DANISH TECHNOLOGICAL INSTITUTE

Biogas upgrading

Evaluation of methods for H_2S removal

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1 Introduction

Hydrogen sulfide (H_2S) is always present in biogas, normally at concentrations between 80 – 4,000 ppmv depending on the feedstock. The primary mechanism for production of this compound is the reduction of sulfur-containing proteins under anaerobic conditions by sulphate-reduction microorganisms (Trogisch, 2004). Inorganic sulfur, particularly sulfates, can also be biochemically converted producing considerable H_2S.

Hydrogen sulfide is corrosive to most equipment (pipelines, compressors, gas storage tanks, engines, etc.) and acts as strong poison for fuel cells and reformer catalysts. Furthermore, H_2S combustion leads to sulfur dioxide emissions, which have harmful environmental effects. Due to the potential problems that hydrogen sulfide can cause, it is recommended to remove it early in the process of biogas upgrading. The level at which gas quality specifications are exceeded and sulfur abatement is required varies by application, equipment and vendor. The following table outlines the typical tolerance of H_2S levels for different biogas utilization equipment.

Table 1: Biogas Utilization Technologies and H_2S requirements (Wellinger, 2000; Trogisch, 2004)

Technology	H_2S tolerance (ppm)
Heating (Boilers) and Stirling Engines	< 1,000
Kitchen stoves	< 10
Internal Combustion Engines	< 500 ppm (depends on the kind of engine; it can be < 50 ppm)
Turbines	< 10,000
Micro-turbines	< 70,000
Fuel Cells : PEM PAFC MCFC SOFC	 < 1 < 20 < 10 in fuel (<0.1 – 0.5 at the anode) < 1
Natural Gas Upgrade	< 4 (variations among countries)

A large number of technologies exist to remove H_2S from gas streams. These techniques can be evaluated for their suitability with biogas systems. Selecting the best one depends on the gas final use, the composition, variability and volume of the gas to be treated, the concentration of H_2S present, and the absolute quantity of H_2S to be removed. Each technology has pros and cons. Additionally, two or more processes can be combined to achieve higher H_2S removal. Hydrogen sulfide can be removed either in the digester, from the crude biogas, or in the upgrading process.

In general, H_2S removal methods can be classified in two big groups according to their principle: the physical-chemicals, which are the traditional ones and currently still dominate the market, and the biotechnological. In the past two decades increasing attention has been paid to biotechnological methods and they have experience a large development as having the same or even higher efficiency than the physical-chemical methods (> 99%) their operating costs are lower, they avoid catalysts, and they do not generally produce secondary streams that have to be specifically treated. Nevertheless, basic and applied research for optimisation of the biological systems is in general still

required. Methods that combined physical-chemicals and biotechnological technologies have been also developed.

Table 2: H_2S removal technologies from gas streams. The most suitable methods for removal of H_2S from biogas are marked in bold and blue

Physical – Chemical	**Addition of iron salts/oxides to the digester slurry**	
	Adsorption	– **Activated carbon** – Molecular sieve – **Iron oxides (iron sponge, SulfaTreat®, Sulphur–Rite®)** – Zinc oxides – Alkaline solids
	Absorption/ Scrubbing	– **Water** – **No–water physical solvents (Selexol®)** – Alkaline solutions – Zinc oxide slurries – Iron oxide slurries – **Iron salts, chelated and no chelated (Lo–Cat®, SulFerox®, Sulfothane®)** – Quinone and vanadium salts (Stretford) – Chemical oxidants: hypochlorite, H_2O_2, $KMnO_4$ ... – Amines
	Membrane purification	
	Claus process (+ SCOT / + Superclaus)	
	Incineration	
Biotechnological	**Air/Oxygen dosing digester slurry**	
	Biofilter/Biotrickling filter (BiogasCleaner®, Biopuric®, DMT filter®)	
	Bioscrubber (Thiopaq™)	
Combined physical-chemical/biotechnological	Chemical absorption with iron salts and microbial regeneration of the solution.	

The applicability of some of these methods regarding gas flow and H_2S concentration are showed in Figure 1.

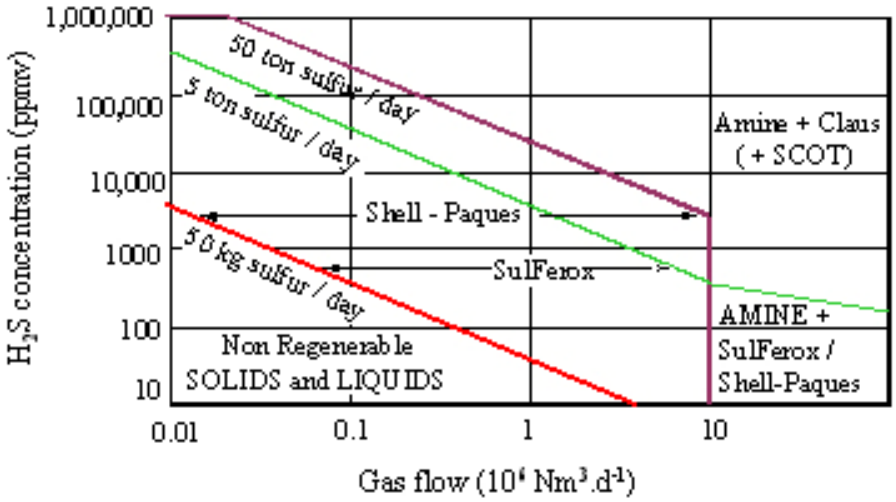

Figure 1: Applicability of some H_2S removal methods according to gas flow and H_2S gas concentration (Janssen, 2007)

For H_2S biogas removal the most employed methods are adsorption in activated carbon and iron oxides and absorption with chelated iron salts. For biogas upgrading to natural gas quality H_2S is often combined with CO_2 removal in water or alkaline scrubbers or by absorption in non-water physical solvents as the Selexol process. The addition of iron chloride or air/oxygen to the digester is widely used for a rough reduction of H_2S when using for example boilers or engines. Biofilters and biotrickling filters are also commonly used in Denmark and other countries for H_2S removal before CHP engine units. But for those applications that required very low levels of H_2S (< 50 ppm) an additional method or a second cleaning step after the biological method must be utilized. Moreover biological system introduced normally oxygen for the biological process as air, which reduces the quality of the biogas by increasing the N_2 concentration. In some cases, lower levels of H_2S can be reached with biological systems. For example, BiogasCleaner can supplied plants with a performance guarantee of 10 ppm.

2 In-situ (digester) sulfide abatement by addition of iron salts/oxides to the digester slurry

Iron chlorides, phosphates or oxides are directly added into the digester slurry or into the feed substrate in a pre-storage tank. The addition of $FeCl_2$, which is a liquid, is the most regularly practiced. Iron hydroxide ($Fe(OH)_3$ or $Fe(OH)_2$) in solid form and ferrous chloride ($FeCl_3$) can also be added. They react then with the produced hydrogen sulfide and form insoluble iron sulfide salts. Due to this precipitation stripping of H_2S into the biogas is prevented.

Ferrous chloride:	$Fe^{+2} + S^{-2} \rightarrow FeS$	Eq. 1
Ferrous hydroxide:	$2Fe(OH)_3 + H_2S \rightarrow 2Fe(OH)_2 + S + 2H_2O$ $Fe(OH)_2 + H_2S \rightarrow FeS + 2H_2O$	Eq. 2
Ferric chloride:	$2FeCl_3 + 3H_2S \rightarrow 2FeS\downarrow + S\downarrow + 6HCl$	Eq. 3

The addition of divalent or trivalent iron ions in the fermentation substrate is related to the hydrogen sulphide equilibrium between the liquid and gas phase. The requirement for iron (in grams per day) can be determined by the following formula (Ries, 1993):

$$Fe = \beta . \frac{M_{Fe}}{M_S} . \left(\frac{H_2S_{aq}}{f_{H2S}} . \dot{V}_{Substrat} + \frac{\Delta H_2\dot{S}_g}{1000} . \rho_{H2S} . \dot{V}_{Biogas} \right) \qquad \text{Eq. 4}$$

where:

Fe = iron ions (g/d)
H_2S_{aq} = total dissolved hydrogen sulphide (g/m^3)
f_{H2S} = portion of the total sulphur dissolved as H_2S_{aq}
ΔH_2S_g = amount of H_2S removed from the biogas (ppmv)
$V_{Substrate}$ = flow of the substrate (m^3/d)
V_{Biogas} = biogas flow (m^3/d)
P_{H2S} = H_2S density (g/l)
M_{Fe} = iron molecular mass (g/mol)
M_s = sulfur molecular mass (g/mol)
B = factor of over dosing: 1.7 – 2.3 (Ries, 1993) or 3 – 5 (Oechsner, 2000). This extra factor is due to the presence of phosphorus, organics, and other entities which consume also iron in the system.

This method is very effective in reducing high H_2S levels, but less effective in attaining a low and stable level of H_2S in the range of vehicle and injection into the gas grid demands. Reductions of H_2S concentrations in the biogas down to 200 – 100 ppmv have been achieved. Removal to lower concentrations required a large excess of iron ions. At this respect, this method can only be regarded as a partial removal process and must be used in conjunction with another technology to go down 10 ppmv. In Sweden, where H_2S concentration in the gas phase is around 300 ppmv average, 4 g $FeCl_3$ per liter of feedstock are added to achieve H_2S levels lower than 100 ppmv. Oechsner indicates that, for example, for a desulphurization from 2,000 to 20 ppmv a dosing of 120 to 160 g per Nm^3 of biogas is required.

The in-situ removal of hydrogen sulfide is included in the turnkey biogas plant or installed by the plant owner. The investment costs are rather low since the only equipment needed is a dosing

system for iron chloride. Operational costs for this method depend on the amount of hydrogen sulfide that is formed by the digestion process. When using raw materials that are rich in protein and other sulfur containing molecules this method is rather expensive.

3 In-situ biological H2S reduction by air/oxygen dosing to digester slurry

For biogas coming from anaerobic digestion the simplest method of desulfurization is the addition of oxygen or air directly into the digester or in a storage tank serving at the same time as gas holder. In this way it takes place the biological aerobic oxidation of H_2S to elemental sulfur and sulphates by *Thiobacillus* bacteria. They grow on the surface of the digestate, which offers the necessary microaerophilic surface and at the same time the necessary nutrients. The small amount of oxygen (3 – 6% air to biogas) required in this method is introduced in the biogas system, e.g. by using an air pump. Depending on the temperature, the reaction time and the amount and place of the air, full scale digesters have claimed 80 – 99% H_2S reduction, down to 20 – 100 ppm H_2S (McKinsey, 2003). The oxygen content in the biogas after desulfurization will be about 0.5 – 1.8 % per volume. Sulphur concentration is monitored, however, only in a small number of slurry digesters and in practice most of the applications work less effectively. An investigation conducted in 1999 indicated that, despite the air feed, in more than half of the biogas plants the sulphur concentration of the gas going into gas engines exceeded 500 ppm and in 15% of cases the sulphur concentration was > 2,000 ppm (Weiland 2003).

This is likely the least expensive and most easily maintainable form of scrubbing for on-farm use where no further upgrading of biogas is required, i.e. when the biogas is cleaned only to prevent corrosion and odour problems. So, the internal biological desulfurization inside the digester is the most applied method for primary desulfurization at agricultural biogas plants using CHP engine units.

The crucial disadvantage of a desulfurization in the digester is the coupling to the anaerobic degradation process as well as the necessity to supply oxygen to the anaerobic fermentation process. Thus the fermentation is disturbed and the methane formation impaired. As consequence the biogas yield decreases. In addition, the remaining of sulfur or sulfate in the system can lead to a renewed formation of H_2S and yellow clusters of sulfur are deposited on surfaces, increasing chances of corrosion. Moreover, measures of safety have to be taken to avoid overdosing of air for example in case of pump failures as biogas in air is explosive in the range of 6 to 12% depending on the methane content. Furthermore H_2S peaks cannot be reduced sufficiently. A further disadvantage is the accumulation of O_2 and N_2 in the biogas stream. Nitrogen is an inert gas very difficult to remove from the biogas during upgrading. Therefore this method can mostly not applied as pretreatment for biogas upgrading systems because most upgrading technologies are not able to remove O_2 and N_2 out of the gas stream, and the further cleaning of this compounds is an expensive process. It is only possible if the biomethane will be injected in a natural gas grid that contains natural gas with L-gas quality. To minimize or avoid the dilution with N_2 there is the possibility to inject pure O_2 into the digester. Because buying bottles of pure O_2 is mostly too expensive a better option is to generate pure oxygen directly at the biogas plant. This strategy is sporadic applied in large scale biogas upgrading plants.

Figure 2: Sulfur precipitation in a digester (Beil, 2010)

4 Adsorption

It is the trapping of pollutants on a solid with a high-surface area. The solid is typically an activated carbon or a crystalline material with high internal porosity (silica gel, zeolites, activated alumina, etc.) whose surface holds the pollutant through intermolecular forces. There are two types of adsorption: the physical, where the pollutant molecules are held in place in the pores by relatively weak physical attraction forces and the chemical, in which much stronger chemical bonding forces are also present. Eventually the solid is saturated and either it may be discarded or sent back to the manufacturer to be cleaned out, or it may be regenerated in place. In the regeneration heat or lower pressure are used to reverse the adsorption process and volatilize the absorbed compounds. Direct steam injection is the most widely used method of providing heat for regeneration.

The conventional adsorber vessel is a fairly long cylinder that can be installed in either a vertical or a horizontal position. Regeneration steam is frequently introduced from the bottom of the vessel. For continuous processes in which regenerative adsorption is used, two or more adsorbers are installed.

Adsorption systems are typically suitable for flow rates between 10 – 10,000 m^3/h and pollutants concentrations between 0.1 – 8 g/m^3 (Shareefdeen, 2005). Adsorption H_2S removal techniques have historically been used at facilities with less than 200 kg S/d in the U.S. Adsorption is one of the most competitive technologies for precision desulfurization because it is simple and effective (> 99%). Major drawbacks include a continually produced waste stream of spent media, and growing environmental concern over appropriate waste disposal methods. The most competitive products for H_2S biogas removal are impregnate activated carbon and iron oxides (McKinsey, 2003).

Adsorption in zinc oxides (ZnO) is preferred from gases at elevated temperatures 200 – 400 °C and adsorption of H_2S from biogas in alkaline substances is very expensive due to the fact that CO_2 is co-removed at extremely high product utilization. So these two methods are not further comment in this chapter (see Annex I).

4.1 Adsorption on impregnated activated carbon

Among the available adsorbents activated carbon (AC) is the most often used for removal of H_2S if low concentrations are required. In addition to the physical adsorption, activated carbon provides a catalytic surface for oxidation to elemental sulfur and sulfate, which significantly enhances the removal capacity of H_2S. In presence of oxygen the following reaction takes place:

$$2H_2S + O_2 \rightarrow \tfrac{1}{4} S_8 + 2H_2O \qquad \text{Eq. 5}$$

The elementary sulfur being adsorbed onto the internal surface of the activated carbon.

The AC must have 20 – 30% of moisture content and the required volume of oxygen. In large biogas plants air is injected into the gas stream but for small scale, regular removal of AC and exposure to ambient air suffices. The reaction works best at pressures of 7 to 8 bar and temperatures of 50 to 70 °C. The gas temperature is easy to achieve through the heat formed during compression. Usually, the carbon filling is adjusted to an operation time of 4,000 to 8,000 hours. If the gas has high levels of H_2S (> 3,000 ppmv) regeneration is periodically required (Wellinger, 2000).

Impregnation of AC to optimize H_2S abatement with chemical adsorption is normally done using alkaline or oxide coatings. Besides of potassium iodine, sodium hydroxide, sodium carbonate, potassium hydroxide, and metal oxides are the most common coatings employed. Impregnated products enhance H_2S removal capacity from a normal 10 – 20 kg H_2S/m^3 carbon for virgin carbon to 120 – 140 kg H_2S/m^3 carbon. Drawbacks of impregnated carbons are that the spent carbon must either be landfilled or re-impregnated with costly, hazardous chemicals and that they are highly susceptible to exothermic reactions and notorious for causing bed fires if careless operation (Zappa, 2001).

Dust and water from biogas must be normally removed before the AC system.

Distributors of impregnated activated carbon include: Calgon Carbon Corporation (FCA, Sulfusorb®), US Filter–Westates Carbon, Carmeron Carbon, etc.

4.2 Adsorption on molecular sieve

Molecular sieves (zeolites) are excellent products to separate different compounds in gas streams. The selectivity of adsorption is achieved by different mesh sizes and/or application of different gas pressures. Polar compounds, such as water, H_2S, SO_2, NH_3, carbonyl sulfide, and mercaptans, are very strongly adsorbed and can be removed from such non-polar systems as methane.

Both activated carbons and hydrophobic molecular sieves present advantages and drawbacks. The former are rather cheap materials, readily available from many companies. Moreover, they have high initial adsorption capacities. On the other hand, the latter, despite their limited initial capacity, are thermally and chemically very stable products and generally do not lead to side reactions. Their relatively high cost prevents their extensive use for the moment.

4.3 Adsorption using iron oxides

As one of the oldest methods still in practice, iron oxides remove hydrogen sulfide by forming insoluble iron sulfides. It is possible to extend bed life by admitting air, thereby forming elemental sulfur and regenerating the iron oxide. This regeneration process is highly exothermic.

Purification:

$$FeO + H_2S \rightarrow FeS + H_2O \qquad \text{Eq. 6}$$

$$Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O \qquad \text{Eq. 7}$$

Regeneration:

$$FeS + ½\,O_2 \rightarrow FeO + S \qquad \text{Eq. 8}$$

$$Fe_2S_3 + 3/2O_2 \rightarrow Fe_2O_3 + 3S \qquad \text{Eq. 9}$$

Regeneration is possible for a limited number of times (until the surface is covered with natural sulfur), after which the tower filling has to be renewed. If using one column systems the regeneration can be applied by injecting 1 – 5% air into the reaction column but loading is limited when compared to a two-column system. In a two-stage system the raw biogas streams through the first column and

iron sulfide is generated. In parallel in the second column air is injected and the regeneration takes place.

The purification step is optimal between 25 and 50 °C and since the reaction with iron oxide needs water the gas stream should not be too dry. However, condensation should be avoided because the iron oxide material (pellets, grains, etc.) will stick together with water reducing the reactive surface (Wellinger, 2000).

The iron oxide removal technology is simple and effective (up to 99.98%). H_2S output concentrations < 1 ppm (related to 1,000 ppm H_2S in the raw gas stream) are possible. Its general drawbacks are that the process is highly chemical intensive, the operating cost can be high, and a continuous stream of spend waste material is accumulated. Moreover, it is difficult to automate the regeneration and/or removal phase and this can be troublesome if the heat from the regeneration is not dissipated properly.

Typical iron oxide media are iron oxide wood chips (iron sponge) and iron oxide pellets. Recently, proprietary iron-oxide media such as SulfaTreat®, Sulphur–Rite®, SOXSIA® and Sulfa–Bind® have been offered as improved alternatives.

Iron Sponge

Iron-oxide-impregnated wood chips are the most well-known iron oxide product. The primary active ingredients are hydrated iron-oxides (Fe_2O_3). Iron oxide or hydroxide can also be bound to the surface of pellets made from red mud (a waste product from aluminum production). These pellets have a higher surface-to-volume ratio than impregnated wood chips, though their density is much higher than that of wood chips. At high H_2S concentrations (1,000 to 4,000 ppm), 100 grams of pellets can bind 50 grams of sulfide. However, the pellets are likely to be more expensive than wood chips (Krich, 2005).

Grades of iron sponge with 100, 140, 190, 240 and 320 kg Fe_2O_3/m^3 are traditionally available, with the 190 Fe_2O_3/m^3 grade being the most common. Bulk density for this grade is consistently around 800 kg/m^3 in place (Revell 2001).

As seen in Eq. 7, 1 kg of Fe_2O_3 stochiometrically removes 0.64 kg of H_2S.

Iron sponge is a mature technology so there are design parameter guidelines that have been determined for optimum operation. For example, 40% moisture content ±15% is necessary to maintain activity, down-flow gas is recommended for maintaining bed gas moisture, temperature should be kept between 18 and 46 °C, 140 kPa is the minimum pressure recommended for consistent operation, residence time should be greater than 60 seconds, etc. (McKinsey, 2003).

The application of wood chips for biogas cleaning is very popular particularly in USA (Wellinger, 2000). Different scales of operation have been employed ranging from gas flow rates of ~2,500 m^3 CH_4/h, e.g. Avenue Coking Works, down to much smaller scale plants ~100 m^3 CH_4/h, e.g. SCA paper recycling plant in Lucca, Italy and Camelshead Waste Water Treatment Works in Plymouth, UK (Environment–Agency, 2004).

Commercial sources for iron sponge include for example Connelly GPM, Inc., of Chicago, IL, Physichem Technologies, Inc., of Welder.

Perhaps the most important drawback of this kind of iron oxide media, which have led to decreased usage in recent years, is that the safe disposal of spent iron sponge has become problematic, and in some instances, spent media may be considered hazardous waste and requires special disposal procedures. Additionally, the regenerative reaction is highly exothermic and can, if airflow and temperature are not carefully controlled, result in self–ignition of the wood chips. Thus some operations, in particular those performed on a small scale or that have low levels of H2S, elect not to regenerate the iron sponge on-site. Precautions must be also taken during removal of spent material to prevent fires. Due to buildup of elemental sulfur and loss of hydration water, iron sponge activity is reduced by 1/3 after each regeneration. Therefore, regeneration is only practical once or twice before new iron sponge is needed.

Proprietary formulations of iron oxide as Sulphur–Rite® and SulfaTreat® products address this problem by using an inert ceramic base. Initial costs of Sulphur–Rite® and SulfaTreat® products are higher than iron sponge products, but those costs are at least partially offset by easier change-out procedures and transportation and disposal costs. Other proprietary formulations are Sulfa-Bind® Media-G2® and Soxsia®.

- **SulfaTreat®**

SulfaTreat® is a proprietary sulfur scavenger, consisting mainly of Fe_2O_3 or Fe_3O_4 compounds coated onto a proprietary granulated support commercialized by M-I SWACO. SulfaTreat® is used similarly to iron sponge in a low-pressure vessel with down-flow of gas and is effective with partially or fully hydrated gas streams.

Conversion efficiency in commercial systems is in the range of 0.55 – 0.72 kg H_2S/kg iron oxide, which is similar to, or slightly higher than, values reported for batch operation of iron sponge (Kohl, 1997).

Multiple benefits over iron sponge are claimed due to uniform structure and free-flowing nature. SulfaTreat® is reported to be easier to handle than iron sponge, thus reducing operating costs, labor for change-out, and pressure drops in the bed. Also, SulfaTreat® claims to be non-pyrophoric when exposed to air and thus does not mean a safety hazard during change-out. Buffering of pH and addition of moisture are not necessary as long as the inlet gas is saturated.

SulfaTreat® is non-regenerable, and similar to iron sponge the spent product can be problematic or expensive to dispose of properly. The manufacturer has suggested that spent product may be used as a soil amendment or as a raw material in road or brick making, but they state that every customer must devise a spent-product disposal plan in accordance with local and state regulations.

- **Sulphur-Rite®**

Sulphur-Rite® is an iron-oxide product offered by GTP-Merichem. Sulphur-Rite® is unique in their claim that insoluble iron pyrite is the final end product. Sulphur-Rite® systems come in prepackaged cylindrical units that are recommended for installations with less than 180 kg/d with pre-engineered units handling gas flow rates up to 4,300 m^3/h (i.e. H_2S gas concentrations < 1,765 mg/m^3). Sulphur-Rite® costs approximately the same than SulfaTreat®. Around 8.5 kg of SulfaTreat® or Sulphur-Rite® remove 1 kg of H_2S. Company literature claims spent product is non-pyrophoric and landfillable and has 3 – 5 times the effectiveness of iron sponge (Environment–Agency, 2004).

- **SOXSIA®**

SOXSIA® (Sulfur Oxidation and Siloxanes Adsorption) is a catalyst developed by Gastreatment Services B.V. that absorbs siloxanes and removes H_2S from the raw gas. Up to 2,000 ppm of H_2S can be removed from the gas at 40 °C, atmospheric pressure and with a capacity of 1,000 Nm^3 raw gas/h (Petersson and Wellinger, 2009).

5 Absorption/Scrubbing

In physical absorption H_2S is removed by absorption in water or other solvents such as methanol and ethers of polyethylene glycol. In chemical absorption the water solubility of the H_2S is enhanced by making the water alkaline or by its oxidation to more water-soluble compounds.

If liquid regeneration is possible usually regeneration columns are operated in conjunction with the absorber to facilitate continuous processing. The stripper gas of the regeneration unit contains the displaced H_2S if it has not been converted to elemental sulfur.

The primary disadvantage of the absorption is that usually eliminates a problem with a contaminated gas stream only to create a contaminated liquid stream or a more concentrate gas liquid stream (if regeneration) that must be further treated. Other disadvantages are high initial investment costs as well as high consumption of water and/or chemicals. Advantages are high efficiency removal (up to 99%), small footprint and ability to handle a wide range of pollutant concentrations. Absorption systems are suitable for flow rate approximately between 100 – 10,000 m^3/h and pollutant concentrations between 8 – 30 g/m^3.

Traditionally absorption processes as amine are not feasible for low-flow and low-pressure applications, typical conditions of small biogas plants, due to increased cost of operating at high pressure, high energy requirements for recirculation pumps and regeneration vessels, or higher media costs. Nevertheless some of them like the iron-chelated process are viable with small biogas systems (McKinsey, 2003). For large scale biogas plants these methods become economically more feasible.

Chemical absorption by oxidation with iron- and zinc- oxide slurries has been generally replaced by the more efficient chelated-iron based processes. Pipeline-gas specifications are easily met, but the high cost of non-regenerable reactant usually limits use of this process to removing trace amount of sulfur. Processes using quinones with vanadium salts, such as the Streford process, account for a large portion of the absorption natural gas purification market, but because of high capital and operating costs quinone-based H_2S technologies are generally not used for small gas streams which is usually the case of biogas plants.

A description of the most common H_2S removal absorption methods that are used for biogas cleaning is given in the next paragraphs. Physical absorption by water scrubbing and no water solvents as polyethylene glycol also removed CO_2. Costs associated with selective removal of H_2S using these kinds of absorption are not competitive with other methods for selective removal of H_2S. Thus, they would only be considered for simultaneous removal of CO_2 and H_2S. Nevertheless, previous rough desulfurization is recommended.

5.1 Water scrubbing

The basis of these processes is high-pressure scrubbing of the biogas with pressurized water. This removes a significant proportion of the acid gas contaminants (including carbon dioxide), which can be released from the wash water in an air- or steam stripping tower. The resulting ‘regenerated’ water can be recirculated for further use (Figure 3) or just used one time (Figure 4). It is important to note that non-regenerative water wash is primarily used with biogas from WWTP because they have access to large supply of water and wastewater treatment capacity on site. But the use of WWTP water can cause problems in pipes and vessels due to bacterial growth. In these cases

cleaning is necessary. Cleaning may have to be performed several times a year by washing the column with detergent or removing the media and cleaning it externally. When using a non-regenerative process it can be performed without stopping the biogas flow.

In non-regenerating process, water use is approximately 150 l/Nm^3 raw biogas. A hundred times less water can be consumed by plants reusing water. Used water will require proper treatment prior to discharge into the environment.

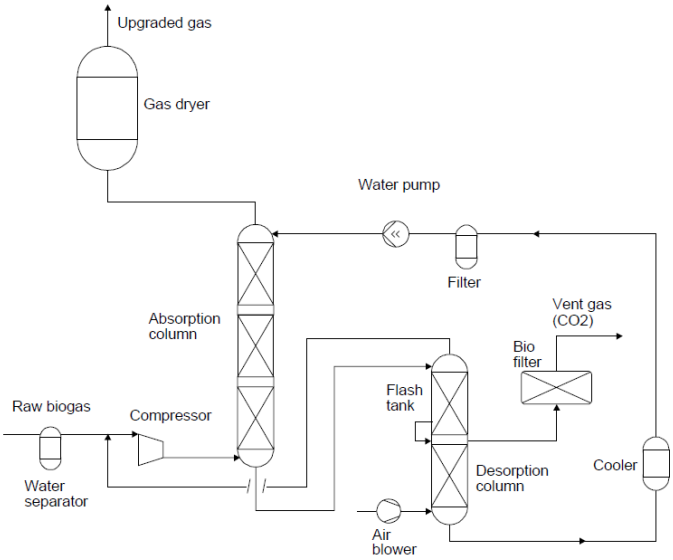

Figure 3: Scheme of a water scrubbing system with regeneration (Hagen, 2001)

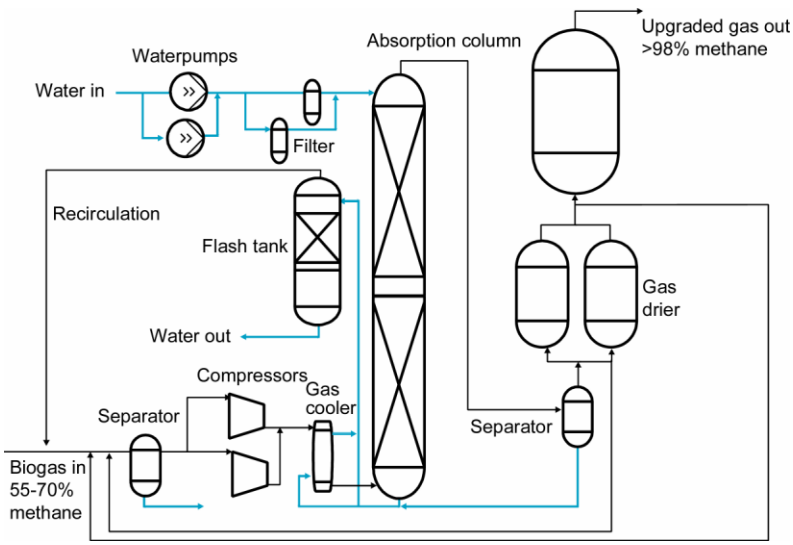

Figure 4: Scheme of a water scrubbing process without regeneration (Hagen, 2001)

H_2S solubility in water is no as high as in other liquids, but it has the advantages of availability and low cost. H_2S has a slightly higher solubility than CO_2, nevertheless cost associated with selective removal of H_2S using water scrubbing (due to the high water consumption and the very large power consumption associated with pumping and handling the circulating flows) have not yet shown competitive with other methods. H_2S will be removed down to 5 mg/m^3 by the process but a rough desulfurization to < 500/300 ppmv can be helpful to avoid plugging and fouling in the regenerative system and significant H_2S emissions into the atmosphere by the exhaust gas, or alternatively if there is an exhaust gas treatment technology installed, it will avoid SO_2 emissions.

5.2 Physical Absorption

The physical absorption technology using organic solvents is basically comparable to the water scrubber technology. Instead of water, organic solvents such as methanol, propylene carbonate, and ethers of polyethylene glycol, with high H_2S selectivity are used. A well know commercial solvent is the Genosorb® 1753 mainly constituted of polyglycol dimethyl ethers and used in the so-called Selexol® process (Figure 5).

Like water scrubbing the cost for selective H2S removal has not yet shown to be competitive and this process will most likely only be considered for applications in which upgrading to relatively pure methane is desired (Wellinger and Lindberg, 2000). Moreover, only if very large gas flows are treated, it can be economically interesting to use Selexol for H_2S removal.

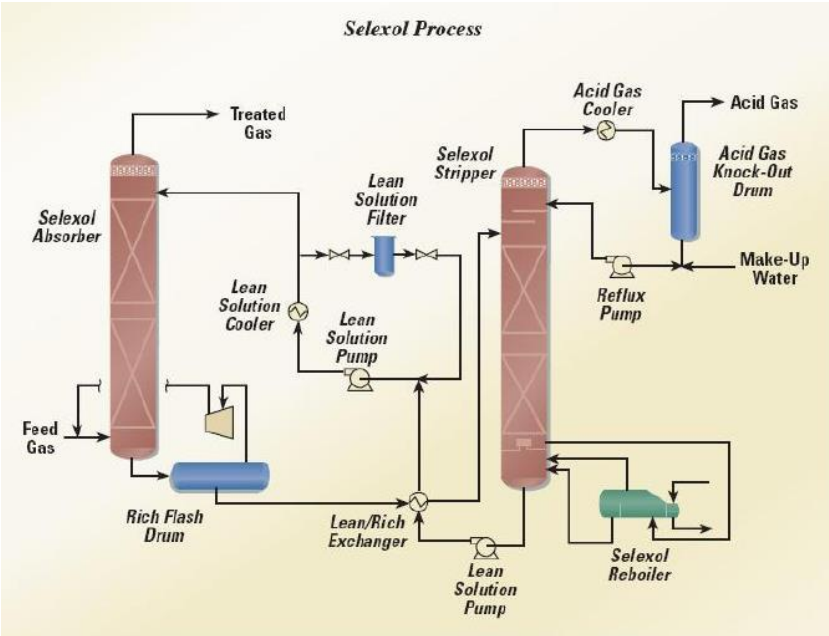

Figure 5: Biogas upgrading with the Selexol chemisorption process (BC Innovation Council, 2008)

5.3 Chemical absorption by catalytic oxidation with chelated-iron salt solutions

Chelated-iron solutions utilize iron ions bound to organic chelating agents. The oxidation of hydrogen sulfide into elemental sulfur is achieved by the reduction of a soluble ferric chelated iron [Fe^{3+}] into a ferrous chelated iron [Fe^{2+}]. The chelating agents prevent the precipitation of iron sulfide or iron hydroxide such that the reduced (ferrous) iron can be re-oxidised to ferric iron by air stripping.

Chelated iron [Fe^{3+}] participates in the absorption process as a catalyst; indeed, in the absence of catalysts, the chemical oxidation of aqueous H_2S by dissolved oxygen proceeds at an imperceptibly slow rate.

Purification: $$H_2S + 2[Fe^{3+}] \rightarrow S + 2[Fe^{2+}] + 2H^+$$ Eq. 10

Regeneration: $$2[Fe^{2+}] + 0.5O_2 + 2H^+ \rightarrow 2[Fe^{3+}] + H_2O$$ Eq. 11

Sulfur removal efficiencies of 99.99% or higher can be achieved with this technology. However, many of the units based in this technology are plagued by plugging and foaming problems.

Catalytic scrubbing processes on the market are for example the LO-CAT® and MINI-CAT® redox chemistry technology (Gas Technology Products–Merichem), the SulFerox® (Shell), the Sulfothane® (Biothane corporation) and the Apollo Scrubber (Apollo Environmental Systems Corp.). The LO-CAT® process is offered in several configurations, the anaerobic one for digester gas is showed in Figure 6.

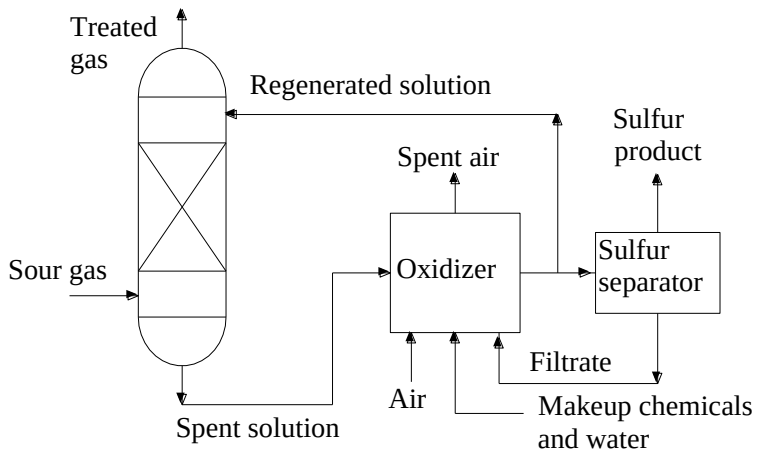

Figure 6: Typical anaerobic LO-CAT® unit (Nagl, 1997)

The LO-CAT® process is attractive for biogas applications because it is > 99% effective, the catalyst solution is non-toxic, and it operates at ambient temperatures, requiring no heating or cooling of the media. The two principal operating costs are for power for pumps and blowers, and chemicals for catalyst replacement due to losses via thiosulfate and bicarbonate production in side reactions (Kohl, 1997).

LO-CAT® systems are used for removing over 1,000 – 10,000 kg S/d. The MINI–CAT® process, born out of the LO-CAT®, treats smaller H_2S loads using (200 – 1,000 kg S/d) the same chemistry than the LO-CAT® and it is therefore especially suitable for biogas systems. Landfills and wastewater treatment plant digesters have implemented MiNI-CAT® H_2S removal systems successfully.

6 Membrane separation

It consists in the use of semipermeable membranes to separate H_2S from a pollutant gas stream by establishing a partial pressure gradient across a semipermeable glassy or rubbery surface that constitutes the membrane. The membrane is designed to allow either gas molecules or pollutant molecules to pass preferentially, resulting in more concentrated pollutant stream on one side of the membrane. Two types of membrane systems exist: high pressure with gas phase on both sides, and low pressure with a liquid adsorbent on one side. A single-stage separation unit cannot achieve complete separation and multistage separation is required.

Membranes can be used for simultaneous removal of CO_2 and other impurities, although today, to extend membrane life, H_2S is separated before high pressure membranes. Due to their high cost membranes are not yet competitive for selective removal of H_2S. Low-pressure gas-liquid membrane processes are a promising technology for H_2S removal.

7 Biofilters and biotrickling filters

In these systems the biogas is forced through a moist, packed bed that contains microorganisms. Microbes grow on the surface and crevices of the support, forming a biofilm. The H_2S in the biogas is transferred from the gas phase into the biofilm, where is used as energy source by the microorganisms producing mainly sulfur if the oxidation is partial or sulfate if it is total. Parameters influencing the process include bed medium, moisture content, temperature, pH, contact time, nutrient and oxygen levels. The bacteria normally used for H_2S removal are aerobic, and therefore they require oxygen. The conventional way of supplying oxygen into a biofilter/biotrickling filter is injecting directly air (4 – 10%) into the gas stream.

The main difference between biofilters and biotrickling filters is the nature of the carrier material, organic in biofilters and inert in biotrickling filters. Therefore, as nutrients are not available in the carrier material of the biotrickling filters they are supplied to the microorganisms by recirculating continuously a liquid phase, counter o co-current to the gas flow, through the reactor. This liquid phase provides too moisture and a means to control the pH or other operating parameters.

The major problem found in biofilters is the acidification of the media due to sulfuric acid formation by the degradation of the H_2S. To counteract the pH drop, special measures are usually taken. The general approach is to enhance the buffering capacity of the media by adding alkaline compounds or using a carrier base that itself has some alkaline properties and/or washing periodically the filter media with water. This problem is avoided in biotrickling filters due to the fact that the acid reaction products are washed out of the media continuously.

Several commercial systems are available. The Biopuric process (Biothane Corporation) was developed in Germany in the 1980s. This process is capable of treating biogas effectively with hydrogen sulfide concentrations ranging from 1,000 to 15,000 ppmv, and single modules loads up to around 200 kg H_2S/d. Removal rates consistently range from 90 to 99%. The Biopuric system is a biotrickling filter working in a pH range of 1 to 3, mesophilic temperatures and under microaerophilic conditions. A define volume proportion of air is injected into the biogas before entering in the biological reactor. In a typical scenario over two thirds of the hydrogen sulfide removed in the Biopuric system is converted into elemental sulfur. Most of this sulfur accumulates in the biofilm on the reactor media. The excess biofilm is periodically flushed from the reactor. Depending on actual operating conditions, this may have to be carried out four to twelve times per reactor per year. Apart from this periodic flush, reactor operation requires little attention and is fully automated. The acidity in the reactor is usually controlled by purging the circulation liquid with a source of clean water (McKinsey, 2003).

The Dutch company DMT Environmental Technology has commercialised the BioSulfurex® which claims a reduction of more than 95% in H_2S for incoming biogas with up to 1% vol. Other Dutch company, Colsen B.V has developed the Bidox® system, which claims H_2S level reduction from > 10,000 ppm to < 50 ppm, with a power consumption of 0.21 kWh/kg H_2S removed, and the combined operational and maintenance costs mount up to around 0.10 – 0.25 €/kg H_2S removed. EnviTec biogas has as well developed a biological trickling filter to desulphurise biogas. The oxidation product of this process is elementary sulphur which drops to the bottom of the filter and is then discharged. EnviTec claims a desulphurization performance of more than 94 % on average.

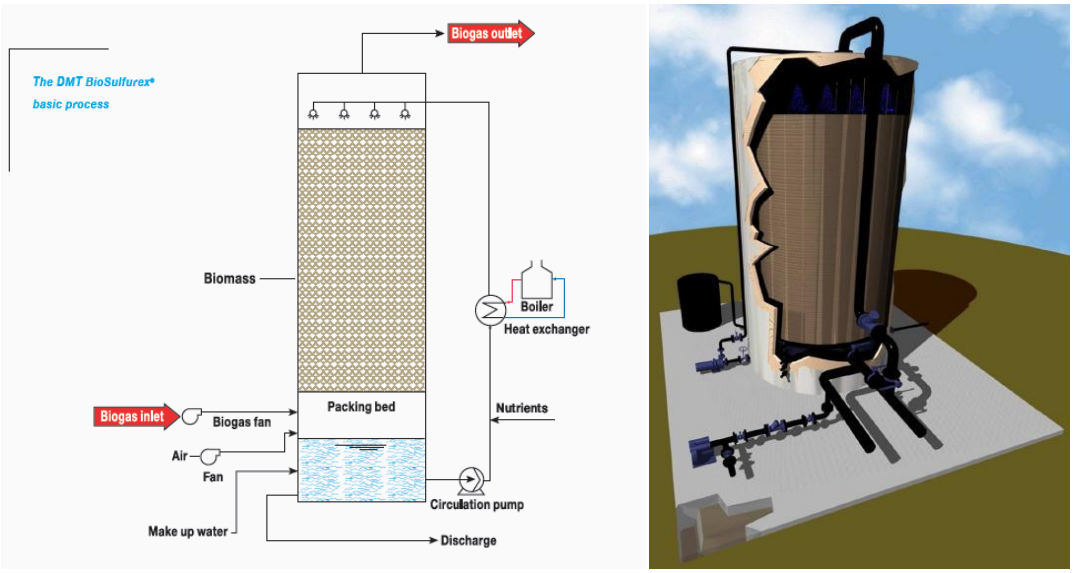

Figure 7: DMT BioSulfurex® basic process (left) and Bidox® system (right)

The Danish company BioGasclean has supplied more than 100 BiogasCleaner® desulfurization plants. They comprise a biotrickling filter working at low pH in one or more tanks of fiberglass or steel tanks with acid-proof liner. Air is injected directly into the system and the main product is sulfate. In case of clogging BioGasclean's gas cleaners are designed to be cleaned completely in less than one working day, without manually removing the filter material from the tank, with the so called system QSR® (Quick Sludge Remover). This system has been installed in biogas facilities with H_2S concentrations up to 5% of H_2S and sulfur loads up to 5,500 kg/d. BioGasclean is guaranteeing as low as 10 ppm H_2S in the clean gas and it can use pure oxygen instead of atmospheric air for upgrading projects. For high loads several BiogasCleaner towers are used in line or in parallel

Figure 8: BioGasclean Måbjerg plant

Biological systems need still to be improved regarding to H_2S peak control and to guaranty continuous removal to very low H_2S concentrations. For injection in the natural gas grid or vehicle fuel use a second cleaning section as a small activated carbon bed is necessary. Moreover biogas quality is reduced when introducing the oxygen for the bacterial process as air.

8 Bioscrubber

A bioscrubber consists of two reactors. The first part is an absorption tower, where pollutants are absorbed in a liquid phase. This liquid phase goes to a second reactor, which is a kind of activated sludge unit. In the latter, microorganisms grow in suspended flocks in the water degrading the pollutants. The effluent of this unit is recirculated over the absorption tower. Nutrient addition, oxygen and pH are continually controlled to maintain microbial growth and high activity. The excess biomass and byproducts are continually purged from the system.

The most well-known scrubber system for removal of H_2S from biogas is the THIOPAQ™ Process licensed by Paques. The THIOPAQ™ system can be regarded as a caustic scrubber in which the spent caustic solution is continuously regenerated in a bioreactor by natural occurring microorganisms. In the scrubber the H_2S contained biogas is brought in a counter-current mode with the alkaline liquid of the bioreactor (pH ranging from 8.2 to 9) causing the H_2S in the biogas to be absorbed into the liquid phase. The solution leaving the scrubber ($NaHS + H_2O$) is directed to the bioreactor. The bioreactor operates near atmospheric pressure and is aerated (constant mix) with a controlled inflow of ambient air. Colorless sulfur bacteria react with the spent scrubber solution and convert the dissolved sulfide to solid elemental sulfur ($NaHS + 0.5O_2 \rightarrow S_o + NaOH$). A small portion of the dissolved sulfide (less than 5%) is completely oxidized to sulfate ($2NaHS + 4O_2 \rightarrow NaHSO_4 \rightarrow Na_2SO_4 + H_2SO_4$). According to this, the solution alkalinity is partially regenerated during the production of elemental sulfur and to maintain pH above 8.2 less than 5% of NaOH must be added as compared to a conventional chemical caustic scrubber. A continuous bleed stream is required to avoid accumulation of sulfate and the produced elemental sulfur is removed from the system. This can be used as raw material in sulfuric acid production factories or it is disposed of. H_2S removal efficiency is claimed to be typically about 99% for properly operated systems.

An advantage of this process regarding to the biofilters/biotrickling filters is that there is not injection of oxygen or nitrogen into the biogas stream. Disadvantages are higher specific cost.

In general, the H_2S content in the biogas is reduced from about 2 vol.-% down to 10 to 100 ppmv, although levels of only a few ppmv can also be achieved. Gas flows normally range from 200 to 2,500 m^3/h (Cline, 2002).

IETL is an Indian company that has also developed a biological scrubber called Bioskubber™, as in the THIOPAQ™ process H_2S is absorbed in a caustic solution which is regenerated in a bioreactor where colorless sulphur bacteria transform the H_2S into elemental sulfur. The company claims removal efficiencies of more than 99 %.

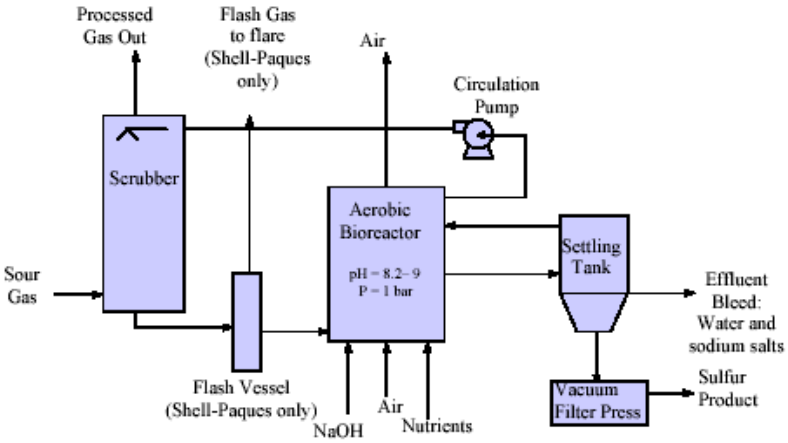

Figure 9: Simplified THIOPAQ™ and Shell-Paques System Schematic (Greenhouse Gas Technology Center, 2004) and picture of a THIOPAQ™ plant (Beil, 2010)

9 Chemical absorption with $Fe_2(SO_4)_3$ and microbial regeneration (Bio-SR)

A combined system for the elimination of H_2S from waste gas have been described (Figure 10) where, in the first step, H_2S is oxidized to elemental sulphur with ferric ion in an absorber and, in the second step, the ferric ion is regenerated by *T. ferrooxidans* (Pagella, 1996). An advantage of this method is that the first reaction (Eq. 12) is so fast and complete that there remains no danger of discharging toxic waste gas. Moreover, sulphur can be recovered from the medium.

$$H_2S + Fe_2(SO_4)_3 \rightarrow 2FeSO_4 + H_2SO_4 + S^0 \qquad \text{Eq. 12}$$

Depending on the gas flow rate and the efficiency required, several types of absorbers are suitable, such as jet scrubbers, bubble-cap towers, or packed towers. Elemental sulphur is separated and recovered from the reduced solution of ferrous sulphate in a separator. The sulphur separators can include settlers, filter presses, and sulphur melters, depending on the quality of elemental sulphur required. After recovering the elemental sulphur the ferrous sulphate solution is led to an aerated bioreactor where *T. ferrooxidans* oxidizes the ferrous ion to ferric (**Fejl! Henvisningskilde ikke fundet.**).

$$2FeSO_4 + 2H_2SO_4 + ½\,O_2 \rightarrow Fe_2(SO_4)_3 + H_2SO_4 + H_2O \qquad \text{Eq. 13}$$

The oxidized solution is then recycled to the absorbed to repeat the cycle. An H_2S removal efficiency of more than 99.99% has been attained in an existing commercial plant (Jensen, 1995).

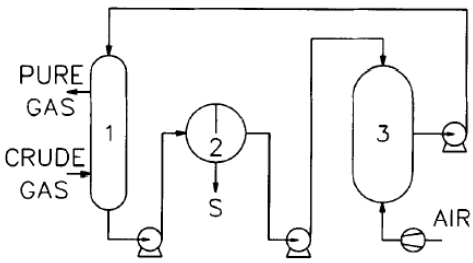

Figure 10: Flow scheme of the BIO-SR process. 1. Absorber, 2. Solid-liquid separator, 3. Bioreactor (Jensen, 1995)

The iron oxidation rate is observed to be five times higher (36 $g.l^{-1}.\ h^{-1}$) in a fixed bed reactor compared to the suspended cell reactor. pH plays a key role both for controlling the growth rate of *Thiobacillus* sp. and the solubility of the materials in the system. The advantages of this process with respect to conventional treatment processes for H_2S abatement are mild pressure and temperature conditions (typical of biotechnological processes), lower operating costs, and closed-looped operation without the input of chemicals or output of wastes. Disadvantages of other microbial processes for H_2S removal are avoided in the BIO-SR process. H_2S does not inhibit the bacteria and SO_4^{2-} does not accumulate in the system. Furthermore, contamination of the purified gas with O_2 is prevented.

10 Cost analysis

It is difficult to find costs estimations in literature for different systems in an unify way. Different cost for several systems with different gas capacities and H_2S removal amounts are given in this chapter. Although comparisons are difficult to make, these costs gives an overall impression.

An overview of three different H_2S removal technologies costs is given in Table 3. For catalytic and chemical-biological scrubbing, the cost estimates include the cost of disposal of solid waste approximately EUR 70 /t. The sulphur cake generated is approximately 60 % water, whereas the produced waste amount is 100-150 t/a (corresponding to 41–58 t/a elemental sulphur removed). The waste produced is non-hazardous and can be utilized as fertilisers. Table 3 compares the costs for these regenerative processes for a 150 kg/day sulphur removal rate from 600 ppm H_2S-laden gas. According to calculations biological scrubbing was the most economical, both in regards to investment and operation costs.

Table 3: Cost estimates of selected desulphurization technologies (Arnol, 2009; based on data from Urban et al. 2009, Lindqvist 2008, Graubard et al. 2007, Pulsa 2008, Carlton et al. 2007).

150 kg/day sulphur removal rate from 600 ppm H2S-laden gas	Investment €	Total cost/year €	Specific capital cost c€/Nm3	Operation and service c€/Nm3	Total c€/Nm3
Catalytic scrubbing with chelated-iron salt solutions *based on figures on MiniCat*	900 000	139 000	0.15	0.06	0.21
Biochemical scrubbing *based on figures on Paques*	900 000	128 000	0.14	0.02	0.17
Biological scrubbing based on figures on Envitec	500 000	73 000	0.08	0.03	0.11

Table 4 presents a group of sulphur removing techniques according to their removal efficiency (kg S/day) as well as expenses. The expense estimates are mostly from US sources and possible expenses for landfill disposal of solid sulphur waste are not taken into account.

Table 4: Sulphur-removing techniques operation costs (Arnol, 2009; based on data from EPRI. 2006; Graubard, 2007; Carlton, 2007)

Medium/technique	Residual	Capacity kg S/day	Running expenses, €/kg S	Observations
Ferrous chloride addition	Ferrous sulphide remains in the sludge	112	0.7	Added into the digester liquid phase
Activated Carbon	Activated carbon impregnated with	< 9	3.5	H_2S outlet < 0.1 ppmv

Medium/technique	Residual	Capacity kg S/day	Running expenses, €/kg S	Observations
	sulphur (landfill waste)			Regeneration possible
Iron sponge	Chipwood impregnated with ferrous sulphide (landfill waste)	< 110	1.7 – 4.5	Chipwood coated with iron oxide
Sulfatreat	Iron pyrite (landfill waste)	> 25 – 135 < 110	2.25 – 4.00 3.5 – 6.2	
Bioscrubber	Used scrubbing liquid to water treatment plant	8 - 450	0.05*	
Catalytic oxidation with chelated-iron salt solutions	Elemental sulphur (landfill waste)	135 – 15 000	0.3 – 1.1	

* depends on the cost of nutrient addition

Costs for the biological H_2S removal system BiogasClean are given in Table 5 (Kvist, 2011; data from BiogasClean). Costs are calculated considering:

Electrical price: 0.11 €/kWh
Running time: 8,500 per year
Life time: 15 year
Rate: 6 %

Table 5: Cost of the biological H2S removal system BiogasClean (Kvist, 2011; data from BiogasClean considering 1€ = 7.4 kr.)

Capacity	m^3/h biogas	200	500	1000	2000
Investing	€	108,100	148,650	175,700	243,250
Operational costs					
Electricity	kWh/year	9,000	12,000	21,000	24,000
Nutrients (NKP)	€/year	334	810	1,622	3,243
Sum:					
Capital cost	€/year	11,100	15,300	18,000	25,000
Electricity	€/year	973	1,297	2,270	2,595
System using air					
Total:	c€/m^3 biogas	0,72	0,41	0.26	0.18
System using oxygen					
Oxygen	€/year	3,200	8,100	16,200	32,400
Total	c€/m^3 biogas	0.92	0.60	0.45	0.38

The Danish company Envidan has reported the following cost information regarding to biological H_2S cleaning (Table 6). Cost for the biological H_2S removal system BioSulfurex® from the Dutch company DMT are given in Table 7 (depreciation 10 years at 5% interest).

Table 6: Costs of a biological H_2S cleaning system (Kvist, 2011; data from EnviDan considering 1€ = 7.4 kr.)

Capacity (Nm^3/h)	NH_3 after cleaning (mg/Nm^3)	H_2S before (mg/Nm^3)	H_2S after (mg/Nm^3)	Plant costs (€)	Plant costs (c€/Nm^3)
500	5	760	304	121,600	0.45
1000	5	3040	304	162,200	0.30
2000	5	3040	304	202,700	0.19

Table 7: Cost for the biological H2S removal system BioSulfurex® (Kvist, 2011; data from DMT)

Capacity (Nm^3/h)	H_2S before (mg/Nm3)	H_2S after (mg/Nm3)	Operational costs (8760 working hours) (€/year)	Plant costs (€)	Total costs (c€/Nm3)
500, 30 °C, 35 vol.% CO_2	7,600	304	25,540	160,500	1.18
500, 10 °C, 35 vol.% CO_2	7,600	304	29,324	174,200	1.30
500, 30 °C, 35 vol.% CO_2	15,200	304	33,920	202,700	1.51

DMT has also developed a caustic water scrubber for H_2S removal for small applications, Sulfurex®. Sulfurex® is designed to remove from 20,000 ppm to 200 ppm H2S. Some costs of this system are given in Table 8.

Table 8: Cost for the caustic desulphurization scrubber Sulfurex® (Kvist, 2011; data from DMT)

Capacity (Nm^3/h)	H_2S before (mg/Nm3)	H_2S after (mg/Nm3)	Operational costs (8760 working hours) (€/year)	Plant costs (€)	Total costs (c€/Nm3)
500, 30 °C, 35 vol.% CO_2	7,600	304	64,595	127,000	1.92
500, 10 °C, 35 vol.% CO_2	7,600	304	56,890	146,200	1.82
500, 30 °C, 35 vol.% CO_2	15,200	304	91,490	132,800	2.56

The company Siloxa Engineering AG produces a system called Siloxa based in activated carbon to remove H_2S and siloxanes. The Danish distributor is EnviDan. The price for purifying 1 m^3 of biogas with a depreciation of 10 years at 5 % rate is 1.08 c€/year of which the operation costs are 0.8 c€/year (see Table 9).

Table 9: Cost for the activated carbon desulphurization process Siloxa (Kvist, 2011)

Capacity (Nm^3/h)	Activated Carbon (kg)	H_2S before (mg/Nm3)	H_2S after (mg/Nm3)	Operational costs (8760 working hours) (€/year)	Plant costs (€)	Total costs (c€/Nm3)
500	2x1400	680	1	35,500	70,300	1.08

In Estabrooks 2013, a cost comparison between the Sulfatreat and the Thiopaq processes is given for two cases (Table 10).

Table 10: Example of cost of the Sulfatreat (adsorption with iron oxides) and Thiopaq (biological scrubber) (Estabrooks, 2013; considering 1$ = 0.7 €)

	Case 1: 4245 m^3/h; from 3,500 to 200 ppmv H_2S ~ 453 kg H_2S/day		Case 2: 4245 m^3/h; from 1000 to 200 ppmv H_2S ~ 113 kg H_2S/day	
	Sulfatreat	*Thiopaq*	*Sulfatreat*	*Thiopaq*
Capital investment cost (€)	2,500,000	4,900,000	1,450,000	4,900,000
Annual operating cost (€)	2,360,000	720,000	755,000	455,000
Annualized total costs (10 years) (€/year)	2,800,000	1,500,000	991,400	1,256,000
Annualized total costs (10 years) (c€/Nm^3)	7.4	4.09	2.67	3.37

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