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Published in:
Journal of Hazardous Materials

Link to article, DOI:
10.1016/j.jhazmat.2023.131334

Publication date:
2023

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
Research Paper

Power-to-X electroscrubbing parameter analysis for biogas desulfurization

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HIGHLIGHTS

- A PtX technology capable of removing hydrogen sulfide from gas has been developed.
- Electrochemically regenerated chlorine oxidizes hydrogen sulfide to solid sulfur.
- The technology can purify gas to a high degree and is quickly adaptable.
- The solvent flow has only a small effect on the efficiency of the process.
- The process is stable over longer periods of operation.

GRAPHICAL ABSTRACT

A new power-to-X desulfurization technology has been examined. The technology uses only electricity to oxidize the hydrogen sulfide (H₂S) found in biogas to elemental sulfur. The process works by using a scrubber where the biogas comes into contact with a chlorine containing liquid. This process is capable of removing close to 100% of H₂S in biogas. In this paper a parameter analysis of process parameters has been carried out. In addition a long term test of the process has been performed. It has been found that the liquid flow rate has a small but notable influence on the process’ performance on removing H₂S. The efficiency of the process largely depends on total amount of H₂S flowing through the scrubber. As the H₂S concentration increases, the amount of chlorine required for the removal process is also increased. A high amount of chlorine in the solvent may lead to unwanted side reactions.

ARTICLE INFO

Editor: Zaher Hashisho
Keywords: Gas scrubbing, H₂S removal, PtX, Electrochemistry, Oxidation

ABSTRACT

A new power-to-X desulfurization technology has been examined. The technology uses only electricity to oxidize the hydrogen sulfide (H₂S) found in biogas to elemental sulfur. The process works by using a scrubber where the biogas comes into contact with a chlorine containing liquid. This process is capable of removing close to 100% of H₂S in biogas. In this paper a parameter analysis of process parameters has been carried out. In addition a long term test of the process has been performed. It has been found that the liquid flow rate has a small but notable influence on the process’ performance on removing H₂S. The efficiency of the process largely depends on total amount of H₂S flowing through the scrubber. As the H₂S concentration increases, the amount of chlorine required for the removal process is also increased. A high amount of chlorine in the solvent may lead to unwanted side reactions.

1. Introduction

Currently, the biogas industry is undergoing a quick growth, and is expected to double in size by 2030 [1–3]. This is largely fueled by concerns regarding carbon emissions from burning of fossil fuel, e.g. natural gas. Biogas offers a sustainable alternative to natural gas and is therefore likely to experience increased use. Particularly in areas where electrical heating is not an option for many years to come [4].

Biogas is a carbohydrate gas made from decomposing organic matter stored in an anaerobic environment. It consists largely of CH₄ (~60%),
CO₂ (~40%) as well as a series of impurities such as H₂S, mercaptans and siloxanes [3,5]. H₂S is found in concentrations of up to several thousand ppm in biogas and needs to be removed before the biogas can be utilized. The sulfur content in the biogas has a large impact on the possibilities for further treatment and use of the gas. Currently most biogas is either burned directly for heat or “upgraded” by capturing and removing the CO₂. After upgrading, the biogas mostly consists of methane which can be utilized in the natural gas grid and used for either heat or power generation [4,6,7].

In the future it might be possible for the biogas to undergo what is known as 2nd generation upgrading [6]. In this process, a reaction is performed between CO₂ and H₂ whereby methane is formed. 2nd generation upgrading technology therefore utilizes a large percentage of the carbon for energy production [6]. This is of further interest when considering advanced refining of the biogas into biomethanol [8].

Both 1st and 2nd generation upgrading requires the biogas to be cleaned of impurities. Especially H₂S is critical, since it will deactivate the heterogeneous catalysts used in the biogas upgrading [9,10]. There are currently several technologies for removing H₂S from biogas, of these the three most commonly used are: Chemical precipitation [11,12], biological scrubbing [13] and activated carbon filtration [14]. The advantages and disadvantages of these technologies are examined in an earlier study by Villadsen et al. [6]. Recent advancements in the field also consider the use of biochar [15,16] or photocatalytic removal of H₂S [17].

The aim of this work is to examine a new electrochemical desulfurization method. This technology uses electrochemically generated active chlorine to remove the H₂S from biogas via oxidation to elemental sulfur. This is a power-to-X process, since only electricity is consumed in the gas cleaning process. The X signifies cleaned biogas, which is produced by the process.

In the future, electricity prices are expected to fall [18], which will make this kind of energy intensive process more attractive. Furthermore, as more electricity is produced by fluctuating energy sources, such as wind and sun, it will be increasingly attractive to find new technologies, which can utilize the energy when a surplus of renewable resources are available [19]. This new technology generates no waste and consumes no chemicals, except the initially loaded liquid. This is especially attractive since biogas plants are often small plants, favoring local regeneration of the solvent [7].

H₂S concentrations can rapidly change in biogas depending on the composition of the feedstock used. This desulfurization process can be quickly adapted to changes in H₂S concentration, since the removal of H₂S is directly dependent on the current applied [20]. This provides a significant advantage compared to conventional desulfurization methods, which are generally slow to adapt to changing H₂S levels.

Furthermore, electroscrubbing processes have been shown to have a high removal rate of even low-concentration pollutants [21–23], which biological scrubbing and chemical precipitation are incapable of [6].

This study is based on the results developed by Villadsen et al. [20], who verified the capability of the process for removing sulfur and determined the efficiency of the process. During the current study, further parameter analysis will be carried out to further determine and quantify their effect on the process.

2. Theory of the electrochemical scrubber

The concept of the process is shown in Fig. 1. The flow of biogas,
containing H$_2$S, enters a scrubber tower and is absorbed in the solvent, see unit a) in Fig. 1. The solvent contains active chlorine compounds which can react with the absorbed H$_2$S. The solvent is sprayed into the tower through a nozzle from the top of the scrubber, as seen in unit b). The H$_2$S absorbed in the liquid reacts with active chlorine and is oxidized to elemental sulfur. The active chlorine is reduced to aqueous chloride, as seen in unit b). The cleaned gas leaves through the top of the scrubber tower, while the spent liquid is pumped through an electrochemical cell, as seen in unit c) in Fig. 1. In the electrochemical cell, power is used to oxidize the chloride ions into elemental chlorine. The chlorine is then absorbed into the liquid, as seen in unit d) in Fig. 1. The active chlorine can then be reused by pumping it through the scrubber yet again. Thus the cycle continues without changing the total amount of chlorine atoms in the system. Reactions take place in the scrubber tower and the electrochemical cell (unit b) and c) in Fig. 1.

### 2.1. Electrochemical cell reactions

In the electrochemical cell (C in Fig. 1), the anodic reaction is the generation of active chlorine, while the cathodic reaction generates elemental hydrogen. The anodic and cathodic reactions are respectively [24]:

\[
2Cl^- (aq) + 2e^- \rightarrow Cl_2 (g), \quad E^0 = -1.36 V \quad (1)
\]

\[
2H^+ (aq) + 2e^- \rightarrow H_2 (g), \quad E^0 = 0 V \quad (2)
\]

Active chlorine generated by this reaction is dissolved into the liquid phase of the system, where it enters into equilibrium with hypochlorous acid, which in turn may dissociate into hypochlorite [24]:

\[
Cl_2 (g) \leftrightarrow Cl_2 (aq) \quad (3)
\]

\[
Cl_2 (aq) + H_2O \leftrightarrow H^+ (aq) + Cl^- (aq) + HClO (aq) \quad (4)
\]

\[
HClO \leftrightarrow ClO^- + H^+ \quad (5)
\]

\[
Cl_2 (aq) + Cl^- (aq) \rightarrow Cl_2^+ (aq) \quad (6)
\]

The active chlorine consisting of chlorine, hypochlorous acid and hypochlorite in aqueous solution is dispersed through the top of the scrubber, where it reacts with H$_2$S.

As seen in reaction (2), hydrogen gas is formed on the cathodic side of the electrochemical cell. Since this gas is not desired in the system, it is vented. In the future it may be possible to use the produced hydrogen for biogas upgrading as outlined in chapter 2.

### 2.2. Scrubber reactions

Inside the scrubber tower (A and B in Fig. 1), the H$_2$S is dissolved into the liquid solvent [25]:

\[
H_2S (g) \leftrightarrow H_2S (aq) \quad (7)
\]

\[
H_2S (aq) \leftrightarrow HS^- (aq) + H^+ (aq) \quad (8)
\]

\[
HS^- (aq) \leftrightarrow S^{2-} (aq) + H^+ (aq) \quad (9)
\]

The sulfide ion created by the above reactions is then mixed with the active chlorine, which is sprayed into the top of the scrubber, and is oxidized. The overall reaction for the oxidation of sulfide by chlorine is [24]:

\[
H_2S (aq) + Cl_2 (aq) \rightarrow S(s) + 2Cl^- (aq) + 2H^+ (aq) \quad (10)
\]

The precise mechanics of the oxidation may not follow this overall reaction. Chlorine, hypochlorite and hypochlorous acid can all participate in the oxidation of H$_2$S, HS$^-$ and S$^{2-}$. The exact reaction path taking place in the scrubber is not part of this study.

Thermodynamically, the produced sulfur is independent of the reaction path. The outcome, mass action, and energy consumption is the same. Three alternative ways of representing the sulfur oxidation are [24]:

\[
HS^- (aq) + Cl_2 (aq) \rightarrow S(s) + 2Cl^- (aq) + H^+ (aq) \quad (11)
\]

\[
HS^- (aq) + HClO (aq) \rightarrow S(s) + H_2O (l) + Cl^- (aq) \quad (12)
\]

\[
HS^- (aq) + ClO^- (aq) \rightarrow S(s) + Cl^- (aq) + OH^- (aq) \quad (13)
\]

These reactions can be obtained by linear combinations of reaction 4–6 and 10. In the above paths, H$_2$S in the biogas is reduced to solid elemental sulfur, which can be filtered out of the system. Since the active chlorine is reduced to aqueous chlorine in the reaction with H$_2$S, no chlorine leaves the system, and the only resource spent during the reaction is the electrical power used to fuel the electrochemical reaction.

Finally, the sulfur obtained by reaction 11–13 can be further oxidized into sulfate. The oxidation from sulfur to sulfate when reacting with hypochlorous acid is [26]:

\[
3HClO (aq) + S(s) + H_2O (l) \rightarrow SO_4^{2-} (aq) + 3Cl^- (aq) + 5H^+ (aq) \quad (14)
\]

When this reaction happens, the pH of the system will gradually fall, due to the accumulation of H$^+$ ions.

Oxygen evolution at the anode is a concern when using electrochemical cells since this will cause decreased efficiency and lead to unwanted gas in the exit stream. During the experiments performed in this article, no oxygen was detected in the outlet gas stream.

### 2.3. Efficiencies

The removal efficiency of this capture process can be calculated as the percentage of H$_2$S removed in the scrubber tower. The efficiency is calculated as:

\[
e_R = 1 - \frac{N_{H_2S, out}}{N_{H_2S, in}} \quad (15)
\]

A removal efficiency of 1 means that all H$_2$S in the gas has been removed, while a removal efficiency of 0 signifies that no removal takes place.

For this process, the removal efficiency is easily changed by adjusting the electrical current flowing through the electrochemical cell. Therefore, it might be interesting to compare the measured electrical current used to a theoretical value.

In this paper the current efficiency of the process is calculated based on the amount of electrons theoretically needed. It can be seen from Eqs. (1)-(15) that chlorine and H$_2$S react to form elemental sulfur in a one to one ratio. As seen in Eq. (1), two electrons are needed to form one molecule of chlorine. The efficiency of the system can be calculated based on the current running through the electrochemical cell, compared to the amount of H$_2$S removed. This can be done with the following equation:

\[
e_C = \frac{N_{H_2S} \times F \times z}{I} \quad (16)
\]

Where $N_{H_2S}$ is the amount of moles of H$_2$S removed per second, F is the Faraday constant and I is the current running through the electrochemical cell. The z signifies the amounts of electrons needed to create one molecule of chlorine. From Eq. (1), z is found to be 2.

An efficiency lower than one suggests that more active chlorine is produced, compared to what is consumed through reaction with H$_2$S. The additional chlorine must therefore either react with other components in the liquid, or alternatively be vented in the gas phase. A current efficiency close to one is desired, since this means that all the electricity consumed is contributing to the oxidation of H$_2$S.
A process flow diagram of the system can be seen in Fig. 2. The setup used in the experimental work was, with the exception of sensors and electrodes, constructed entirely in plastic (PVC and PTFE) due to the highly corrosive and oxidative nature of the system. PVC was chosen since this plastic is already chlorinated. PVC is therefore highly resistant to oxidation from the high chlorine concentration \([27]\) present in the solvent.

During operation, electrical current was adjusted in order to achieve steady state conditions between 1 and 20 ppm \(\mathrm{H}_2\mathrm{S}\) in the outlet gas of the system. Several \(\mathrm{H}_2\mathrm{S}\) measurements were made at each steady state to ensure representative data.

Biogas containing \(\mathrm{H}_2\mathrm{S}\) enters the scrubber, Fig. 2 (A), through the bottom at flow G1, where it is mixed with the solvent containing active chlorine, which is pumped (P1) through flow 4 and then sprayed through a nozzle into the scrubber. Thereby the \(\mathrm{H}_2\mathrm{S}\) is oxidized to sulfur and the cleaned biogas leaves through the top of the scrubber via G2 where the \(\mathrm{H}_2\mathrm{S}\) contents are measured at (D). The solvent leaves through the bottom of the scrubber, where it is pumped (P2) through flow 1 into the electrochemical cell (C). The spent solvent is then regenerated by applying electrical current through the electrochemical cell. The liquid flowing through the cell (Flow 2 and 3) enters the reservoir underneath the scrubber. The hydrogen produced at the cathode is vented (G3). The flow and purity of the hydrogen flow is not currently measured.

Solid sulfur is currently not removed in the laboratory setup and as such the amount of absorbed sulfur in the solvent continuously increases. The low amount of \(\mathrm{H}_2\mathrm{S}\) (0.1–1 g/h) captured in the laboratory setup made observing the existence of solid sulfur difficult, since the sulfur can be further oxidized into sulfate (Eq. (14)).

### 3.2. \(\mathrm{pH}\) and ORP sensors

\(\mathrm{pH}\), temperature and redox measurement sensors from Bürkert were placed in the liquid flow before and after the scrubber unit, as well as on the inlet flow to the electrochemical cell, and in the outlet flow from each of the chambers of the electrochemical cell (AP1–4 in Fig. 2).

As seen in Fig. 2, sensors were placed at four different locations of the system: AP1, The liquid flow going into the electrochemical cell; AP2 and AP3, the liquid flow going out of each of the chambers of the electrochemical cell; AP4, the liquid flow entering the top of the scrubber unit.

The AP1 measurement is characterizing the liquid into the electrochemical cell. It is equivalent to the absorber bottom. The residence time of the liquid in the absorber bottom is in the order of 5–10 s.

During normal operations, it is expected that the ORP (Oxidation Reduction Potential) measurements will show: AP2 > AP4 > AP1 > AP3 due to the content of active oxidant in the liquid. The ORP was solely used as an indication of process performance, and not for any further characterization of the process efficiency.

The \(\mathrm{pH}\) of the fresh solvent was between 7 and 8, but rapidly fell during operation due to absorption of sulfur and \(\mathrm{CO}_2\). During steady state the \(\mathrm{pH}\) of the system was between 0 and 1. The \(\mathrm{pH}\) value of the solvent was not found to have any influence on the performance of the process.

Due to the work of the pumps the temperature slowly rose during operation and stabilized at approximately 30 degree Celsius, the heat of absorption of \(\mathrm{H}_2\mathrm{S}\) is considered negligible, due to the low concentration. During the experiments in this study temperature was not found to have any effect the performance of the system.

### 3.3. Gas measurement equipment

After exiting the scrubber, the cleaned biogas was analyzed (see unit D in Fig. 2). The \(\mathrm{H}_2\mathrm{S}\) concentration was measured using an AWITE AWIECO electrochemical analyzer. The equipment contained two electrochemical sensors, which were capable of measuring in a range of 0–20 ppm and 0–1000 ppm, respectively. Since the low range sensor was more accurate, experiments were conducted so the outlet \(\mathrm{H}_2\mathrm{S}\) concentration was kept between 0 and 20 ppm whenever possible. The equipment measured the concentration every 15 min, but since only steady state data was desired, the infrequent measurements were not an issue. The \(\mathrm{H}_2\mathrm{S}\) concentration was supported by additional measurements using gas sampling tubes from Dräger.

To determine the existence of chlorine in the cleaned gas, Dräger tubes were used. During the experiments described in this paper, no chlorine was observed in the cleaned gas.

### 3.4. Coriolis mass flow controllers

The gas used in the experiments was a synthetic biogas consisting of \(\mathrm{H}_2\mathrm{S}, \mathrm{N}_2\) and \(\mathrm{CO}_2\). \(\mathrm{CH}_4\) is a main component of biogas, but during the initial setup and testing of the setup, it was found that the \(\mathrm{CH}_4\) in the gas phase is inert during the process. It was therefore replaced with an equal volume of nitrogen due to considerations of cost and safety.

The flow of each of the component gasses was controlled by a Bronkhorst miniCori Coriolis flow controller (model M13V10I) in order to ensure accurate measurements. The gasses were mixed before entering the scrubber unit.

### 3.5. Electrochemical cell

Due to the highly oxidative and acidic environment, it was chosen to use a titanium oxide alloy for the electrodes. The chambers of the electrochemical cell were divided by a Nafion membrane, which allows water and cations to move through the membrane, but not anions. This ensured that the active chlorine was kept on the anode side of the cell.
The liquid flow through the cell was kept high for all experiments, therefore the process is not expected to be influenced by limitations in diffusion speed.

During initial experiments a small (0.001 m$^3$) cell was used. This cell was later changed for a larger cell (0.02 m$^3$) to reduce the resistance in the system.

3.6. Liquid pumps

The flow of solvent through the scrubber unit was controlled by a Grundfoss membrane pump, which made it possible to adjust the solvent flow with a high degree of accuracy. The solvent flow through the electrochemical cell was achieved by using a smaller centrifugal pump. It was not possible to adjust the solvent flow through the centrifugal pump, why the precise solvent flow through the electrochemical cell is unknown. However, it was approximately 1 L/min for all experiments. The flow rate through the electrochemical cell was measured with a measuring cup and a stopwatch. This flow rate is within the optimal operation parameters given by the supplier. Standard deviation of flow was between 1 and 2 L/h for all experiments.

Due to the corrosive nature of the solvent, the part of the pump in contact with the solvent was constructed entirely in plastic.

3.7. Ion chromatograph for sulfate measurement

To determine the contents of sulfate ions in the liquid of the scrubber, an ion chromatograph was used. This method measures the speed of the ions as they move through a charged resin. Ions with less affinity for the resin will move faster compared to ions with higher affinities. In this way the concentration of the ions can be determined by measuring the conductivity in the outlet liquid as it changes over time [28].

4. Experimental results

To better understand the cleaning process, a parameter analysis was carried out to examine the impact of several parameters on the process. The examined parameters were: 1. Solvent flow through the scrubber; 2. gas flow through the scrubber; 3. H$_2$S concentration in the inlet gas; and 4. the impact on the system from long term operation.

An overview of the different steady states examined during the analysis of the scrubber system can be seen in Table 1. Outlet H$_2$S concentration was kept low in all experiments by adjusting the current applied to the electrochemical cell.

The purpose of Campaign 1 (C1.1-C1.8) was to determine the impact of different solvent flow rates through the scrubber. The focus of Campaign 2 (C2.1-C2.9) was to investigate differing gas flow rates and concentrations. Last, Campaign C3 was a longer term test done to examine the stability of the system over prolonged operation (~30 h).

The gas used in these experiments consisted only of N$_2$, CO$_2$ and H$_2$S. When steady state was achieved, no change in N$_2$ and CO$_2$ concentration was observed through the system.

The power consumption of the scrubbing process varies from 12.68 kWh/kg H$_2$S to 60.35 kWh/kg during the experiments. The deviations in power consumption is mainly caused by large changes in the voltage required to apply the needed current to the electrochemical cell. The cell used for campaign 2 had a maximum capacity of 4 A, and as the current approaches this limit, the voltage needed rises drastically.

During campaign 1 and 3 a slightly larger cell was used. The larger cell reduced the electrical resistance in the system and caused a significantly lower power consumption than the smaller cell.

4.1. Liquid flow influence on H$_2$S removal efficiency

To examine the effect of the solvent flow rate through the scrubber, all process parameters were kept constant while the scrubber flow (flow 4 in Fig. 2) was varied between 36 L/h and 334 L/h. After each change in the pump flow setting, steady state was achieved before changing the pump flow. The experimental parameters at steady state can be seen in Table 1 under Campaign 1 (C1.1-C1.8).

The applied electrical current is proportional to the production of chlorine (Eqs. (1) and (2)). This is utilized in the experiments, where current is maintained constant regardless of the solvent flow rate. The rate of chlorine production remains constant during the experiments but the concentration may vary, depending on flow rate. The concentration of chlorine in the scrubber inlet at 36 L/h is thus approximately 10 times higher than at 335 L/h. The active chlorine concentration in the scrubber inlet is therefore between 0.97 * 10$^{-3}$mol/L and 0.11 * 10$^{-3}$mol/L.

The results for the outlet H$_2$S concentration as a function of the solvent flow through the scrubber can be seen in Fig. 3. On the left Y-axis, the outlet H$_2$S concentration is plotted against the solvent flow. On the right Y-axis, the removal efficiency of the scrubber is plotted. The removal efficiency is defined as seen in Eq. (15).

As solvent flow rate increases from 36 to 149 L/h, the H$_2$S outlet concentration slowly decreases from 80 ppm to 60 ppm. A clear change in removal efficiency is seen at solvent rate from 149 to 194 L/h, where H$_2$S outlet ppm declines from approximately 60 ppm to 40 ppm. For high flow rates, > 200 L/h, it remains constant. This observation is quite

<table>
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<th>Campaign</th>
<th>Chloride conc. g/kg water</th>
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<th>Gas flow g/h</th>
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<th>Current A</th>
<th>Voltage V</th>
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</table>
peculiar, but can be explained in terms of wetting rate of packing. The wetting rate of the packing dictates the amount of liquid which is distributed on the internals of column. At high wetting rates the column is completely wetted and the surface of the packing material is fully utilized. At low wetting rates the packing will be insufficiently wetted and the active surface area in the column will decrease. The minimum required solvent flow rate through the scrubber can be estimated with engineering theory. Common engineering rules dictate, that the wetting is completely wetted and the surface of the packing material is fully distributed on the internals of column. At high wetting rates the column will be insufficiently wetted but at high wetting rates the column will be saturated with chlorine. At this point, the formed chlorine will begin to evaporate to the gas phase instead of taking part in the oxidation of H$_2$S. This evaporation of chlorine will decrease the reaction rate of the system, and lead to increased concentrations of chlorine in the gas phase, which is not desired, due to the toxicity and corrosive nature of chlorine.

In the other experiments in this article, the solvent flow is kept high to optimize the cleaning efficiency.

4.2. Influence of gas flow on scrubber current efficiency

Several gas flows and H$_2$S concentrations were tested in order to examine the effect of the gas flow on the scrubber system. The electrical current flowing through the electrochemical cell was adjusted, in order to achieve an outlet concentration between 1 and 20 ppm H$_2$S. The steady state values achieved during the experiments can be seen in Table 1 under Campaign 2 (C2.1-C2.9).

In Fig. 4 the applied current used to remove the H$_2$S is plotted versus the total inlet gas flow. The experiment was performed for three different H$_2$S gas concentrations and for a series of different gas flows. The experiments for 500, 1000 and 2000 ppm of H$_2$S are represented by the green, blue and red line, respectively. Experiments for a concentration of 2000 ppm were only done up to an inlet gas flow of 250 g/h. Above this value, the current required for cleaning the gas would exceed the limits of the electrochemical cell and thereby damage the equipment.

The removal efficiency is 99% ± 1% for all steady state points. Constant removal efficiency was achieved by tuning the applied current to the electrochemical cell. From Fig. 4 it can be seen that the required current increases approximately linearly as function of gas flow. This is
expected since there is a direct correlation between current use and removed H₂S. Comparing the green, blue and red lines, the current required for desulfurization also increases as a function of the H₂S concentration.

The applied current needed for removing the H₂S does not seem to increase linearly with H₂S concentration, which is surprising. The reason for this may be that an increase in current, facilitates unwanted side reactions due to a proportional increase in chlorine concentration.

This effect can be seen when comparing the steady state for 300 g/h of gas containing 1000 ppm of H₂S (A) to the steady state for 300 g/h of gas containing 500 ppm of H₂S (B) in Fig. 4. The total amount of H₂S at steady state A is twice the amount of steady state B. The required current for removing the H₂S, however, increases from 0.8 to 2.4 A between the two steady states. This suggests that three times as much electrical current was needed to remove twice the amount of H₂S.

The current efficiency, as defined in Eq. (16), can also be used to examine the influence of H₂S concentration on process performance examined by calculating. This is indicated in Fig. 5 where the efficiency is plotted versus the total gas flow rate for three different H₂S concentrations. The steady states used for this graph are the same as the ones seen in Fig. 4 and in Campaign 2 in Table 1 (C2.1-C2.9). The current efficiency of the system generally drops as the total gas flow rate increases regardless of the H₂S concentrations. When comparing the same inlet gas flow between the red, green and blue line, the efficiency also drops as a function of the H₂S concentration. The efficiency is likely dependent on the total amount of H₂S flowing through the scrubber, which can be calculated as the gas flow multiplied by the H₂S concentration.

In Fig. 5, the current efficiency is seen to drop gradually as H₂S increases and reaches a minimum of approximately 22–23% for both 1000 ppm and 2000 ppm of H₂S. While the efficiency seems to slightly at 1000 ppm when going from 225 to 450 g/h, this change is very small and may be caused by small inaccuracies in the measurements.

It is possible that the amount of H₂S does not directly impact the efficiency of the process. Rather, the increased current applied and active chlorine produced might have an adverse effect on the current efficiency. This efficiency loss can be explained by a large concentration of active chlorine facilitating unwanted side reactions, such as the formation of sulfate through oxidation of sulfur. This phenomenon will be examined further in Section 4.4.

The effects of gas and liquid flow rates supports the observations done by Villadsen et al. [20]. It was discovered how reaction between H₂S and chlorine is practically instantaneous. A higher gas flow will lower the residence time in the scrubber, but this plays an insignificant role in the performance of the process.

4.3. 30 h experiment

To examine the longer term stability of the system, a test of the laboratory setup was run for 30 h. During this period the solvent flow, inlet gas flow, and H₂S concentrations were all kept stable. The steady state process parameters can be seen in Table 1 under Campaign 3 (C3.1). The results for the outlet H₂S concentration, as well as the current applied to the electrochemical cell, can be seen in Fig. 6.

On the left Y-axis in Fig. 6, the current applied to the system is plotted as black dots. During start-up, the current was initially changed slightly to find a suitable operating point. It was desired to achieve an outlet H₂S concentration of approximately 25 ppm. On the right Y-axis, the outlet H₂S concentration of the system is plotted versus time as red dots. From Fig. 6 it can be seen that a steady state was reached 10 h into the experiment.

The system is seen to be stable at constant applied current with H₂S outlet concentrations deviating only up to 2 ppm during more than 20 h of continuous operation. This deviation is less than 0.5% of the inlet concentration and can be considered negligible. During the entire experiment, the mean current efficiency of the process was calculated to be approximately 21% when using the definition in Eq. (15). Since the system parameters do not change over long-term operations, it is well suited for industrial processes where long-term stability is key.

During operation, pH decreased gradually from 8 to 0.5 during the initial 3 h of the experiment. The pH then stabilized and was steady until the end of the campaign. This decrease in pH is caused mainly by sulfurous acid formed by the absorption and subsequent oxidation of H₂S and sulfur. Absorption of CO₂ into the solvent will only play a minor role in the pH drop, since CO₂ is not captured at low pH values [30]. H₂S is a sour gas, so it would be expected, that the low pH in the system would lead to reduced efficiency when capturing H₂S. The pH was unexpectedly found to have no impact on the process efficiency over the course of the experiment.

4.4. Power efficiency and sulfate formation

To determine the cause of the efficiency loss, an analysis of the liquid phase in the scrubber system was conducted. During the 30 h experiment, several liquid samples were extracted periodically. This was done to determine whether the elemental sulfur reacted with active chlorine to form sulfate. The sulfate content of the liquid samples was measured using an ion chromatograph as seen in Section 3.5.

The sulfate concentration for the extracted liquid samples compared to the total amount of H₂S captured during the experiment, can be seen in Fig. 7. Note that the amount of sulfate in the system is not exactly 0 moles at time zero, since some sulfate ions remained in from earlier.

![Fig. 5. Calculated current efficiency for the scrubber system, for different total gas flows and H2S concentrations.](image-url)

![Fig. 6. Long term test of the electroscrubbing system.](image-url)
The amount of sulfate measured in the liquid samples is represented by the black line in Fig. 7. It is seen that the amount of $\text{SO}_4^2-$ also increases almost linearly over time. This indicates that a portion of the active chlorine produced in the electrochemical cell is not used for oxidizing $\text{H}_2\text{S}$ to elemental sulfur. Instead the chlorine is consumed by further oxidizing the elemental sulfur into sulfate.

In Eq. (14), oxidation of sulfur to sulfate is seen to use three times as much active chlorine as the reaction from $\text{H}_2\text{S}$ to sulfur (Eq. (10)). Therefore, this reaction constitutes a considerable amount of the electrical current consumed in the cleaning process. In the long term experiment, the reaction from sulfur to sulfate consumed approximately 54% of the total current applied to the system. The oxidation of $\text{H}_2\text{S}$ to $\text{SO}_4^2-$ consumed only 21%, which leaving 25% currently unaccounted for. That a majority of the efficiency loss comes from formation of sulfate fits well with the observation that a large concentration of active chlorine leads to lower efficiency, as discussed in Section 4.2. A large concentration of chlorine may increase the reaction rate of unwanted sulfur oxidation, and thus lead to formation of additional sulfate and a loss of oxidant.

It will be possible to drastically increase the efficiency of the process by developing a method for removing the sulfur before it is oxidized to sulfate. This might be possible with the use of a filter capable of removing the solid sulfur from the liquid phase of the system.

The 25% of the electrical current that is currently unaccounted for, may be used in oxidation to form additional products, or possibly used for hydrolysis in the electrochemical cell. It is likely that some sulfur chlorides may be formed, as this has been seen in previous experiments where sulfur was oxidized by chlorine [31].

In the future it is desired to test the process on real biogas to examine how the process interacts with some of the other impurities (terpenes, ketones etc.) found in biogas. Furthermore, it is desired to test different solvents, since chlorine presents an issue in regards to toxicity and corrosion.

5. Conclusion

The efficiency of the new electro scrubbing desulfurization process increases slightly as the solvent flow rate increases. The efficiency of the process does not depend on the concentration or flow rate of the gas, but rather on the total amount of $\text{H}_2\text{S}$. The $\text{H}_2\text{S}$ increase corresponds to an increase in current applied to the system, which facilitates the oxidation from sulfur to sulfate.

During a 30 h long experiment, it was proved that the system was extremely stable with fluctuations in outlet concentration of under 0.5%. The current efficiency of the process was determined to be 23% during the long term test.

The majority of the systems efficiency loss can be contributed to the formation of sulfate from sulfur, which consumes approximately 54% of the chlorine produced in the electrochemical cell. This loss of efficiency may be mitigated by installing a filtration system, which can remove the solid sulfur from the liquid phase of the system. If the sulfur can be removed, further oxidation can be prevented, and the efficiency should rise significantly.

Overall the process seems to be well suited for industrial use. The process was found to be easily adjustable by changing the current and did not fluctuate over long-term operation.

Environmental implication

Hydrogen sulfide is considered hazardous material, since it is highly poisonous both to humans and to equipment used in the treatment of biogas. Due to the current climate and energy crisis, alternatives to natural gas are highly sought after. If hydrogen sulfide can be removed cheaply and efficiently from biogas, it will significantly raise the potential for utilizing biogas in place of natural gas. Furthermore, biogas may be used for synthesis of biofuels. In order for this process to be possible hydrogen sulfide must be removed, since it is highly toxic to the catalysts used in the upgrading process.

CRediT authorship contribution statement

**Sebastian Borgquist:** Methodology, Validation, Investigation, Writing – original draft, Writing – review & editing. **Sebastian Nis Bay Villadsen:** Conceptualization, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Christina Skitsi:** Validation, Investigation. **Katrine Boesgaard:** Visualization. **Jens Abildskov:** Writing – review & editing, Supervision. **Rodrigo Rivera-Tinoco:** Writing – review & editing. **Jan Boye Rasmussen:** Writing – review & editing. **Philip Loldrup Fosbol:** Methodology, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Philip Loldrup Fosbol reports financial support was provided by The Energy Technology Development and Demonstration Programme.

Data availability

The data that has been used is confidential.

Acknowledgments

Many thanks to the partners in the BE-Clean project: DTU, Pentair Union Engineering, Danish Gas Technology Center, Elplatek and EUDP program journal number 64019-0601 for funding this research project.

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