{H}_2\text{O}_2$  decomposition.

### 3.5. Pilot plant

The pilot plant was constructed and tested at a cofermentation biogas plant that utilized substrates of great variety. Therefore,

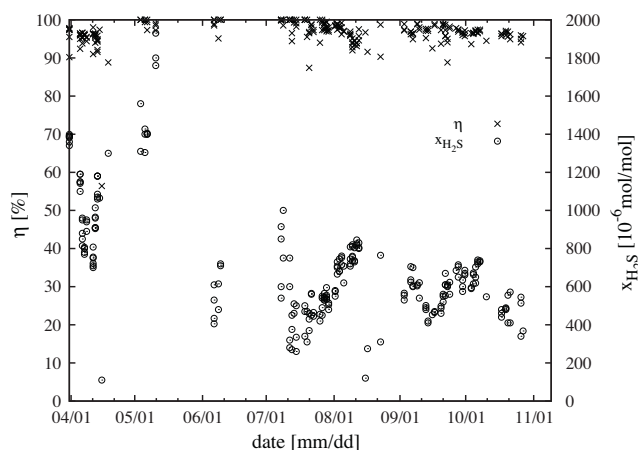


Fig. 9.  $\text{H}_2\text{S}$  content in the raw biogas and the separation efficiency of the pilot plant in a long-term test.

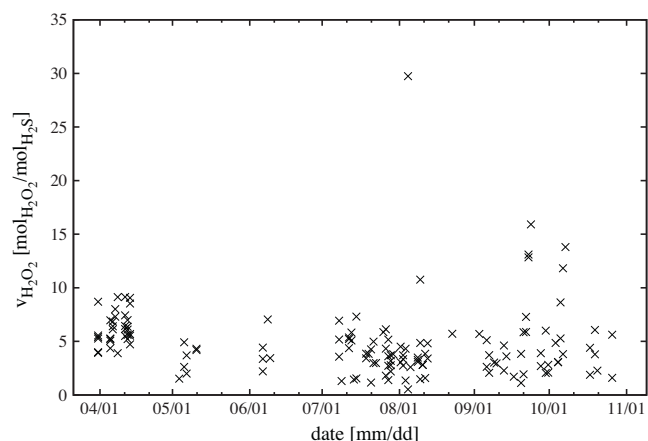


Fig. 10. Specific  $\text{H}_2\text{O}_2$  consumption in a long-term test on the pilot plant.

daily and monthly fluctuations in the  $\text{H}_2\text{S}$  content in the produced biogas were expected. Fig. 9 shows the collected data points on the separation efficiency  $\eta$  and the  $\text{H}_2\text{S}$  content in the raw biogas within a period of several months. It is noticeable that the plant was able to achieve high separation efficiencies, even if relatively high  $\text{H}_2\text{S}$  contents of up to 2000 ppmv were present in the raw biogas. Also, high fluctuations in the  $\text{H}_2\text{S}$  content did not influence the separation efficiency. The average separation efficiency calculated from the documented data points equals 97%.

Figs. 10 and 11 present the collected data points on the specific consumption of  $\text{H}_2\text{O}_2$  and  $\text{NaOH}$ , respectively. The majority of the points representing the  $\text{H}_2\text{O}_2$  consumption can be found in the range of up to  $10 \text{ mol}_{\text{H}_2\text{O}_2}/\text{mol}_{\text{H}_2\text{S}}$ . The average consumption calculated from the data points from the test period is equal to  $4.8 \text{ mol}_{\text{H}_2\text{O}_2}/\text{mol}_{\text{H}_2\text{S}}$ . This value is higher than the values reported in the laboratory experiments (see Fig. 8). It is also higher than the maximum possible stoichiometric amount of  $\text{H}_2\text{O}_2$  that is consumed if all  $\text{HS}^-$  is converted to  $\text{SO}_4^{2-}$  (i.e.  $4 \text{ mol}_{\text{H}_2\text{O}_2}/\text{mol}_{\text{H}_2\text{S}}$ ). The overconsumption might be caused by the loss of  $\text{H}_2\text{O}_2$  during the periodical exchange of the scrubbing solution or to the oxidation of other trace components present in the biogas (typical trace components in biogas are given in [25,26]). Also,  $\text{H}_2\text{O}_2$  decomposition can be a possible explanation, as described in Section 3.4. The average specific consumption of  $\text{NaOH}$  calculated from the collected data points equals  $6 \text{ mol}_{\text{NaOH}}/\text{mol}_{\text{H}_2\text{S}}$ .

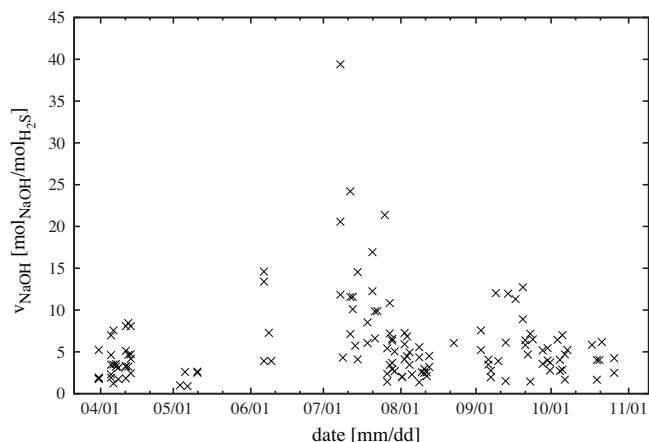


Fig. 11. Specific  $\text{NaOH}$  consumption in a long-term test on the pilot plant.

#### 4. Conclusions

Chemical oxidative absorption is a promising method for the H<sub>2</sub>S removal in the biogas upgrading process, since the irreversible oxidation reactions can guarantee constant and effective H<sub>2</sub>S removal, even at relatively high and strongly fluctuating H<sub>2</sub>S contents in the crude gas, while the CO<sub>2</sub> absorption and thus the consumption of base is kept low. Also, no harmful substances are produced during oxidation, thus the remnant liquid can be fed back into the fermenter and discharged with the digestate.

In the laboratory experiments, virtually complete H<sub>2</sub>S absorption could be ensured at any time by maintaining the pH above 7.7 and the redox potential above 100 mV. Investigations on the solution aging showed that the increasing content of HCO<sub>3</sub><sup>-</sup> ions, which were formed by the previously absorbed CO<sub>2</sub>, provided a pH buffer with increasing strength. Therefore, the aging of the solution had a positive effect on H<sub>2</sub>S absorption and NaOH consumption. However, at high ionic strength a decrease in absorption rates was observed, which can be attributed to limitations in mass transfer.

The H<sub>2</sub>O<sub>2</sub> consumption is directly proportional to the H<sub>2</sub>S content in the crude gas, but it can also be negatively influenced by the overdosage of H<sub>2</sub>O<sub>2</sub>. High concentrations of H<sub>2</sub>O<sub>2</sub> present in the solution lead to a higher specific uptake because the dissociated H<sub>2</sub>S is oxidized all the way to SO<sub>4</sub><sup>2-</sup>, while for low concentrations of H<sub>2</sub>O<sub>2</sub> in the solution elemental sulfur is the final oxidation product.

In the experiments on the pilot plant, high separation efficiencies (with an average of 97%) could be reached, despite strongly fluctuating H<sub>2</sub>S contents in the crude gas. The average H<sub>2</sub>O<sub>2</sub> consumption equaled 4.8 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>/mol<sub>H<sub>2</sub>S</sub>, which is higher than the values reported for the laboratory column (1.2–2.9 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>/mol<sub>H<sub>2</sub>S</sub>). It is also higher than the maximum theoretical consumption (4 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>/mol<sub>H<sub>2</sub>S</sub>). This overconsumption can be attributed to the oxidation of other trace components that are present in biogas, to the loss of the oxidizing agent during the periodical exchange of the scrubbing solution, or to a decomposition of H<sub>2</sub>O<sub>2</sub>. Future work includes the reduction of the specific H<sub>2</sub>O<sub>2</sub> consumption in the pilot plant through an optimized control system as well as optimization efforts in process design.

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#### References

[1] M. Miltner, A. Makaruk, M. Harasek, Application of gas permeation for biogas upgrade – operational experiences of feeding biomethane into the Austrian gas grid, in: Proceedings of 16th European Biomass Conference & Exhibition, Valencia, 2008, pp. 1905–1911.

[2] A. Makaruk, M. Miltner, M. Harasek, Membrane biogas upgrading processes for the production of natural gas substitute, *Sep. Purif. Technol.* 74 (2010) 83–92.

[3] D. Schieder, P. Quicker, R. Schneider, H. Winter, S. Prechtel, M. Faulstich, Microbiological removal of hydrogen sulfide from biogas by means of a separate biofilter system: experience with technical operation, *Water Sci. Technol.* 48 (2003) 209–212.

[4] D. Ramirez-Saenz, P.B. Zarate-Segura, C. Guerrero-Barajas, E.I. Garcia-Pena, H<sub>2</sub>S and volatile fatty acids elimination by biofiltration: clean-up process for biogas potential use, *J. Hazard. Mater.* 163 (2009) 1272–1281.

[5] Y. Xiao, S. Wang, D. Wu, Q. Yuan, Catalytic oxidation of hydrogen sulfide over unmodified and impregnated activated carbon, *Sep. Purif. Technol.* 59 (2008) 326–332.

[6] S. Pipatmanomai, S. Kaewluan, T. Vitidsant, Economic assessment of biogas-to-electricity generation system with H<sub>2</sub>S removal by activated carbon in small pig farm, *Appl. Energy* 86 (2009) 669–674.

[7] B.P. Mandal, A.K. Biswas, S.S. Bandyopadhyay, Selective absorption of H<sub>2</sub>S from gas streams containing H<sub>2</sub>S and CO<sub>2</sub> into aqueous solutions of N-methyldiethanolamine and 2-amino-2-methyl-1-propanol, *Sep. Purif. Technol.* 35 (2004) 191–202.

[8] J. Lu, Y. Zheng, D. He, Selective absorption of H<sub>2</sub>S from gas mixtures into aqueous solutions of blended amines of methyldiethanolamine and 2-tertiarybutylamino-2-ethoxyethanol in a packed column, *Sep. Purif. Technol.* 52 (2006) 209–217.

[9] H. Godini, D. Mowla, Selectivity study of H<sub>2</sub>S and CO<sub>2</sub> absorption from gaseous mixtures by MEA in packed beds, *Chem. Eng. Res. Des.* 86 (2008) 401–409.

[10] A.L. Kohl, R. Nielsen, *Gas Purification*, 5th ed., Gulf Publ. Co., Houston, TX, 1997.

[11] R. Heitz, A. Rocklin, Removal of other acid gases from mixtures containing carbon dioxide, US Patent 2,747,962, May 1956.

[12] G. Astarita, F. Gioia, Simultaneous absorption of hydrogen sulfide and carbon dioxide in aqueous hydroxide solutions, *Ind. Eng. Chem. Fund.* 4 (1965) 317–320.

[13] R.W. Hohlfeld, Selective absorption of H<sub>2</sub>S from sour gas, *J. Pet. Technol.* 32 (1980) 1083–1089.

[14] E. Bendall, R.C. Aiken, F. Mandas, Selective absorption of H<sub>2</sub>S from larger quantities of CO<sub>2</sub> by absorption and reaction in fine sprays, *AIChE J.* 29 (1983) 66–72.

[15] V. Bontozoglou, A. Karabelas, Simultaneous absorption of hydrogen sulfide and carbon dioxide in sodium hydroxide solutions: experimental and numerical study of the performance of a short-time contactor, *Ind. Eng. Chem. Res.* 32 (1993) 165–172.

[16] A. Couvert, I. Charron, A. Laplanche, C. Renner, L. Patria, B. Requieme, Treatment of odorous sulphur compounds by chemical scrubbing with hydrogen peroxide – application to a laboratory plant, *Chem. Eng. Sci.* 61 (2006) 7240–7248.

[17] A. Couvert, C. Sanchez, A. Laplanche, C. Renner, Scrubbing intensification for sulphur and ammonia compounds removal, *Chemosphere* 70 (2008) 1510–1517.

[18] S. Piche, N. Ribeiro, A. Bacaoui, F. Larachi, Assessment of a redox alkaline/iron-chelate absorption process for the removal of dilute hydrogen sulfide in air emissions, *Chem. Eng. Sci.* 60 (2005) 6452–6461.

[19] J. Zhang, Z. Tong, Study on catalytic wet oxidation of H<sub>2</sub>S into sulfur on Fe/Cu catalyst, *J. Nat. Gas Chem.* 15 (2006) 63–69.

[20] J. Zhang, Z. Tong, H<sub>2</sub>S removal with cupric chloride for producing sulfur, *Chin. J. Chem. Eng.* 14 (2006) 810–813.

[21] J.A. Navarro, M.A. De la Rosa, M. Roncel, F.F. De La Rosa, Carbon dioxide-mediated decomposition of hydrogen peroxide in alkaline solutions, *J. Chem. Soc., Faraday Trans. 1* 80 (1984) 249–253.

[22] I. Charron, A. Couvert, A. Laplanche, C. Renner, L. Patria, B. Requieme, Treatment of odorous sulphur compounds by chemical scrubbing with hydrogen peroxide – stabilisation of the scrubbing solution, *Environ. Sci. Technol.* 40 (24) (2006) 7881–7885.

[23] O. Spalek, J. Balej, I. Paseka, Kinetics of the decomposition of hydrogen peroxide in alkaline solutions, *J. Chem. Soc., Faraday Trans. 1* 78 (1982) 2349–2359.

[24] A. Otto, D. Guessbacher, J. Conrad, Möglichkeiten des Einsatzes von Eisenhydroxid fuer die Bindung von Schwefelwasserstoff in Anaerob-Prozessen, <http://deutsche-zeolith.de/images/Schwefelwasserstoff%20.pdf> (accessed: November 2010).

[25] S. Rasi, A. Veijanen, J. Rintala, Trace compounds of biogas from different biogas production plants, *Energy* 32 (2007) 1375–1380.

[26] M. Pawlowska, J. Czerwinski, Variability of the non-methane volatile organic compounds (NMVOC) composition in biogas from sorted and unsorted landfill material, *Arch. Environ. Prot.* 34 (2008) 287–298.