

A review of biogas purification processes

Nicolas Abatzoglou, Université de Sherbrooke, Quebec, Canada

Steve Boivin, Université de Sherbrooke and Bio-Terre Systems, Inc., Quebec, Canada

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Abstract: Biogas is a valuable renewable energy carrier. It can be exploited directly as a fuel or as a raw material for the production of synthesis gas and/or hydrogen. Methane (CH₄) and carbon dioxide (CO₂) are the main constituents, but biogases also contain significant quantities of undesirable compounds (contaminants), such as hydrogen sulfide (H₂S), ammonia (NH₃) and siloxanes. The existence and quantities of these contaminants depend on the biogas source (i.e., landfills, anaerobic fermentation of manure). Their presence constitutes a major problem because (i) they can be detrimental to any biogas thermal or thermocatalytic conversion device (e.g., corrosion, erosion, fouling); and (ii) they generate harmful environmental emissions. It is therefore important to include biogas purification steps upstream of its final use processes. This review is aimed at presenting the scientific and technical state-of-the-art in biogas purification processes. Both mature, already-applied and promising, under-development technologies are reported and described here. © 2008 Society of Chemical Industry and John Wiley & Sons, Ltd

Keywords: review; biogas; physicochemical and biological purification; H₂S; NH₃; siloxanes; removal; reactive adsorption; commercial technologies; cost

Introduction

In a world that is increasingly accepting the imperative nature of sustainable development, the junction of energy and environment has become a field of intense activity, with both R&D and technology implementation given top priority. Biogas, naturally occurring from the decomposition of all living matter, has yielded important industrial products or byproducts, and its commercial value has risen for two reasons: (i) because its release into the atmosphere contributes largely to greenhouse gas concentration, with consequent and significant remediation costs, and (ii) because its energetic content is high, and its exploitation

means significant revenues or avoided costs. Systematic biogas sources linked to anthropogenic activities include non-exclusive units of: landfill, commercial composting, wastewater sludge anaerobic fermentation, animal farm manure anaerobic fermentation, and agrofood industry sludge anaerobic fermentation. The biogas produced by all these activities is rich in CH₄ (typically ranging between 35 and 75%vol), and its higher heating value is between 15 and 30 MJ/Nm³.

Conversion of the chemical energy contained in biogas to heat or electricity is possible through combustion. If heat is the required output, biogas is usually fed into burner-boiler units, and the released heat is transferred to water and

off-gases. If electricity is targeted, biogas is either fed directly to internal combustion engines (Otto cycle engines or turbines) or to combustors-superheaters/boilers generating high-quality steam for electricity production through steam-cycle turbines (Gazmont, Montreal; http://www.cemr.ca/f_business_01.html).¹ In all of these cases, biogas quality is crucial in both its CH₄ content and purity. The latter is highly affected by the presence of contaminants in trace or higher quantities, and whose nature depends on the source of its production. The most common contaminant is H₂S and other malodorous sulfur- (S)-containing compounds (i.e., mercaptans, such as CH₃SH) coming from the anaerobic fermentation of S-bearing organic molecules (i.e., proteins). Depending on the composition of the organic material fermented, the H₂S content of biogas can vary from some 10s to about 10,000 ppmv (0.0001–1%vol). This contaminant, besides its bad smell, is highly non-desirable in energy-recovery processes because it converts to highly corrosive, unhealthy and environmentally hazardous sulfur dioxide (SO₂) and sulfuric acid H₂SO₄. Its removal is a must for any eventual utilization of biogas.

Ammonia (NH₃) is another common contaminant coming from the anaerobic digestion of nitrogen-bearing organic molecules. It, too, is corrosive and represents a health risk, but its combustion only slightly increases nitrogen oxides (NO_x) emissions, and it is not considered as harmful as H₂S.

'Siloxanes' are a group of silicon (Si)-bearing molecules found in landfill biogases. They are considered to be the third most important contaminant. Their presence during combustion is detrimental because they form glassy microcrystalline silica. Their removal is also a must to ensure an acceptable and useful lifespan of process equipment. All other components in biogas (CO₂, H₂O, O₂, N₂, Ar) are considered to be harmless or even useful, as is the case with O₂ which is helpful in some H₂S-removal technologies by partially oxidizing S²⁻ into elemental sulfur (S⁰). CO₂ is sometimes considered to be a nuisance because it is present in large quantities (almost balanced between about 95% and the % of CH₄), and it is an inert gas in terms of combustion, thus decreasing the energetic content of the biogases. There are methods of enriching biogas in CH₄ by separating it from CO₂. The main technique used is pressure swing adsorption (PSA) on zeolites (molecular sieves) with

high selectivity in CO₂ adsorption and selective membrane separation.^{2,3} Nevertheless, since CO₂ is not considered to be a contaminant, its study is outside the scope of this review.

Biogas purification methods can be divided into two generic categories:

1. Those involving physicochemical phenomena (reactive or non-reactive absorption; reactive or non-reactive adsorption).
2. Those involving biological processes (contaminant consumption by living organisms and conversion to less harmful forms).

Review of physicochemical biogas purification methods and techniques

In the first category belong the following processes which are reviewed in subsequent parts of this review: *chemical absorption in aqueous solutions; chemical adsorption of H₂S on solid adsorbents; and scrubbing with solvents or other liquid phases.*

In the second category belong the biological processes. The focus is on different species of chemotrophic thiobacteria serving as S-oxidizing agents in biofilter, biotrickling filter and bioscrubber units.

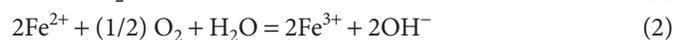
H₂S and NH₃ removal

Chemical absorption in aqueous solutions

The chemical affinity of H₂S for metallic cations is at the basis of processes employing chemical absorption. These processes can be divided into two categories, those involving oxidation of S²⁻ to S⁰, and those based on the capture of S²⁻ through precipitation of its metallic salts owing to their very low K_{sp} (water solubility product). Another option, which belongs to the second category, is the capture by aqueous alkaline solutions which rapidly react with diffused H₂S. Nevertheless, this option is not examined here extensively because of its low importance. The low interest is attributed to the high reactivity of CO₂ with alkaline solutions. Thus, this method is much less selective for H₂S, and the captured CO₂ consumes relatively expensive alkaline reactants (i.e., NaOH or CaO).

Processes involving H₂S conversion to S⁰

The first published work reporting on complexes of Fe³⁺-chelates with H₂S and mercaptans appears to be that of Philip and Brooks⁴ in 1974. In 1984, Neumann and Lynn⁵ published their findings on the oxidative absorption of H₂S and O₂ by Iron (Fe)-chelated solutions. The redox reactions involved were:



In 1991, a patent was filed by the Dow Chemical Company,⁶ probably to protect the Sulferox[®] process commercialized by Shell and Dow. Obviously, the interests of these companies in this technology came from their oil and coal activities which produced large quantities of sour gases, so far desulfurized in Claus units, and certainly not from the biogas industry. Although the technology is well-described in the patent, no data are available on process kinetics. In 1994, Wubs and Beenackers studied the kinetics of H₂S absorption into aqueous ferric solutions of ethylenediaminetetraacetic acid (EDTA) and hydroxy-ethylethylenediaminetriacetic acid (HEDTA).⁷ They found that only the hydroxyl forms of Fe-chelates reacted with H₂S and, consequently, the reaction was possible at high pH values. The approximate models considered were completed by Demmink and Beenackers⁸ in 1998, who incorporated mass transfer and reaction kinetics based on penetration theory in their mathematical paradigm. They proposed and validated a reaction mechanism clearly depicting the higher reactivity of the hydroxyl species. The major finding is, however, the significant effect of near-interface concentration gradients which, depending on operating conditions, can render H₂S diffusion the controlling step of the process. The comprehensive model proposed seems to be scalable, but the influence of operating conditions on the H₂S mass transfer coefficient through the liquid film (K_L) is not a known function of operating conditions and this limits the applicability of the model. As in virtually all other studies reported in this work, they determined that the reaction kinetics were of order 1 with H₂S and the same with Fe³⁺. More recently, in 2003, Iliuta and Larachi⁹ proposed the application of this method in Kraft paper mills. They combined O₂- and H₂S-containing atmospheric effluents with iron chelate solutions in a scrubber. Two other

patents^{10,11} referring to Dow Chemical one,⁶ were filed by the Institut Français du Pétrole (IFP). The only noticeable differences were: (i) the non-use of a separate nanofiltration step to remove water and chelant degradation products, and (ii) operation of the process at high pressures (up to 1 MPa).

In 2004, Horikawa *et al.*¹² used the method in a lab-scale counter-current gas-liquid contactor at room temperature (RT) and low gas pressure (P). Their work was aimed at (i) presenting a more reliable, Fe-chelated solution preparation; (ii) proving the higher absorption capacity and efficiency of the method compared to pure water adsorption; and (iii) producing data for scale-up calculations and techno-economic evaluation of the process. In this method, gaseous H₂S diffuses in a Fe-chelated aqueous solution where it participates in a redox reaction. S²⁻ is converted to S⁰ while the Fe³⁺ cation is reduced to Fe²⁺. The S⁰ is water-insoluble and remains as a dispersed solid phase in the solution. The spent Fe-chelated solution is filtered or submitted to sedimentation to remove solid S and then regenerated back to the Fe³⁺ form through oxygenation in a secondary air-solution counter-current contactor (bubbling air column).

The Fe-chelated solution was prepared successfully with Fe powder and HBr as starting materials to synthesize FeBr₂. The latter, less sensitive than the previously reported FeCl₂, was used to prepare a homogeneous Fe-EDTA solution of 0.2 mol/L. The experimental set-up included simulated biogas (a synthetic mixture) containing about 80%vol CH₄ and H₂S = 2.2–2.4%vol. Cylindrical absorber unit dimensions were: internal diameter (ID) = 5.4 cm and height (H) = 36 cm. The solution flow rate was L = 68–84 ml/min for a gas flow rate of 1000 ml/min at pressure (P) = 1.2–2.2 bar. For low P and high L, H₂S removal efficiency can reach 100%. Batch experiments allowed the rate of solution deactivation and subsequent regeneration to be determined. It is noteworthy that the CO₂ capture rate from this solution is negligible in opposition to alkaline solutions. The data permitted easy calculation of residence times, but it is probable that scale-up will not be a straight-forward process because the authors did not provide kinetic data which could determine whether the process was diffusion- or reaction-controlled. Consequently, additional data are required to avoid trial and error in an eventual scale-up. Besides, although process severity is low (RT and low P), it involves

fairly complex steps, and industrial applications are possible only for high-capacity units. So far, there are no known industrial applications, and the probability of seeing the process applied on pig or other animal farms is rather low.

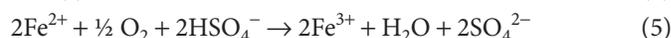
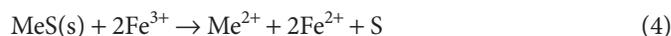
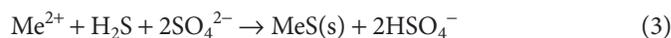
LO-CAT[®] (US Filter/Merichem) and SulFerox[®] (Shell/Dow) processes are currently available chelated-Fe H₂S removal technologies. The SulFerox[®] licence is jointly handled by Dow and Shell; Dow licenses the technology externally, and Shell markets the process among its own company divisions. IFP has one such license, and Gaz Integral Enterprise of France, a company like IFP, markets the SulFerox[®] process¹³ for S removal rates between 100 and 20000 kg/day and high CO₂/H₂S ratios. CO₂ is not removed significantly, but 50–90% of mercaptans can be removed in either low- or high-P applications. S removal with SulFerox[®] costs around \$0.24–\$0.3 per kg. LO-CAT[®] can effectively treat any stream containing S and, consequently, any biogas. Since its typical economic niche¹⁴ is the removal needs of more than 200 kg of S/day, farm applications of this technology are not economically sustainable. However, the technology can be envisaged for landfill biogases. The company reports the following application: the Broward County, Florida, landfill collects approximately 3 Nm³/s of landfill gas from 300 wells and converts it to electricity on site at the nation's largest landfill gas-turbine-to-energy plant. Increasing H₂S concentration in the landfill gas caused severe odor problems, corrosion in the compressors, and SO₂ emission problems in turbine exhaust gas. A LO-CAT[®]II H₂S oxidation system was installed to treat up to 5 Nm³/s of landfill gas containing up to 5000 ppmv H₂S. This gives a total amount of S to be captured of about 3000 kg/day.

In 2005, Lee *et al.*¹⁵ worked on a magnesia-supported, iron III+ oxide (Fe³⁺/MgO) catalyst in a slurry batch reactor to remove H₂S from a gaseous stream composed of an O₂ and H₂S mixture at a 100/5 molar ratio and at room temperature. The redox reactions occurring are the same as with Fe³⁺-chelated solutions, as shown by the XPS spectra of fresh and spent catalysts. The best-performing formulation was that having an iron load of 15%wt; its measured H₂S removal capacity was 3.74 g H₂S/g catalyst, but this number was obtained by stopping the experiment when H₂S removal efficiency dropped to 50%. Consequently, the real capacity for a successful industrial process must be fairly

lower. No SO₂ was detected at the exit gas, showing that all S²⁻ was converted to S⁰ or reacted with Fe to form sulfides. It could be expected to have *in situ* regeneration of Fe³⁺ due to the high O₂ concentration in the gas, but one must consider the batch character of the runs. Unfortunately, there is no other information regarding regeneration of the catalyst, i.e., under steady-state bubble-column operation. The same authors¹⁵ also examined the catalytic properties of a magnesia-supported copper II+ oxide (CuO/MgO) catalyst under the same conditions and according to the same experimental procedure. They showed that the optimal Cu loading was 4%wt. So far, no other data have been published in this area, but the usefulness of the process and its techno-economic feasibility cannot be evaluated without knowing catalyst costs and consumption per unit of S removed.

Processes involving H₂S conversion to low solubility metallic sulfides

In 1992, Broekhuis *et al.*¹⁶ presented a medium T process for H₂S removal from sour gas coming from oil refineries using metal sulfate solutions. Although the process takes CuSO₄ or ZnSO₄ to form metal sulfides which are quasi-insoluble in water and apparently belong to this category, it also uses Fe³⁺ to oxidize S²⁻ to S⁰ while regenerating Fe²⁺ solution by air oxidation under ambient conditions. Thus, it is closer to the first rather than the second category. The process deploys a venture scrubber as a gas-liquid contactor-reactor. The H₂S-containing gas diffuses in sulfates containing aqueous solutions and reacts with metallic cations to form insoluble sulfates. The metal sulfides react (redox reaction) with ferric cations to form S⁰, thus liberating cations for new S²⁻ capture. The ferrous cations formed from the reduction of the ferric ones are then submitted to reoxidation under air in a separate counter-current bubble-column contactor operated at RT. The reactions taking place can be represented by the following equations:



Zn and Cu sulfate solutions have been tested. Zn performance was not satisfactory in the pH range tested (acidic due

to the addition of H_2SO_4) while Cu gave excellent S retention efficiency, even at pH as low as 2.6. Cu solutions allow fast absorption rates but, even in this case, tests showed that the process was diffusion-limited. The best results were obtained at temperatures around 60°C . Reoxidation of the Cu solution with ferric cations must be undertaken at temperatures typically higher than 100°C to reach conversions higher than 99% for residence times of 5 min. The process targets coal gas because of similarities to technologies mentioned earlier. Its application at lower scales is rather improbable owing to the relatively high complexity and costs. Besides, this process is more intensive, and the severity of the reactions is higher. Thus, all operations occur at temperatures above 60°C , and the environment is quite corrosive due to the low pH and the presence of strong acids like H_2SO_4 . More recently, in 2005, H. ter Maat *et al.*¹⁷ reported, in Parts I and II of their work, a study on H_2S removal from gas streams (more generally), using aqueous solutions of metal sulfates. They focused on CuSO_4 and regeneration of the derived CuS to CuO. They determined the optimal pH range for sulfide precipitation. There is nothing to improve the severity of the reactions presented previously and the probability of seeing this technology applied to biogases in the near future.

Processes involving chemical adsorption of H_2S on solid adsorbents

These processes are based on the selective adsorption of H_2S on solid adsorbents. They are also called 'dry' because they do not involve liquid phases. These processes use fixed-bed upward or downward flow gas-solid contactors. Like almost all adsorption processes, they are semi-batch because there is a continuous gas-stream flow and a fixed bed of adsorbent which is gradually saturated with the adsorbate. These processes are not employed for large-scale desulfurization, mainly because the adsorbent cannot be regenerated and its useful lifespan is relatively short. They are, consequently, considered more appropriate for the purification of small-scale biogas production (e.g., fermentation of manure and dairy effluents and small-to-medium landfills). Subcategories of these processes are defined by adsorbent type. These categories are analyzed below.

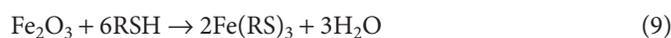
Iron oxides

The iron sponge is the best-known iron oxide adsorbent. Iron-oxide-impregnated wood-chips selectively adsorb H_2S and mercaptans. The primary active ingredients are hydrated iron oxides (Fe_2O_3) of alpha and gamma crystal-line structures. The mixed oxide, Fe_3O_4 ($\text{Fe}_2\text{O}_3 \cdot \text{FeO}$), also contributes to the activity present.¹⁸ Typical specifications for the iron sponge were given in 1997 by Kohl and Neilsen.¹⁹

The chemical reactions involved are shown in the following equations:²⁰



The iron sponge is also capable of removing mercaptans according to the following equation:²¹



Like all gas-solid adsorption processes, iron-sponge-based H_2S removal is operated in batch mode with separate regeneration, or with a small flow of air in the gas stream for continuous, at least partial, regeneration. The iron sponge can be operated in batch mode with separate regeneration, or with a small flow of air in the gas stream for continuous revivification. In batch mode, operational experience indicates that only about 85% ($0.56 \text{ kg } \text{H}_2\text{S}/\text{kg } \text{Fe}_2\text{O}_3$) of theoretical efficiency can be achieved as reported by Taylor in 1956.¹⁹ The same authors discerned that regeneration takes place under the following conditions: 8%vol O_2 concentration in the gas stream and at space velocity $0.3\text{--}0.6 \text{ m}^3/\text{m}^3$ of the iron sponge/min. Alternatively, the sponge can be removed, spread out in a 0.15 m-thick layer, and continually wetted for 10 days. It is imperative to manage heat build-up in the sponge during regeneration to maintain activity and prevent combustion. Due to S^0 build-up and loss of hydration water, iron-sponge activity is reduced by about one-third after each regeneration cycle. Therefore, regeneration is only practical once or twice before a new iron sponge is needed.

Removal rates as high as $2.5 \text{ kg } \text{H}_2\text{S}/\text{kg } \text{Fe}_2\text{O}_3$ have been reported in continuous-regeneration (in fact, it is rather a revivification) mode with a feed-gas stream containing only a few tenths of a percent of oxygen.¹⁹

At Huntington's Farm in Cooperstown, NY, a removal level of 1.84 kg H₂S/kg Fe₂O₃ was reported, with a 140 kg Fe₂O₃/m³ grade sponge and continuous revivification with 2.29% air recirculation.²²

Because the iron sponge is a mature technology, design parameter guidelines have been established for optimum operation. In 2003, McKinsey Zicari²² presented a collection of these design guidelines in his Master's thesis. Based on these criteria, and considering that the biogas to be purified has the following characteristics at 25°C and gauge P lower than 2 kPa:

Biogas composition: 60% CH₄/40% CO₂

S content: 4000 ppmv H₂S

Water content: saturated biogas

Biogas flow rate: 1400 m³/day,

the following techno-economic data can be calculated:

- Adsorbent useful lifespan: 20–80 days
- Annual iron-sponge consumption: 4–16 tn
- Annual operating costs: \$1000–\$4500

Biogas operations currently using the iron sponge are located in Cooperstown, NY, Little York, NY, and Chino, CA, among others. H₂S levels at one farm digester were consistently reduced from as high as 3600 ppmv (average 1350 ppmv) to below 1 ppmv with a 1.5-m diameter × 2.4-m-deep iron sponge reactor.²²

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

Inc., of Welder, TX. Both companies provide media for around \$6 per bushel (~50 lb); shipping costs may be more significant than actual media costs. Varec Vapor Controls, Inc. sells its Model-235 treatment units for around \$50 000, including the cost of initial media. Such a unit could last up to two years before change-out would be necessary.²²

While the benefits of the iron sponge also comprise simple and effective operation, there are critical drawbacks to this technology that have led to its decreased usage in recent years. The process is highly chemical-intensive; operating costs can be high; and a continuous stream of spent waste material is accumulated. Additionally, the change-out process is labor-intensive, and can be troublesome if heat is not dissipated during regeneration. Perhaps most importantly, the safe disposal of spent iron sponges has become problematic, and in some instances, spent media may be considered as hazardous waste requiring special disposal procedures. Landfilling on site is still practiced, but has become riskier due to fear of the need for future remediation.

Recently, proprietary iron oxide media, such as SulfaTreat[®], Sulfur-Rite[®], and Media-G2[®], have been offered as improved alternatives to the iron sponge. A fairly detailed description of these technologies is presented by McKinsey Zicari.²² Table 1 gives comparisons based on these data:

As seen on the last line of Table 1, characterization of the spent adsorbent becomes critical in evaluating the techno-economic sustainability of these technologies. In fact, for

Table 1. Comparison of iron-sponge technologies: data for 4000ppmv H₂S in biogas.

	SulfaTreat [®]	Sulfur-Rite [®]	Media-G2 [®]
No. of vessels	2 in series	1	2 in parallel
Vessel dimensions	1.22 m × 1.65 m × 1.83 m	2.29 m diameter × 3.43 m height	0.91-m diameter × 1.52-m height
Gas-flow rate	0.94 m ³ /min	0.94 m ³ /min	0.94 m ³ /min
Investment for vessel(s) only	\$8 000	\$43 600	\$13 000 (estimated)
Empty-bed residence time	4 + 4 = 8 min	15 min	1 min
Mass of adsorbent	3 636 kg each	9 100 kg	760 kg each
Air recirculation rate	2.4%	Off-line regeneration	2.4%
Expected bed lifespan	86 days	98 days	47 days
Annual adsorbent consumption	15 450 kg	33 900 kg	5 900 kg
Annual adsorbent cost	\$13 500	\$23 840	\$8 290
Spent adsorbent	Special waste	Non-pyrophoric and landfillable iron pyrite	Non-hazardous

small- to medium-scale applications (i.e., farms and landfills) the cost associated with final disposal of the spent adsorbent can determine project feasibility. The author of this work kept the wording used by the companies to characterize their spent material. From a purely scientific standpoint, all of these adsorbents are iron-based, and they will definitely contain S^0 and sulfides. S^0 must not be fixed in the adsorbent matrix while the pyrites could be either free powders or grains attached to a matrix, like the diatomaceous support of Media-G2[®] or the doped montmorillonite of SulfaTreat[®].

In 2005, Truong and Abatzoglou²³ demonstrated that the active ingredient of the adsorbent Sulfatreat 410-HP[®] is a combination of iron oxides (Fe_2O_3 , Fe_3O_4) and an activator oxide attached to a calcined montmorillonite carrier matrix; the latter is thought to catalytically enhance the reactive adsorption phenomenon. Based on data available from the manufacturer, it is known that the amount of activator is 0.125–5% w/w of the adsorbent. The activator is constituted of one or more oxides in a group of metals consisting of platinum, gold, silver, copper, cadmium, nickel, palladium, lead, mercury, tin and cobalt.²⁴ The active ingredients are supported on a non-porous silica (SiO_2) matrix containing small amounts of alumina (Al_2O_3), an aluminosilicate coming from montmorillonite. Thus, it can be said that the adsorbent is a 2D (two-dimensional) formulation in which the active ingredients are at the surface of a coarse-size

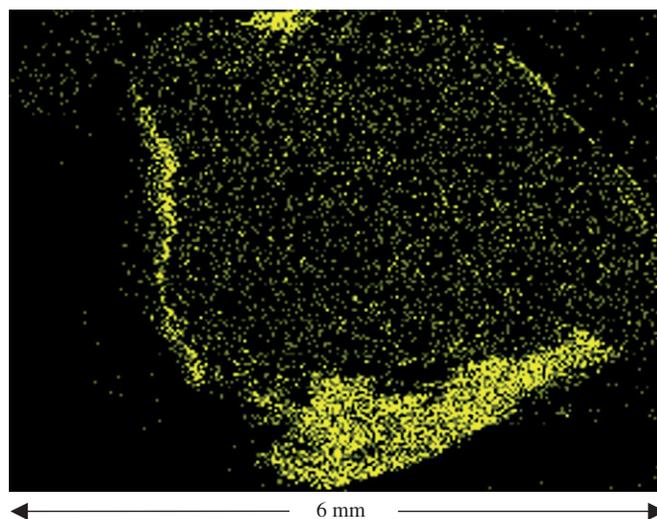


Figure 1: Iron distribution on adsorbent by SEM (active+support) particles.²³

support matrix; silica particle diameter varies between 4.0 and 6.5 mm. These data are corroborated by Scanning Electron Microscopy (SEM) analyses. Figure 1 depicts Fe distribution at the surface of the adsorbent before use.

In 2006, Abatzoglou and Truong,²⁵ based on lab-scale and farm-scale data as well as kinetic calculations published earlier,²³ presented interesting data on Sulfatreat 410-HP[®] (Table 2).

Data on a biogas flow rate of 0.125 m³/min have come from the fermentation of manure in a swine farm annually

Table 2. Data on Sulfatreat 410-HP[®].²⁵

Data on adsorbent use		
Average H ₂ S content in biogas	1 000	ppmv
Adsorption capacity	0.15	kg H ₂ S/kg adsorbent
Mass of adsorbent in unit	286	kg adsorbent
Daily consumption of adsorbent	1.70	kg adsorbent/day
Cycle length	169	days
Adsorbent use and cost estimation		
Cost of unit and media	1 542	\$
No. of replacements per year	2.17	
Real purchase cost of adsorbent	2.07	\$/kg
Replacement cost per unit	592	\$/replacement
Annual operating cost	1 281	\$/year
Initial investment cost	1 542	\$

producing 2650 pigs. This means 40 m³ of biogas/pig, an annual operating cost for H₂S removal of about \$0.5/pig or \$0.015/m³ of biogas. This cost does not include capital amortization and the final disposal cost of the spent adsorbent. If we consider a 5-year constant amount amortization period and a conservative cost of transport, management and disposal of \$500/tn of spent adsorbent, the added costs are: \$642 for disposal and \$308 for annual capital costs. Manpower costs for the operation, replacements and maintenance are very low and surely less than three days per year, that is, about \$300 less per year. Consequently, the total cost for the studied case will be \$2 531/year, about \$1/pig or 0.0254/m³ of biogas.

These numbers change proportionally with the H₂S content of biogas and they are highly sensitive to the H₂S tolerance level. Thus, in these calculations, the operation is stopped and the adsorbent is replaced when H₂S content in the biogas reaches the level of 500 ppmv. If this tolerance level is decreased, as is the tendency now (typically lower than 100 ppmv), the associated H₂S removal costs will be higher. In Table 3, these calculations are compared with McKinsey Zicari's data²² for biogas containing 1000 ppmv H₂S.

The observed difference in cost per unit volume of biogas treated is due to the higher cut-point (500 ppmv in the calculation reported in Abatzoglou and Truong.²⁵ It was left intentionally to show the sensitivity of the calculations.

In 2005, Nguyen-Thanh *et al.*²⁶ examined the possibility of modifying sodium (Na)-rich montmorillonite with iron to introduce active centres for H₂S adsorption. They proposed

different types of modifications, among which the most successful in terms of H₂S adsorption capacity are the one (i) where interlayer Na was replaced by Fe cations; and (ii) where the montmorillonite was first changed by replacing interlayer Na with Al cations, thus forming aluminum pillared-clay, then doped with Fe. These transformations increased the capacity of the initial montmorillonite to adsorb H₂S by a factor of 15–20. This leads to an H₂S breakthrough capacity of 10–12 mg H₂S/g of material (stopped at 1000 ppmv H₂S!), still far from about 150 mg H₂S/g which can be calculated from the results reported (Figure 9 in Abatzoglou and Truong²⁵) for Sulfatreat 410-HP[®] stopped at 500 ppmv H₂S.

Activated carbons (AC) and doped AC

There are three basic types of AC: catalytic-impregnated (regenerable), impregnated carbons and non-impregnated carbons (virgin). A detailed description is given below for each carbon type:

1. Catalytic-impregnated AC

Catalytic AC are manufactured by treatment with urea or some other chemical containing nitrogen (i.e. NH₃). These chemicals react with the surface sites on AC particles and add nitrogen functionalities. Catalytic carbons are said to be water-regenerable. Practically, this is not true because of the large volume of water required and the acidic stream produced during regeneration. The few locations that undertake water-regeneration achieve 2–3 cycles of diminishing efficiency.²⁷ Fresh catalytic AC have specified H₂S-loading capacities of around 0.10 g/g of AC (ASTM D-6646 test method).

2. Impregnated AC

Impregnated AC are those to which a solid or liquid chemical has been mixed with carbon substrate before, during, or after activation. The main chemicals serving as impregnates are sodium bicarbonate (NaHCO₃), sodium carbonate (Na₂CO₃), sodium hydroxide (NaOH), potassium hydroxide (KOH), potassium iodide (KI), and potassium permanganate (KMnO₄). Mixtures of these chemicals are sometimes used. A typical H₂S loading capacity for caustic, impregnated carbons is 0.15 g/g of AC. Strong base-impregnated carbons are considered regenerable by re-application of the strong

Table 3. Comparison of costs from data published.^{22,25}

	Ref. (22)	Ref. (25)
Gas flow rate (m ³ /min)	0.940	0.125
Investment for vessels (\$)	8000	1542
Mass of adsorbent per vessel (kg)	3636	286
Adsorbent-bed lifespan (days)	86	169
Annual adsorbent consumption (kg/year)	15450	620
Annual adsorbent cost (\$)	13500	1281
Cost per unit of biogas treated (\$/m ³)	0.046	0.025

base. Such regenerations are rather cumbersome for small-scale applications and can lead to the spent adsorbent being classified as hazardous, including the treatment area.

3. Non-impregnated AC

The non-impregnated AC employed for H₂S removal have H₂S-loading capacities around 0.02 g/g of AC. Norit presents its product DARCO[®] H₂S (<http://www.norit-america.com/pressrelease3.html>) as having an H₂S-loading capacity of 0.2 g/g of AC. DARCO[®] H₂S costs about the same as other non-impregnated AC used for H₂S removal and has 4–10 times the loading capacity. Spent AC disposal issues are also reduced with DARCO[®] H₂S.

AC are well-known, highly specific area adsorbents for the removal of volatile organic compounds from industrial gas streams. In 2005, Dabrowski *et al.*²⁸ published a review on AC deployed for the removal of phenolic compounds. This work also provides a comprehensive review on AC preparation methods and properties as functions of their physico-chemical traits. Because of its relatively lower affinity for H₂S, AC utilization for H₂S removal has been limited.

In 1999, Abid *et al.*²⁹ first showed that the local pH has a significant role on both the adsorption capacity and the distribution of the products. Thus, when the carbon surface is very acidic the S is highly oxidized producing more water-soluble species and less elemental S, but the total sorption capacity decreases with the acidity increasing. Only a slight increase in an average pH (half a unit) results in more than a 15-fold higher capacity, owing to the dissociative adsorption of hydrogen sulfide ions and their oxidation, with only one-third decrease in the yield of water soluble sulfur species. Moreover, additional works from the same group on two series of carbons (coconut shell and bituminous coal origins), Abid *et al.*³⁰ and Bagreev *et al.*³¹ have shown that the choice of non-impregnated activated carbons as H₂S adsorbents should be made based on surface parameters related to its acidity. While at pH values above 5 considerable H₂S adsorption capacities are reported, a more acidic environment, which decreases the dissociation of H₂S, quickly suppresses the process. The capacity significantly drops when the number of acidic groups exceeds a threshold value of approximately 0.85 mequiv/g of carbon.

However, when AC are treated (i.e. through impregnation) with acidic or alkaline functionalities, they become good H₂S adsorbents. In 2002, Bandosz³² published a fairly comprehensive study on this topic. She used AC derived from various sources and showed that AC efficiency in adsorbing H₂S depended on the combination of surface chemical properties and porosity. An acidic surface environment promoted H₂S oxidation to SO₂ and H₂SO₄ but exhibited small removal capacity while an alkaline environment evoked H₂S conversion to S⁰ and reached higher removal efficiency. As with iron adsorbents, surface-water concentration also plays a positive role in H₂S removal efficiency.²³ In 2006, Seredych and Bandosz³³ showed that the performance of the catalytic AC in the removal of H₂S from digester gas depends on the state of water present in the system. The best capacities are obtained when the pre-humidification of adsorbents was done and the gas mixture contained no water. This is, however, not practical when the AC are used for the removal of H₂S from biogas which is already water-saturated or close. The reason for the lower activity when the biogas contains water is that this gas-borne water reacts with CO₂ forming carbonates and contributes to the formation of sulfurous acid, which deactivates the basic catalytic sites, resulting in decrease in capacity. When catalyst consists of mineral-like structures based on iron and calcium, the performance is not affected to a great extent by the carbonated.

Wood-derived AC in an 80% relative humidity (RH) environment have presented better breakthrough capacities (the tests were stopped at 500 ppmv H₂S), mainly because of their higher specific surfaces. These were close to 300 mg H₂S/g of AC and were obtained by the ASTM D6646-01 (accelerated) standard dynamic test. This work examined the carbon chemistry of the AC surface and proposed mechanisms explaining the results observed. The mechanisms showed that the rate-limiting step of the H₂S-removal phenomenon was the surface reaction of HS⁻ with the O^{*} radical. This means that [HS⁻]_{liq}, which comes from the H₂S dissociation reaction, is critical. Calculations revealed that, to achieve effective H₂S removal, [HS⁻] must be higher than [H₂S]_g, and this is possible only at pH theoretically higher than 4.2. Experiments demonstrated that this threshold was rather 4.5. Bandosz³² concluded that pH (calculated as defined by

the ASTM D3838 procedure) must be typically higher than 5 for good H₂S efficiency. Regeneration tests have also been presented, by water-washing and heat-treating the spent AC. The so-regenerated AC recovered only 40% of their efficiency.

In 2002, Bagreev and Bandoz³⁴ examined the role of NaOH-impregnation on various types of AC. Four activated carbons of various origins were impregnated with different concentrations of NaOH and used as H₂S adsorbents in accelerated tests. The results showed that, with increasing loading of NaOH, the H₂S breakthrough capacity increases 4–5 times until maximum capacity is reached at about 10% NaOH. This capacity per unit volume of the carbon bed is the same for all carbons and independent of their pore structures and surface areas. The specific capacity per unit surface area is also the same for all materials studied, including activated alumina. This indicates that the amount of NaOH present on the surface is a limiting factor for the capacity. By increasing the pH value of the carbon, sodium hydroxide causes an increase in the HS⁻ ion concentration. These ions can be further oxidized to elemental sulfur or sulfuric acid, as suggested by changes in the surface pH values. The reactions proceed until all of the NaOH reacts with H₂SO₄ or CO₂ (a product of surface reactions or gas present in the atmosphere) and the basic environment is no longer maintained.

In 2004, Yan *et al.*³⁵ brought more insight into the mechanisms involved in H₂S removal by AC. They tested two types of KOH-impregnated, coal-derived AC. Lab-scale experiments were performed in a fixed-bed glass tube (4.8-cm internal diameter and 22.9-cm height) with 80% RH air containing 10 000 ppmv H₂S. H₂S breakthrough capacity was determined by the ASTM D28-2000 norm. pH of the AC surface was measured according to a protocol of thorough carbon washing with ultrapure water for 16 h under stirring conditions. Based on their data, they proposed a mechanism characterized by the following claims:

- At carbon surface pH typically higher than 7.0, H₂S chemisorption on OH⁻ (alkaline) sites dominates, thus creating a high HS⁻ concentration at the water film and, consequently, at the adjacent solid surface of the AC. A high molar ratio of HS⁻/O* leads to the partial oxidation of S species, and the phenomenon is driven towards the generation of various forms of solid S⁰.
- At carbon surface pH typically higher than 4.5 but lower than 7.0, physical adsorption on the wetted AC surface becomes significant, and the so-derived low HS⁻/O* ratio results in the formation of SO_x species which acidify the surface and block the AC pores under the form of H₂SO₄.
- At carbon surface pH typically lower than 4.5, physical adsorption dominates, and the H₂SO₄ relative rate of formation increases considerably. Then, a part of the H₂S participates in a redox reaction with H₂SO₄, namely, producing various forms of solid S⁰. However, when these conditions (acidic surface) prevail, the rate of H₂S adsorption is considerably lower than in the alkaline surface case, and the H₂S removal rate is proportionally lower.

Although this mechanism seems quite general, the experimental data clearly depict the importance of AC surface properties. Without entering into details which can be found in this paper, it can be easily claimed that AC with a greater specific volume of micropores in the size range between 0.5 and 1 nm (5–10 Å) have higher H₂S adsorption capacities. Moreover, the nature and density of chemical functional groups at the surface of AC have been shown to play an equally important role. The conclusions at this point are not definite, and more work is needed to quantify the phenomena. Tests have disclosed that the breakthrough capacity of these alkaline-impregnated AC was 21 and 23% respectively, but there are no data on the possibility of regeneration and adsorption efficiency recovery after regeneration.

Regarding the role of the H₂S content on the adsorption capacity of the activated AC, Bagreev *et al.*³⁶ showed in 2005 that the lower the H₂S concentration, the higher the capacity of adsorbent. Various contents of oxygen (1 or 2%) and an increase in the temperature of the reactor (from 38° or 60° C) have no significant effect on the performance of the materials. This behavior has been linked to the fact that low H₂S concentration slow down the oxidation kinetics, thus decreasing the rate of the AC surface acidification which is responsible of the adsorption activity loss.

In 2008, Xiao *et al.*³⁷ examined the activity of coal-based AC and Na₂CO₃-impregnated AC as low-concentration H₂S oxidation catalysts. Na₂CO₃-impregnated AC manifested

the best activity, with a retention capacity of 420 mg H₂S/g of AC. Since the tests were performed with N₂ containing 600 ppmv H₂S and four times the stoichiometric quantity of O₂ for complete H₂ oxidation (molar H₂S/O₂ = 1/2), breakthrough capacity coincided with maximum retention capacity if the test was stopped at H₂S exit concentrations of 500 ppmv; the same as in almost all other published tests. In real-time applications, lower breakthrough capacities are expected, probably closer to the value of 300 mg H₂S/g of AC, as can be seen in Fig. 2 of their publication. They have also confirmed the highly important role of humidity and the inhibitory effect of H₂SO₄ if adsorption conditions allow its formation due to pore blockage. Tests with Na₂CO₃-impregnated AC were done at Gas Hourly Space Velocity (GHSV) = 45 000 h⁻¹; this is a very high space velocity, equivalent to a gas residence time of less than 0.1s! These data are sufficient to calculate AC consumption per unit of biogas treated. Unfortunately, there are no data regarding the feasibility of spent AC regeneration. In 1998, Przepiorski and Oya³⁸ worked with a K₂CO₃-impregnated AC and found that regeneration was possible by heating the spent AC at 500°C for 2 h under an N₂ blanket. This process allowed the evaporation of S⁰. They did not determine the maximum number of regenerations (after the third regeneration, the AC were still behaving with essentially the same efficiency). Nevertheless, this regeneration is process-intensive and

cannot be done *in situ* for small-to-medium biogas productions. Considerable cost must be added, which could even be of the same order of magnitude of fresh AC production costs. Considering that AC can be used once, the following cost can be calculated:

Distributors of AC include Calgon Carbon Corporation (CENTAUR[®] 4x6), Molecular Products, Ltd (Sofnocarb KC[®]), USFilter-Westates (Midas OCM, US patented), Norit Americas, Inc., (DARCO[®] H₂S and NORIT ROZ 3) and Bay Products, Inc. Typically, 20–50% loading by weight of H₂S can be achieved, 2–3 times higher than the best non-impregnated granular AC.

In 2003, McKinsey Zicari²² reported on a non-regenerable KOH-AC bed (USFilter-Westates) for H₂S removal from anaerobic digesters and landfill gas for use in fuel cells. Oxygen (0.3–0.5% vol) was added to facilitate H₂S conversion to S⁰. Two beds, 0.6 m in diameter by 1.5-m high, were piped in series and run with space velocities of 5300 h⁻¹. Inlet H₂S concentration ranged from 0.7 to 50 ppmv, averaging 24.1 ppmv; 98+% removal was demonstrated. A loading capacity of 0.51 g S/g carbon was reported, which is substantially greater than the normally reported range of 0.15–0.35 g S/g AC for KOH-AC. Media costs were estimated at \$5/kg for the adsorbent. Assuming an average loading capability of 25% and non-regeneration of KOH-AC, we compare the case with that reported in Table 4.^{22,37}

Table 4. Comparison between Fe adsorbents and alkaline AC for same volume adsorption vessels.

	McKinsey Zicari ²² for Fe adsorbents)	Xiao <i>et al.</i> ³⁷ for Na ₂ CO ₃ -impregnated AC
H ₂ S concentration (ppmv)	1 000	1 000
Gas-flow rate (m ³ /min)	0.94	0.94
Loading capacity	0.15	0.25
Investment for vessels (\$)	8 000	8 000
Mass of adsorbent per vessel (kg) (*)	3 636	1 057
Adsorbent-bed lifespan (days)	86	129
Annual adsorbent consumption (kg/year)	15 450	2 991
Cost of adsorbent (\$/kg)	0.87	5 (approximation from USFilter-Westates KOH-AC)
Annual adsorbent cost (\$)	13 500	14 959
Cost per unit of biogas treated (\$/m ³) with 5-year capital cost amortization	0.031	0.034

(*) This quantity was calculated by taking into account that the specific gravity of bulk AC (packing density) was 0.3 and that of SulfaTreat[®] was 1.1.

Table 5. Comparison between Na₂CO₃- and KOH-impregnated AC.

	McKinsey Zicari ²² for KOH-impregnated AC)	Xiao <i>et al.</i> ³⁷ (for Na ₂ CO ₃ -impregnated AC)
H ₂ S concentration (ppmv)	25	1 000
Volume of the vessels (m ³ /min)	Two vessels of 0.6 m in diameter by 1.5-m high each 0.424 m ³ each	2.0 m ³
Gas-flow rate (m ³ /min)	37.1 (calculated from the space velocity of 5 300h ⁻¹)	0.94
Loading capacity	0.51	0.25
Investment for vessels (\$)	8 000	8 000
Mass of adsorbent (kg)	250*2 = 500	1 057
Adsorbent-bed lifespan (days)	126	129
Annual adsorbent consumption (kg/year)	1 450	2 991
Cost of adsorbent (\$/kg)	5	5 (approximation)
Annual adsorbent cost (\$)	7 250	14 959
Cost per unit of biogas treated (\$/m ³) with 5-year capital cost amortization	0.0005	0.0340
Cost of adsorbent per unit of H ₂ S removed (\$/kg)	12 (*)	20 (*)

(*) Fairly proportional to loading capacity

Table 5 shows the good techno-economic performance of the proposed KOH- impregnated AC. The results in this case, however, concern a gas of low H₂S concentration, and the kinetics of adsorption are necessary to evaluate performance under conditions of high H₂S concentrations.

Use of sludge-derived adsorbents

Sludge coming from biological activity is quite a complex mixture of organic and inorganic matter. Its ability to chemically adsorb H₂S from gaseous streams has been examined by a limited number of researchers. In 2004, Bagreev and Bandoz³⁹ tested the adsorbent capacity of pyrolyzed mixtures of sewage-sludge-derived granulated fertilizer (terrene) and spent mineral oil. Pyrolysis was performed under N₂ atmosphere at temperatures between 600°C and 950°C. The resulting products had alkaline surfaces. Adsorption capacity was calculated by H₂S breakthrough capacity tests. These tests were conducted with 80% RH moist air containing 3000 ppmv H₂S in a 6-cm³ adsorption column and gas-flow rate of 0.5 L/min. They were stopped at exit H₂S concentration of 500 ppmv. The best breakthrough capacity (0.115 g H₂S/g of adsorbent) was obtained with samples pyrolyzed at 950°C. Under these conditions, the volume of pores in the range of 0.7 nm and mesopores

(1–10 nm) increased because of the decomposition of inorganic salts and oxides with the simultaneous production of O₂ acting as a pore former. In addition, under the same conditions, the volume of the larger pores decreased, most probably due to physical change of the inorganic matter (melting). As reported in 2004 by Yan *et al.*,³⁵ pores in the size range between 0.5 and 1 nm had higher H₂S adsorption capacities. The mechanism of adsorption is complex owing to the existence of more than one type of active sites. Thus, after the physical adsorption of gaseous H₂S on the liquid (H₂O) film at the surface of the preconditioned (1 h under 80% RH moist air flow) adsorbent, H₂S and its dissociation species reacted with:

1. Metal oxides (CuO, ZnO, Fe₂O₃) to form sulfides.
2. Alkaline species (K₂O, CaO, CaCO₃) to give neutralization products.
3. Surface O species eliciting redox reaction products, mainly S⁰ but also small quantities of SO₂ and H₂SO₄. Sulfides coming from steps 1 and 2 can also participate in redox reactions and produce S⁰.

This work showed that these new adsorbents can technically replace the majority of non-impregnated AC. Their efficiency is close to that of iron adsorbents, but they are less

efficient than impregnated AC. Their cost of production is not known because they are still in the research stage and, so far, there is no known commercialization endeavor. A major question to be answered is the effect of sewage sludge and mineral-oil source on the properties of the final product. Since metal content seems to play an important role, it will be a rather challenging task to ensure a constant quality product in a commercial production line.

In 2007, Yuan and Bandosz⁴⁰ also published on the exploitation of pyrolyzed sewage and metal sludge as H₂S removal adsorbents. This work utilizes the methodology described by Bagreev and Bandosz in 2004³⁹ and investigates the effect of pyrolysis conditions and humidity. Although the authors claim, in their conclusions, that these adsorbents show capacities comparable to those obtained with catalytic AC, the highest breakthrough capacity reported is lower than 21 mg H₂S/g of adsorbent, which is close to average virgin AC.

In 2007, Seredysz and Bandosz⁴¹ worked on the mechanism elucidation of the H₂S reactive adsorption on pyrolyzed metal-containing industrial-derived sludge and waste oils and demonstrated the complex dependence of the H₂S adsorption capacity on the surface chemistry, porosity (volume and sizes of pores), and water content. In all cases, elemental sulfur has proven the predominant product of the surface reactions. The reactivity is linked to the presence of Ca, Mg, and Fe, which are known catalysts for H₂S oxidation. When water is not present, CO₂ quickly deactivates alkaline-earth-metal-based centers, leading to lower H₂S removal capacity.

Recently, Seredych *et al.*⁴² tested mixtures of various compositions of New York City sewage sludge and fly ashes from SASOL, South Africa, produced by pyrolysis at 950°C, as H₂S adsorbents. It was found that the addition of fly ash decreases the desulfurization capacity in comparison with the sewage-sludge-based materials. The extent of this decrease depends on the type of ash, its content and the composition of biogas. The addition of ashes has a more detrimental effect when the adsorbents are used to remove H₂S from air, likely due to the hydrophobicity of ashes. Besides, the addition of ashes strongly decreases the porosity of materials where sulfur, as a product of H₂S oxidation, can be stored.

Kante *et al.*⁴³ recently reported their work on using pyrolyzed, spent mineral-oil-impregnated sewage sludge as H₂S

adsorbent. The results indicated the importance of new carbon phase from the oil precursor. This phase provided mesoporosity, which increased the dispersion of catalytic phase and space for storage of surface reaction products. The results indicated that the adsorbents obtained at 950°C are much more active in the process of hydrogen sulfide oxidation than those obtained at a lower temperature (650°C). Moreover, longer heat treatment is also beneficial for the development of surface catalytic properties. Extensive pyrolysis stabilizes carbon phase via increasing its degree of aromatization and provides activation agents for this phase coming from decomposition and rearrangement of inorganic phase.

In his Master's thesis, McKinsey Zicari²² published results on cow-manure compost as H₂S removal media. The data were rather inconclusive. The removal efficiency reported was around 80% for a gaseous stream containing 1500ppmv H₂S. The removal rate was estimated to be 16–118 g H₂S/m³ solids/h for residence times (empty bed) of 100 s. He did not have sufficient data to distinguish between the physical, chemical and biological mechanisms of H₂S retention. The main utility of this work is the fairly comprehensive presentation of available technologies, including those essentially employed in scavenging H₂S in the oil industry on a large scale (solvent-based absorption and solid oxide scavengers). In addition, this review fairly well covers the technical and market survey in the field.

Processes involving scrubbing

Although there are several solvent-based gas-scrubbing technologies for scavenging H₂S from gaseous streams in large-scale industrial operations (mainly refineries), applications of such technologies in biogas are not known. Couvert *et al.*⁴⁴ very recently published their results on a new compact scrubber used to remove H₂S, mercaptans and NH₃ from wastewater treatment (WWT) plant gaseous emissions. Scrubbing has serious drawbacks which hamper the application of this technology for biogas purification from odorous compounds. The main problems are:

1. It is impossible to remove all contaminants in one stage; thus, S-containing compounds (H₂S, mercaptans) require alkaline scrubbing, and N-containing compounds (NH₃) require acidic conditions.

2. During alkaline scrubbing, CO₂ is also retained intensively, thus increasing the cost of alkaline chemical (i.e., NaOH or Na₂CO₃) consumption and cost.
3. Gas-liquid transfer coefficients are relatively low at low velocities and turbulence, thus requiring high severity treatments.
4. The gas-liquid transport rate is low, even at high mass transfer coefficients because of low contaminant concentrations.
5. Because of points 3 and 4, contactors must have a very high, gas-liquid contact surface and long residence times, thus necessitating large volumes and, consequently, high capital investment.
6. A high contact surface means a high P drop through the contactors, which is not tolerated in biogas production facilities.

The main conclusions of this work are as follows:

1. The compact scrubber is based on a two-stage co-current configuration.
2. Use of a free chlorine agent (NaClO) under acidic conditions in Stage 1, and alkaline conditions in Stage 2.
3. Removal efficiencies higher than 99.5%wt of H₂S and NH₃ and 96%wt of CH₃SH (methyl-mercaptan) are possible for superficial gas velocities higher than 15 m/s and with superficial liquid velocities higher than 4 cm/s.
4. A one-stage configuration is not recommended because of the formation of NH₃-Cl-derived dangerous by-products (chloramines).

The conclusion is that this method has a lot of drawbacks to be considered for biogas applications.

In the same category, we can classify the 2006 effort of Lee *et al.*⁴⁵ who examined the possibility of selectively oxidizing H₂S to S⁰ by means of a magnesia-supported iron catalyst (Fe/MgO) in a three-phase (slurry) reactor. The iron loadings tested, between 1 and 30%wt, were prepared by the classical, wet impregnation technique with iron nitrates as precursor. They showed that good results can be obtained only when Fe is well-dispersed, and this is possible at loading below 15%wt. For a H₂S load of 50,000 ppmv in a 105-ml/min O₂ stream, the maximum H₂S retention reached was 3.8 g H₂S/g-catalyst. These results are of theoretical interest because the catalyst is expensive, and there are no data on its regenerability and useful lifespan.

Siloxane removal

The term 'siloxane' refers to silicones containing Si-O bonds with organic groups. They are widely employed by industry because of their interesting properties, including low flammability, low surface tension, thermal stability, hydrophobicity, high compressibility and low toxicity. Moreover, they are not environmentally persistent compounds and generally have very low allergenicity.⁴⁶ Among others, they can be found in shampoos, pressurized cans (i.e., hair sprays, shaving foams), detergents, cosmetics, pharmaceuticals, textiles and paper coatings. During the anaerobic digestion of waste sludges and in landfills, siloxanes do not decompose; they are significantly volatilized and, thus, they are transferred to biogas. The main problem with siloxanes in biogas is that they produce microcrystalline silica (MCS) when biogas is used as an energy vector (during combustion). MCS has glass properties, and the fouling of metallic surfaces leads to abrasion; ill-functioning spark plugs; overheating of sensitive parts of engines due to coating; and general deterioration of all mechanical engine parts. It is noteworthy that biogas coming from anaerobic fermentation of manure on farms does not contain this type of substances. Consequently, the problem concerns only biogas from landfill operations or waste composting. The only possible remediation of the problem is through siloxane removal from the gas before its use as energy carrier. There are four possible techniques.

Reactive absorption (extraction) with liquids (also called Chemical abatement)

In 2001, Schweigkofler and Niessner⁴⁷ published a study on siloxane removal in biogases. They performed lab tests to compare reactive liquid extraction and solid adsorption techniques. In the case of reactive liquid extraction, the methods work by cleavage of the Si-O bond catalyzed by strong acids or alkalis. Alkaline extraction has the drawback that CO₂ is also retained, thus considerably increasing the consumption and cost of treatment. HNO₃, H₂SO₄ and H₃PO₄ have been employed at relatively elevated temperatures (around 60° C). H₃PO₄ has proven to be ineffective. High concentration (33%) HNO₃ leads to siloxane abatement typically lower than 75%, whereas in the case of H₂SO₄, nearly 100% siloxane removal is possible only when acid concentration is close to 50% at 60° C. Moreover, since this reactive extraction process must use gas-liquid contact

columns of relatively high superficial velocities to ensure high mass transfer surfaces and coefficients, entrainment of acid droplets in the gaseous phase will be significant. These results prove that the process is highly intensive because of ultra-high acidities, and its techno-economic feasibility is questionable for the majority of applications.

Adsorption on AC, molecular sieves, alumina, silica gel (SG) or polymer pellets

In the same work the authors investigated various siloxane removal techniques with solid phase adsorption.⁴⁷ They tested two kinds of polymers: molecular sieve (zeolite 13X), SG, and 2 AC-based adsorbents (activated charcoal and Carbopack B). Batch tests were done; 0.5 g of every adsorbent was put in contact with a total of 5 mg of various types of siloxanes. For this, a fixed 0.5-g bed of the tested adsorbent was in contact with N₂ flow of 200 ml/min containing 1.2 mg of siloxane/Nm³ for 2 min. The measured dependent variable was siloxane breakthrough in the effluent stream as a fraction of influent siloxane mass. The major conclusions are:

1. Adsorptive capacity largely depends on siloxane type, i.e., in every case, D5 siloxane (decamethylcyclopentasiloxane) adsorbs better than L2 siloxane (hexamethyldisiloxane). This means that siloxane composition must be seriously taken into account.
2. Some siloxanes (like D5) adsorb very well in all tested adsorbents.
3. SG proved to be the most efficient of the adsorbents tested, but gas-drying must be considered. In fact, a gas of 30% RH decreases the adsorption efficiency of SG, measured as siloxane loading, by 50% if compared to a dry gas (0% RH). Since biogas comes near saturation, this method must be undertaken in two steps: drying followed by siloxane removal.
4. The maximum SG loading capacity (in the case of dry gas) is close to 0.1 g of siloxane/g of SG.
5. SG regeneration has proven possible by thermal treatment at 250°C for 20 min. Almost 95% of the siloxane is desorbed, but efficiency varies with siloxane volatility. Consequently, the adsorption efficiency of SG as well as of all other tested adsorbents is expected to decrease after each use-regeneration cycle.

6. Testing with real sewage biogas has established the effect of humidity and shown that the measured loading capacities for SG are similar.
7. Additionally, the authors tested the siloxane retention efficiency of a Fe-based adsorbent (meadow ore) to remove H₂S in 2 different sites. They found removal efficiencies varying between 31 and 75%.

Recently, in December 2007, a patent was issued for siloxane removal by means of a regenerable, activated alumina bed.⁴⁸ According to this invention, biogas released from landfills and sewage treatment plants is freed of siloxane contaminants by passing the biogas through a bed containing activated alumina, which absorbs them. When the activated alumina becomes saturated with siloxanes, its absorption capability can be recovered by passing a regeneration gas through the bed. A system containing two or more beds of activated alumina can use one bed to remove siloxanes from biogas while one or more of the other beds are being regenerated.

Absorption

This method relies on the preferential solubility of siloxanes in some organic solvents of high boiling points (i.e., tetradecane). Spray and packed columns are employed. Tetradecane was tested in 1996 by Huppmann *et al.*⁴⁹ and proved to have a collection efficiency of 97% for D4 siloxane. The application of this method in small- to medium-scale units is not techno-economically sustainable.

Cryogenic condensation

Freezing to -70°C is necessary to achieve siloxane removal of more than 99%. At -25°C, only 26% of siloxanes condense as liquids.⁵⁰ A US patent was issued in 2004 based on this method.⁵¹ According to the patent, the method is aimed at continuously removing siloxanes and H₂O from a waste gas stream. The process includes the following modules: (i) cooling the waste gas stream in a primary heat exchanger to a T higher than -17°C to condense a portion of the H₂O from the waste gas stream; (ii) chilling the waste gas stream in a first gas-refrigerant heat exchanger to a temperature of about -29°C to condense the siloxanes and freeze the remaining H₂O; (iii) directing the cooled waste gas stream from the primary heat exchanger to a second gas-refrigerant

heat exchanger, while the first gas-refrigerant heat exchanger is defrosted to remove frozen H₂O and siloxanes. Based on the information provided,⁵⁰ a temperature of −29°C is not enough to appropriately condense all siloxanes. The method seems efficient at temperatures around −70°C, but is energy-intensive, and techno-economic analysis is needed to prove its sustainability.

Table 6 presents an overview of the information published so far.

Review of biological biogas purification methods and techniques

Biological processes are widely employed for H₂S removal, especially in biogas applications. They are usually cited and considered as economical and environmentally friendly, notably because chemical use is limited.

An established methodology calls for chemotropic bacterial species (*Thiobacillus* genus) for biogas conditioning. Many bacterial strains studied in the laboratory have the following process characteristics, or respect these design strategies:^{53,55,58}

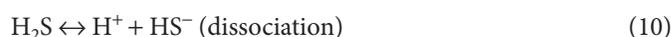
- Capability to transform H₂S into S⁰ (used as fertilizer).
- Minimum nutrient input (with CO₂ as carbon source).
- Easy separation of S⁰ from biomass.
- No biomass accumulation (avoiding clogging problems).
- High robustness to fluctuation (e.g., temperature, moisture, pH, O₂/H₂S ratio).

The use of microalgae cultures has also been examined but the available literature⁵⁶ is short and cannot help in appropriately evaluating this option. Another methodology deploys anaerobic phototrophic bacteria (*Cholorobium limicola*) capable of oxidizing H₂S in the presence of light and CO₂.⁶⁹ No known commercial applications at this time use prototrophic bacteria. The following text focuses on chemotropic bacteria.

Chemotropic thiobacteria are organisms which could be employed for H₂S purification in both aerobic and anaerobic pathways. The chemotropic biological process produces cell material through CO₂ (autotrophic species) and chemical energy resulting from the oxidation of reduced inorganic compounds such as H₂S. Mainly, SO₄²⁻ and S⁰ arise from such biological activity. On the

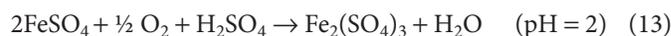
other hand, some thiobacteria (i.e., *Thiobacillus novellus*, *Thiothrix nivea*) are called mixotrophic and can grow heterotrophically, having the capability of using available organic material as carbon source (i.e., glucose, amino acids). In contrast, biogas, which contains around 30% CO₂, is a good source of inorganic carbon, rendering it more suitable for autotrophic bacteria.

Thiobacillus bacteria evoke a redox-reaction which, under limited oxygen conditions, produces S⁰ (Eqn 11). Conversely, an excess oxygen condition will lead to SO₄²⁻ generation and, thus, acidification, as shown in Eqn 12.⁶⁵



In 1996, Chung *et al.*⁶⁶ isolated *Thiobacillus thioparus* from swine wastewater. The bacteria were immobilized with Calcium alginate to produce pellet-packing materials for a lab-scale biofilter (5-cm diameter, 25-cm working length). Growth was optimum at pH 6–8 under facultative autotrophic and heterotrophic conditions. The biofilter was operated under air-H₂S mixture flow between 36 to 150 L/h containing 5 to 100 ppmv of H₂S. Removal efficiency was more than 98% at residence times higher than 28 s. Optimal S-loading was 25 g m⁻³ h⁻¹. The main product was (i) S⁰ (72%) at high H₂S concentration (60 ppmv), and (ii) sulfate (75%) at low H₂S concentration (5 ppmv). No pH fluctuation was observed. The experiments showed no temperature influence on removal efficiency between 20° and 37°C.

Thiobacillus ferroxidans is an example of a chemotropic aerobic which can oxidize FeSO₄ to Fe₂(SO₄²⁻)₃. The resultant Fe⁺³ solutions are capable of dissolving H₂S and oxidizing it to S⁰. This allows S⁰ separation and permits biological FeSO₄ regeneration. Besides, these bacteria are acidophilic and are able to grow at low pH levels (1 to 6). The main biochemical reaction is detailed in Eqn 13.



Acidithiobacillus thiooxidans AZ11 was isolated from H₂S-enriched soil and incubated by Lee *et al.* in 2006.⁶⁷ The bacteria can live in a very acidic environment, as low as pH = 0.2, with high sulfate concentration (74 g l⁻¹). A lab-scale biofilter (4.6-cm diameter, 30-cm working length) was

Table 6. Review of published information.

No	Technologies	Literature	Methodology	Process modules	Conditions of main unit
1	Physicochemical				
1.1.	Chemical absorption in a Fe-chelated solution	BJChE, 21 (3): 415–422 ¹²	Absorption into Fe-chelated solutions Overall reaction: $H_2S + 1/2O_2 = S + H_2O$ through a cycle of reduction/oxidation of Fe ³⁺ /EDTA complex at ambient T and low P conditions	<ul style="list-style-type: none"> • Biogas/Fe-EDTA solution contactor • S recovery by particle separation from aqueous solutions • Fe³⁺ regenerator: Air-solution bubble column contactor • Treated biogas scrubber 	<ul style="list-style-type: none"> • Simulated biogas • H₂S = 2.2–2.4% vol. • G = 1000 ml/min • L = 68–84 ml/min • Fe-EDTA = 0.2 mol/l • P = 1.2–2.2 bar • H₂S removal efficiency = up to 100% for low P and high L • CO₂ removal is negligible • Conversion of H₂S to solid S⁰
1.2.	Chemical adsorption in a mixed-metal sulfate solution	S&PTech 43 : 183–197 ¹⁷	In aqueous mixed-metal sulfate solution	<ul style="list-style-type: none"> • Biogas/sulfates (Fe²⁺, Zn²⁺ and Cu²⁺) aqueous solution contactor (bubble column) • Precipitated sulfide filtration from the aqueous solution 	<ul style="list-style-type: none"> • Simulated biogas • H₂S = 1–4% vol. • Gas-phase mass transfer limited process • Trickle flow: packed column • Cu concentration = 90–370 mol/m³ • G = 1000 ml/s (orders of magnitude) • L = 39–280 g/s • Fe-EDTA = 0.2 mol/l • P = barometric • T = 5–12° C • Residence time = 16–22 s • H₂S removal efficiency = 0.85–0.99 • CO₂ removal is negligible only with Cu and at specific pH for Zn
1.3.	Chemical adsorption on a solid adsorbent	B&B 29 : 142–151 ²³	In a Fe oxide-based adsorbent	<ul style="list-style-type: none"> • Reactive adsorption in a fixed-bed • Twin-bed operation for commercial applications 	<ul style="list-style-type: none"> • Simulated biogas • H₂S = 0.3–1% vol • Lab-scale results • Sulfatreat (commercial); detailed SEM characterization • G = 20 L/h • P = barometric • T = ambient • Residence time = 30–60 s • Role of humidity (important) • H₂S removal efficiency = up to 100% • H₂S removal rate = 3–8 mmol/m³.s • Sulfatreat adsorption capacity = 0.1–0.2 g H₂S/g adsorbent • Breakthrough curves available • Kinetic study proves that diffusion control may be important; depends on experimental conditions • Phenomenological model available

(continued overleaf)

Table 6. continued

No	Technologies	Literature	Methodology	Process modules	Conditions of main unit
1.4.	Chemical adsorption on a solid adsorbent	Chemosphere, 59 : 343–353 ²⁶	In a Fe oxide-based adsorbent: Na-based montmorillonites doped with Fe oxides	<ul style="list-style-type: none"> • Na and Al-montmorillonite functionalization with Fe or FeO_x. – Stirred tank reactor with suspension and addition of FeCl₃ or FeCl₃/NaOH. Duration of 24 h; load of 10 mmol of Fe³⁺ per g of clay – Washing, filtering (11 μm); drying and calcination at 400 °C for 4 h • Fixed-bed contactor 	<ul style="list-style-type: none"> • H₂S in moist air (80% RH) • H₂S = 6% vol • Fixed bed: 60 mm length *9 mm diameter • Adsorbents in granules of 2–3 mm • G = 0.5l/min • P = barometric • T = ambient • Residence time = 0.7 s! • Maximum adsorption capacity at breakthrough (FeAl-M) = 12.7 mg/g (small!) • Breakthrough curves available
1.5.	Adsorption and oxidation on AC	JofColloid&InterfaceSci, 246 : 1–20 ³²	Acid and basic AC have been tested	Fixed-bed column	<ul style="list-style-type: none"> • Standard dynamic ASTM 6646–01 test and other tests for breakthrough calculations • H₂S in moist air (80% RH) • H₂S = 3000–10,000 ppmv • Boehm titration for surface oxygenated group measurement • G = 0.5 L/min • P = barometric • T = ambient • Breakthrough curves available • Basic AC produce S⁰ and show higher S removal efficiencies
1.6.	Catalytic oxidation over AC	S&PTech, 59 : 326–332 ³⁷	Coal-based and impregnated AC as oxidation catalysts	Fixed-bed contactor	<ul style="list-style-type: none"> • AC: Coal-based commercial • IAC: AC Ground to 550–830 μm and impregnated with 6% sol. Na₂CO₃; dried at 120 °C for 10 h • N₂ flow containing H₂S and 4 times the stoichiometric amount of O₂ (O₂/H₂S = 2/1) • T = 30 °C; P = barometric • GHSV = 2400–45 000 h⁻¹ • Various relative humidities • H₂S = 200–600 ppmv • G = 120 ml/min • Amount of AC per run = 1.5 g • Residence time = 30–60 s • Role of humidity (important) • H₂S removal efficiency = up to 100% • H₂S removal rate = 3–8 mmol/m³.s • Breakthrough curves available • AC adsorption capacity = Anoxic: 6.8 mg H₂S/g AC Oxidative: 140 mg H₂S/g AC • IAC adsorption capacity = Anoxic: 11.2 mg H₂S/g AC Oxidative: 407 mg H₂S/g AC • Role of RH: very positive

Table 6. continued					
No	Technologies	Literature	Methodology	Process modules	Conditions of main unit
					<ul style="list-style-type: none"> • Proposal of a gas-liquid-solid catalytic oxidation mechanism • BET surface decreases drastically in the exhausted IAC • Some sulfate ions are detected in the final products but the main product is S⁰
1.7.	Adsorption and reaction on basic AC: influence of surface properties	EnvSci&Tech, 38 : 316–323 ⁵²	Influence of AC surface properties on the mechanisms		<ul style="list-style-type: none"> • ASTM D28–2000 used to perform the tests and measure breakthrough curves. H₂S in moist air (80% RH) • Two AC impregnated with KOH • H₂S = 10000 ppmv • Boehm titration for surface acidic and basic site measurements • G = 5.20 l/min • Reactor: glass tube (diameter = 4.8 cm; length = 22.9 cm) • P = barometric • T = ambient • Breakthrough curves available • Clear proof that various mechanisms co-exist and that surface properties change with AC exhaustion • Basic AC have a great tendency to form S⁰ instead of higher oxidation products (i.e., H₂SO₄)
1.8.	Adsorption on pyrolyzed sewage sludge-derived granulated fertilizer impregnated with spent mineral oil	EnvSci&Tech, 38 : 345–351 ³⁹	Evaluation of the adsorption efficiency of pseudo-composite materials produced by pyrolysis of 'terrene+spent car oil'	<ul style="list-style-type: none"> • Reactive adsorption in a lab-scale fixed-bed of 6 cm³ • Twin-bed operation for commercial applications 	<ul style="list-style-type: none"> • H₂S in moist air (80% RH) • H₂S = 3000 ppmv • Test stops at breakthrough concentration of 500 ppmv (Interscan LD–17 monitor) • Boehm titration for surface acidic and basic site measurements • G = 0.5 L/min • Reactor: column (diameter = 9 mm*length = 36 cm) • P = barometric • T = room • The adsorbents are pre-humidified for 1 h with moist air (80% RH) • Pore size distribution evaluated according to the density functional theory • Breakthrough curves available • The original adsorbents are basic (pH around 11) and the spent ones have pHs around 10. • The breakthrough capacity of these adsorbents varies: 35–115 mg/g • Porosity decreases with H₂S removal • Mechanisms of H₂S removal: <ol style="list-style-type: none"> (a) Physical or ionic adsorption on carbonaceous sites (b) Chemisorption on metal (Fe, Cu, Zn and Cu) oxides with sulfide formation

(continued overleaf)

Table 6. continued

No	Technologies	Literature	Methodology	Process modules	Conditions of main unit
					<p>(c) Chemisorption on Ca and K oxides and carbonates (neutralization reactions)</p> <p>(d) Oxidation of H₂S by O atoms on carbonaceous adsorption sites or catalytically-active oxides of transition metals to oxidized forms of S (S, SO₂, H₂SO₄)</p>
1.9.	Adsorption of siloxanes	US Patent 7,306,652, Dec. 11, 2007 ⁴⁸		Classical fixed-bed adsorption on activated alumina (γ -Al ₂ O ₃) with regeneration (twin-beds).	A purification process for removing siloxanes from biogas from landfill or sewage treatment plants; passing the biogas through a bed comprising activated alumina; adsorbing at least a portion of the siloxanes on to activated alumina in the biogas; and regenerating the activated alumina by removing at least a portion of the siloxanes adsorbed
1.10.	Siloxane removal by selective gas permeation membranes	Desalination, 200 : 234–235 ⁵³	Only Aspen calculations available		No runs; identification of membrane candidates (rubbery type: i.e., polydimethylsiloxane)
1.11.	Siloxane abatement techniques reviewed	EnerConv & Management, 47 :1711–1722 ⁴⁶	Review of the following technologies: adsorption, absorption, cryogenic condensation, chemical abatement (caustic or acidic catalyzed hydrolysis of the Si-O bond)		<ul style="list-style-type: none"> • Adsorption on AC, molecular sieves or polymers <ul style="list-style-type: none"> – AC: Costly; regeneration almost impossible; AC adsorb other compounds too, and a specific study is needed. Twin-bed operation is a must. – Silica gel: High adsorption capacity; it also dries the biogas; siloxane desorption up to 95% at 250°C for 20 min; clean-up efficiency up to 99%. • Absorption on high boiling point organic solvents <ul style="list-style-type: none"> – In spray or packed-bed columns – Low efficiency for highly volatile siloxanes (stripping) – Chemical absorption improves efficiency but regeneration is almost impossible – Tetradecane as collector oil gave a 97% removal efficiency for D4 siloxanes • Cryogenic condensation: at 5°C, 88% of siloxanes are still in the gaseous state. –70°C are needed to remove 99.3% of siloxanes. 74% of volatile siloxanes are still in the biogas at –25°C. • Chemical abatement: caustic or acidic hydrolysis of siloxanes: <ul style="list-style-type: none"> – With acids: 95% elimination with H₂SO₄ (48%) or HNO₃ (65%) at 60°C – With bases: NaOH not very successful; moreover, CO₂ forms carbonates with NaOH

Table 6. continued

No	Technologies	Literature	Methodology	Process modules	Conditions of main unit
1.12.	Siloxane removal from biogases	JofHazMat, 83 (2–3): 183–196 ⁴⁷		Lab tests on: solid adsorption, liquid (solvents) absorption	<p>Adsorption on activated charcoal, molecular sieve 13X, XAD–II resins, Tenax TA, Carbopack B</p> <ul style="list-style-type: none"> – AC: Costly; regeneration almost impossible; AC adsorb other compounds too, and a specific study is needed. Twin-bed operation is a must – Silica gel: High adsorption capacity; it also dries the biogas; siloxane desorption up to 95% at 250°C for 20 min; clean-up efficiency up to 99%. – Polymer beads: see also 1.11 – Absorption on high boiling point organic solvents – In spray or packed-bed columns – Low efficiency for highly volatile siloxanes – Chemical absorption improves efficiency but regeneration is almost impossible – Tetradecane as collector oil gives a 97% removal efficiency for D4 siloxanes • Cryogenic condensation: at 5°C, 88% of the siloxanes are still in the gaseous state. –70°C are needed to remove 99.3% of siloxanes. 74% of volatile siloxanes are still in the biogas at 25°C. • Chemical abatement: caustic or acidic hydrolysis of siloxanes: <ul style="list-style-type: none"> – With acids: 95% elimination with H₂SO₄ (48%) or HNO₃ (65%) at 60°C – With bases: NaOH not very successful; moreover, CO₂ forms carbonates with NaOH
1.13.	Chemical scrubbing Absorption + Reaction	Chemosphere, 70 : 1510–1517 ⁴⁴	+H ₂ S, mercaptans (CH ₃ SH) and NH ₃	Proprietary technology: Aquilair Plus™. Wire mesh packing for co-current gas-liquid contact. Use of NaOH or H ₂ SO ₄ with the presence or not of Cl ₂ . Very short residence times allow for low NaOH consumption by CO ₂ . Two stages are required because of the possibility of forming volatile chlorine compounds	<ul style="list-style-type: none"> • Reactor geometry <ul style="list-style-type: none"> – diameter = 2.5 cm*length = 32 cm (V = 0.15 L) – Void fraction = 0.975 – Geometric surface = 176 m²/m³ – Packing factor = 6667 m²/m³ • Complex analyses of the products when chlorination is used • T = ambient; P = barometric; pH 11 or higher • Increase of liquid superficial velocity (U_{SL} = 0.016–0.055 m/s) improves removal efficiency (mass transfer enhanced and higher 'fresh L'/G ratio • Increase of gas superficial velocity (U_{SG} = 5.6–28 m/s) also improves removal efficiency (mass transfer enhanced) within the range tested. • H₂S = 200–600 ppmv

(continued overleaf)

Table 6. continued

No	Technologies	Literature	Methodology	Process modules	Conditions of main unit
					<ul style="list-style-type: none"> Residence time = 0.01–0.06 s! <p>The most important finding is the low consumption of NaOH by CO₂ due to the very low residence time. This is possible at the expenses of Cl₂ which enhances S and NH₃ removal at pH around 12. An additional drawback is the presence of secondary byproducts due to oxidation reactions</p>
4	Biological				
4.1.	Biological oxidation	Chemosphere, 71 : 10–17 ⁵⁸	<ul style="list-style-type: none"> Under microaerobic conditions Autotrophic sulfide oxidizing culture H₂S ↔ H⁺ + HS⁻ HS⁻ + 0.5O₂ → S⁰ + OH⁻ HS⁻ + 2O₂ → SO₄⁻² + H⁺ 	<ul style="list-style-type: none"> Two lab-scale biotrickling filters (upflow, counter-current mode, fed with a mimic of biogas or fuel gas containing mostly nitrogen, CO₂ and H₂S): Two different packing materials. A: open pore polyurethane B: polypropylene Automated control of pH Inlet gas composition fluctuation problem: 5 000 ± 2 000 ppm 	<ul style="list-style-type: none"> Inlet H₂S concentration 900–12 000 ppmv Outlet H₂S concentration maintained below 500 ppmv Maximum S removal 280 and 250 g H₂S/(m³·h) Residence time: A:167 s; B:180 s ΔP: 1–2 cm H₂O Significant pH drop (as low as 3.5) after day 28 (A) and day 20 (B) but no impact on EC Low (about 30 days) adaptability of bacteria to high H₂S concentration Specific surface area A: 600 m²/m³ B: 433 m²/m³ Predominant species of S are SO₄⁻² and S⁰ (98%) SO₄⁻²/S⁰ ratio depends on O₂/H₂S ratio. High O₂ concentration gives high sulfate production Reactor A clogged after three months because of fine mesh resulting in P drop > 10 cm H₂O. Not the case for reactor B Compromise between surface area and opening mesh pH control is an issue at high H₂S concentration
4.2.	Autotrophic aerobic degradation of H ₂ S	Biotech & Bioeng, 92 (4): 462–471 ⁵⁵	<ul style="list-style-type: none"> Bacteria from WWT sludge In air; parametric study (pH, CO₂, flow) 	<ul style="list-style-type: none"> Biotrickling filter 75–mm diameter; 70–cm length Packed with polypropylene pall ring (height 15 mm) 	<ul style="list-style-type: none"> Specific area of packed bed = 350 m²/m³ and porosity = 91% H₂S concentration inlet ranging from 0 to 190 ppmv Gas flow rate of 7 L/min (24 s) Liquid mineral medium at constant flow of 2.77 L/h Nutrient solution renewed every day Operated in counter-current mode for most of the experiment Under 50 ppm of inlet concentration, CO₂ concentration has no impact on removal efficiency (RE) Above 50 ppmv, RE is limited by CO₂ mass transfer in biofilm CO₂ concentration has an impact on RE at concentrations between 1087 and 1309 ppmv

Table 6. continued

No	Technologies	Literature	Methodology	Process modules	Conditions of main unit
					<ul style="list-style-type: none"> pH effect between 2 and 7 studied and each specific pH maintained for two days RE above 97% between pH 3 and 7 and 95% RE at pH 2 EC ranging from 13.25 to 31.12 g H₂S/m³/h during pH impact test Optimal pH = 6 Without pH control, pH stabilizes at 2 and around 60% of sulfide were converted to sulfate Test with CaO to precipitate sulfate in CaSO₄
4.3.	Biological removal of H ₂ S from biogas	46 th Purdue University Industrial Waste Conference Proceedings, 1992 ⁵⁴	<p>Full-scale and pilot data</p> <p>Mesophilic oxidation of H₂S under micro-aerophilic conditions; biopuric process</p>	<ul style="list-style-type: none"> Nutrient recycle analyzed during experiment Biogas in-out composition 3 reactors with 25 L of packing material 	<p>On-site operation data:</p> <ul style="list-style-type: none"> Removal efficiency % ranging from 94–98% with biogas flow from 1500 to 7000 m³/day H₂S input from 1000 to 10000 ppmv H₂S output from <50 to 600 ppmv Experiment at 27000 ppmv H₂S inlet gives RE = 85% and H₂S output of 4000 ppmv Operating cost: 25¢/kg S entering the system (45% labor, 15% tap water, 10% electricity, 15% temperature control) <p>Pilot plant operation results</p> <ul style="list-style-type: none"> Temperature higher than 25°C Biomass yield: 8% Biofilm growth: 40% H₂S converted RE 92% and 96% and kept stable even at H₂S loading twice the initial design
4.4.	Aerobic CO ₂ and H ₂ S removal by microalgae	BiotechLetters, 16 (10): 1087–1090 ⁷⁰	<ul style="list-style-type: none"> Biogas desulfurization with <i>Thiobacillus ferrooxidans</i> 2FeSO₄ + 1/2O₂ + H₂SO₄ → Fe₂(SO₄)₃ + H₂O (bacteria) H₂S + Fe₂(SO₄)₃ → H₂SO₄ + FeSO₄ + S₀ Analysis of Fe²⁺ and Fe³⁺ 	<ul style="list-style-type: none"> Bacteria isolated from acid mine drainage Polytene fibrefill used as packed bed Packed bubble tower bioreactor operating volume: 1,000 L Liquid is pumped from the top to the bottom of the tower, then to the S separator and, finally, to the bioreactor. Biogas is introduced with air at the base of the bioreactor 	<ul style="list-style-type: none"> RE: up to 99% H₂S inlet = 901 to 5401 ppm H₂S outlet = 10 to 203 Aeration: 30 m³/h T = 30°C pH = 2 Residence time = 4 h Operated for 30 days Ferric iron productivity = 1 g/(L*h) V_L/V_g has an important impact on RE
4.5	Microbiological removal of H ₂ S from biogas using a separate biofilter	Water Science & Technology, 48 (4): 209–212 ⁶⁵	<ul style="list-style-type: none"> The Bio-Sulfex biofilter operated in WWT and agricultural plant flow ranged from 150 to 350 m³/h and H₂S content up to 5000 ppm 	<ul style="list-style-type: none"> S⁰ production preferred Cleansing liquid in sufficient flow to evacuate the formed S Use of fresh liquid 	<ul style="list-style-type: none"> In normal operation: 90% RE and more Outlet H₂S concentration less than 100 ppmv and 50 ppmv could be achieved Several days shutdown does not affect performance No clogging observed

(continued overleaf)

Table 6. continued

No	Technologies	Literature	Methodology	Process modules	Conditions of main unit
4.6.	Study of <i>Thiobacillus thioparus</i>	JofApplied Microbiology, 101 : 1269–1281 ⁷³	Insight into the dynamics of this bacterium in an activated sludge bioreactor used to treat wastewater and degrade H ₂ S	<ul style="list-style-type: none"> • Pilot activated sludge bioreactor comprising aeration and clarifier bioreactors • VSS was used as the approximate measurement of active biomass • Gradient gel electrophoresis was used to confirm the presence of Thioparus • PCR was used to quantify Thioparus 	<ul style="list-style-type: none"> • 25 ppmv H₂S diffusion with regular peak of 100 ppmv • Increase of MLVSS with H₂S diffusion at 25 ppm suggests increase of biomass • Time has a greater impact on community structure than the addition of H₂S • Increase of Thioparus has been observed with H₂S diffusion • RE = 98–99% for H₂S inlet of 50 or 100 ppmv • Thioparus population size in the pilot plant showed a marked increase after 6 weeks
4.7.	H ₂ S removal by <i>Acidithiobacillus thiooxidans</i> AZ11	JofBioscience & Bioengineering, 101 (4): 309–314 ⁶⁷	<ul style="list-style-type: none"> • Reaction rate calculation in a fixed-bed porous ceramic biofilter inoculated with AZ11 	<ul style="list-style-type: none"> • Lab-scale biofilter (46-mm diameter pyrex column) 	<p>Inoculum test</p> <ul style="list-style-type: none"> • After comparing 3 strains of thiobacteria, AZ11 appears to have better tolerance to high H₂S load at low pH • AZ11 performance: specific oxidation rate = 6.8 g-S/g-DCW/d at high sulfate level (74 g/L) = 2.9 g-S/g-DCW/d <p>Experimental conditions and results</p> <ul style="list-style-type: none"> • H₂S inlet = 200–2000 ppm • H₂S out = less than 0.1 ppmv • Space velocity = 200 h⁻¹ • H₂S loading = 47–670 g-S/(m³*h) – high value corresponds to the limit of H₂S detection at the outlet • Removal efficiency = 98% at 500 h⁻¹, 94% at 600h⁻¹, and 99.9% below 400 h⁻¹ • RT experiment ranging from 6 to 18 s • At 2 000 ppm of H₂S inlet, Space velocity of 200 h⁻¹ (residence time of 18 s)
4.8	H ₂ S removal from biogas using cow-manure compost for biofiltration	Master Thesis, Cornell University, 2003 ²²	<ul style="list-style-type: none"> • Study of the biological removal of H₂S using cow-manure compost 	<ul style="list-style-type: none"> • 2 columns made of polyvinyl chloride cylinder – 0.1-m diameter and 0.5-m length • Mature cow-manure compost mixed 1:1wt with maple woodchips 	<ul style="list-style-type: none"> • RE = 90% at the beginning and around 50% after 44 days (end of the experiment) • EC ranged from 16 to 118 g H₂S m³/h • Concluded that optimal T is tight which can explain some reduction in RE • Economic analysis for biogas injection in pipeline
4.9	Removal of H ₂ S from anaerobic biogas using a bio-scrubber	Water Science & Technology, 36 (6–7): 349–356 ⁶⁸	<ul style="list-style-type: none"> • Airtight multiple bubble-tray contact tower • Use of sulfate-reducing bacteria and S-oxidizing bacteria • Simulation model for contact tower 	<ul style="list-style-type: none"> • The biogas from an anaerobic WWT process is introduced into a multiple bubble tray contact tower (bio-scrubber) and scrubbed with activated sludge liquor from an aeration tank. 	<ul style="list-style-type: none"> • K_La for bubble tray = 200 h⁻¹ • Contact tower with 13 bubble trays (V = 3 m³) • Liquid/gas ratio of 50% good RE • Reactor volume and O₂ addition should include extra volume for BOD removal

Table 6. continued

No	Technologies	Literature	Methodology	Process modules	Conditions of main unit
			<ul style="list-style-type: none"> Using simulation model criteria to design a full-scale plant for treating biogas from a UASB process for potato-processing wastewater 	The sludge liquor containing sulfides is then returned to the aeration tank, where the sulfide is oxidized to sulfate by S-oxidizing bacteria, such as <i>Thiobacillus</i>	<ul style="list-style-type: none"> Simulation results: H₂S IN = 2000 ppmv – gas velocity = 40 m/h – liquid/gas ratio = 100% – liquid T = 25°C Aeration tank volume = 550 m³ Gas flow rate = 40 m³/h H₂S outlet less than 20 ppm Average H₂S inlet = 300–2500 ppm (average 1,300) RE = more than 99% 6-month operation No clogging problem S oxidation rate step 1 = 870 mg–S/g–VS/d, step 2 = 50 mg–S/g–VS/d Consumption of 1056 kWh of electricity/month Operating cost evaluated at \$2660/month
4.10.	Evaluation of packing material for the biodegradation of H ₂ S and product analysis	Process Biochemistry, 37 (8): 813–820 ⁶⁰	A packing material based on pig manure and sawdust was used for biofiltration purposes	<ul style="list-style-type: none"> Biofilter made up of three exchangeable modules 	<ul style="list-style-type: none"> The operation was carried out for 2500 h, during which the H₂S mass loading rate was increased from 10 to 45 g/(m³*h) with 2 superficial gas velocities (100 and 200 m/h) Main by-product obtained in the biodegradation process was S⁰ (82% of total S) S deposition does not plug the bed for operating periods of 2500 h
4.11	Removal of H ₂ S from gas streams using biological processes - A review	CanBiosystemsEng, 48 : 2.1–2.14 ⁵⁷	A review of all biological processes used for the removal of H ₂ S from gas streams		

inoculated with these inocula on a crushed, porous ceramic support. The study showed that, at a low flow rate (space velocity = 200 h⁻¹) and residence time of 18 s, this species was capable of degrading high H₂S concentration (2 200 ppmv) and S-loading of 670 g/(m³*h). Removal efficiency ranged from 94% to 99.9% and was demonstrated to be dependent on residence time (the studied range was 6 to 18 s).

Process approach and design consideration

As described by Syed *et al.* in 2006,⁵⁷ there are mainly three different design approaches in biological desulfurization: biofilter, bioscrubber, and biotrickling filter. The biotrickling filter is similar to a biofilter, with the difference being that the packing bed is trickled over with a nutrient solution. In both cases, the packing material is a crucial design parameter.

Porosity, alkalinity, pressure drop, fluidic behavior, nutrient content, and solid accumulation can have an impact on global removal efficiency and process stability. Moisture, pH, O₂ and H₂S concentration are critical attributes (parameters) to control in a biofilter operation.

Fortuny *et al.*⁵⁸ recently inoculated non-identified species of chemotrophic thiobacteria on a biotrickling filter. This system was tested with high H₂S concentrations ranging from 900 to 12,000 ppmv. The set-up consisted of two lab-scale biotrickling filters (volumes of 0.5 and 2.15 L, respectively) using two kinds of synthetic packing materials (polyurethane and polypropylene), and fed with a mimic of biogas (N₂-H₂S-CO₂). One of the filters had an automated system to control pH, its optimum level being established at 6. The system provided an elimination capacity of 280 g

$\text{H}_2\text{S}/(\text{m}^3\cdot\text{h})$. Predominant species of S are SO_4^{2-} and S^0 , both totalling 98% of total S. Analysis of the $\text{SO}_4^{2-}/\text{S}^0$ ratio shows dependency on the $\text{O}_2/\text{H}_2\text{S}$ ratio. The higher H_2S concentration tested produced almost no sulfate.

In 1997, Nishimura and Yoda⁶⁸ experimented on a full-scale bioscrubber treating $40 \text{ m}^3/\text{h}$ of a biogas (up to 2500 ppmv H_2S) produced from potato-factory wastewater. The system included an airtight contact tower (Volume = 3 m^3) with 13 bubble trays flushed with recycled liquid from the aeration tank ($V = 550 \text{ m}^3$) of the UASB process. The outlet removal efficiency obtained was more than 99%, with outlet H_2S concentration less than 20 ppmv. Annual operating costs were estimated to be US\$2660. In 1994, Guoquiang *et al.*⁷⁰ tested a full-scale bioscrubber treating $1000 \text{ m}^3/\text{day}$ of biogas in a packed bubble tower coupled to an aerobic bioreactor ($V = 1 \text{ m}^3$) inoculated with *Thiobacillus ferrooxidans*. Bioreactor conditions were: pH = 2, T = 30°C , aeration = $30 \text{ m}^3/\text{h}$, Fe^{2+} maintained above 5 g/L. Removal efficiency in the contact tower was up to 98%.

Commercial applications

Thiopaq[®] is one of the most cited technologies for large-scale industrial biogas desulfurization by chemotrophic thiobacteria operated in an alkaline environment. The system includes a scrubber operating at pH 8–9, dissolving H_2S by chemical reaction with hydroxide ions (Eqn 14). Then, the liquid is sent to the bioreactor where thiobacteria oxidize sulfide in S^0 , regenerating simultaneously hydroxide (Eqn 15). This process is claimed to be suited for flow ranging from $200 \text{ Nm}^3/\text{h}$ to $2500 \text{ Nm}^3/\text{h}$ with H_2S concentrations of up to 100%. The redox potential is maximized by controlling airflow in function of H_2S concentration. Outlet concentrations below 4 ppmv are guaranteed. These systems are generally most economical for larger quantities of S, up to 50 tons/day, equivalent to $1000 \text{ m}^3/\text{h}$ with concentrations of 7000 ppmv in H_2S .⁷¹



MVLLC Inc.,⁷² commercialized a patent-pending purification process which combines both chemical and biological principles. The $\text{H}_2\text{SPLUS SYSTEM}^{\text{®}}$ consists of an iron-sponge-bed filter inoculated with thiobacteria. Nutrients are fed to the vessel on a weekly basis and a constant air supply is provided. According to the developer, around one-third of the S is transformed into S^0 through a biological pathway.

The bed has to be changed after approximately six months, depending on process parameters. The spent bed material can be used as fertilizer. About 30 systems are currently in operation throughout the USA. Most of these are agrifood projects treating biogas generated by the treatment of wastewater produced from organic processing factories (slaughter houses, potato factories, alcohol plants). These units are suited for smaller systems ranging from 17 to $4200 \text{ m}^3/\text{h}$, with removal capacity of up to 225 kg of H_2S per day. Operating costs are evaluated to be US\$2.20 per kg of S removed. Capital investment for $1700 \text{ m}^3/\text{h}$ of biogas concentrated to 5000 ppmv H_2S is US\$450 000.

In Europe, many industrial applications and a majority of on-farm anaerobic digesters include a system to maintain 4 to 6% of air in the bioreactor headspace. Such air addition allows the development of facultative aerobic thiobacteria, which precipitate H_2S oxidation to S^0 . It seems that residence time in the bioreactor headspace can be sufficient to achieve significant H_2S removal with biogas outlet below 200 ppmv H_2S . Often, wood beams are added in the headspace to give bacteria an extra support area for their development. The technique is very simple and economical. Essentially, it requires an air blower with security control to ensure that the air concentration does not reach the lower explosive limit, e.g., 5% CH_4 . Thiobacteria are naturally present in many substrates treated by anaerobic digestion, particularly manure and compost. The result is a deposit of S^0 at the liquid interface and on the wood beam.

Commercial technologies

Table 7 lists integral technical solutions offered commercially worldwide for biogas purification, as well as some new solutions coming from patented works and presenting interest for the future.

Conclusion

Purification is a 'must-do' step independently of biogas final use. The reasons have been clearly given in previous sections of this review. S-containing contaminants, mainly H_2S , are the principal concern.

Physicochemical methods, adopting chemical adsorption and absorption processes, have been explored, both scientifically and technically, and most of them are now offered commercially by companies owning or licensing the

Table 7. Integral commercially available biogas purification solutions.

Companies or other	Elements	Characteristics	Applications	Other data
Schmack – Biogas AGCarboTech Process ⁶¹	1. Compression 2. Dehumidification 3. Desulfurization 4. Decarbonization 5. Siloxane removal	1. Up to 5 bars 2. By moderate quenching 3. Fixed-bed catalytic adsorption on AC 4. PSA adsorption on molecular sieves 5. Same as Point 4 They do not give costs but claim that the overall specific costs for gas purification are very weak (unclear...)	Not specified Unlimited	– Capacities between 500 and 5000 Nm ³ /h – They sell a ‘Zero emission technology’ option (ZETECH4 [®]); it seems that they recycle the separated CO ₂ back to the CH ₄ production step (unclear...)
Eco-Tec Inc. BgPur™ BioGas Purification System ^{63,63}	Removal of H ₂ S and particulate matter by liquid scrubbing	– 99%+ H ₂ S removal – Automatic adjustment for H ₂ S and flow levels – Small, skid-mounted, pre-assembled, pre-tested, easy-to-install and operate – Capacity according to specific needs	– Municipal WWT – Industrial WWT – Food and beverage processing – Meat rendering – Landfill gas – Pulp and paper mills – Agri/livestock farms	The adsorbing solution contains NaOH and a proprietary chemical additive (Eco-BGA-1 solution); pH around 8. The adsorbing solution is regenerated using O ₂ to oxidize S ²⁻ to S ⁰ ; the solution is then re-used. NaOH is consumed as a make-up.
Guild Associates, Inc. Guild PSA Technology ⁶²	1. Compression: 4–7 atm 2. The Guild PSA system removes water, CO ₂ , and H ₂ S to meet pipeline specifications. 3. The tail gas can be used as local fuel or flared, as necessary, since it has a relatively low heating value.	The system: removes water to pipeline specifications of less than 0.11 g/Nm ³ ; removes H ₂ S to a typical requirement of 4 ppm; and removes CO ₂ as required by pipeline specifications (typically in the range of 1 to 3%vol).	No limitations reported	
Shell-Paques/ Thiopack™ Technology ⁷¹	H ₂ S removal with bioscrubber	Alkaline absorption H ₂ S + OH ⁻ → HS ⁻ + H ₂ O followed by biological oxidation in a liquid phase bioreactor HS ⁻ + ½ O ₂ → S ⁰ + OH ⁻ – pH=8–9	– High-scale system – Oil industry – Wastewater plant	– Flow between 500 and 2500 Nm ³ /h – Economical for removal capacity higher than 50 tons S/day
MVLLC Inc. H ₂ S PLUS™ Technology ⁷²	Iron sponge with thio-bacteria – Chemical and biological H ₂ S removal	– Heated vessel with nutrient recycle loop – S oxidizes to S ⁰ – 1/3 of S ⁰ is produced by the biological pathway	Agrifood processing factories (slaughter houses, potato factories, alcohol plants)	– Flow between 17 and 4200 m ³ /h – 225 kg of H ₂ S per day – US\$2.20 per kg of S removed. – Capital investment for 1700 m ³ /h of biogas containing 5000 ppmv H ₂ S is US\$450 000

associated rights. Significant research efforts are ongoing; they mainly focus on the following:

1. Understanding the H₂S capture mechanism to model the phenomena taking place and optimizing efficiency.
2. Understanding the nature of the captured S and its physicochemical impact on the adsorbing or absorption media to evaluate and maximize the useful lifespan of the latter and, consequently, decrease purification costs.

- Proposing new solutions based on new or improved (i) functionalized adsorbents, and (ii) a controlled oxidative absorption technique.

The biological methods are less well known, and more intensive research activities are needed. Although separate gas treatments in fixed-bed or other bioreactor configurations seem to be a clear option for medium-to-large-scale biogas producers (i.e., landfills and special WWT units), *in situ*, compact, one-stage S-removal has to be optimized, especially for small-scale applications (i.e., animal farms). Both biological activity mechanisms and reaction kinetics as well as physicochemical methods of captured S withdrawal and use/disposal must be studied at the fundamental and applied research levels.

A comparative assessment of the benefits generated through these research activities leads to the opinion that the eventual success of a proposed technique will come from a combination of better S-capture efficiency, low media and operating costs, energy prices and socio-economic policies. The currently prevailing sustainable development context is clearly positive for the proliferation of biogas use, and biogas purification will be an important component in all such endeavors.

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Nicolas Abatzoglou, Eng.

Dr Nicolas Abatzoglou is full professor at the Department of Chemical Engineering, Université de Sherbrooke, Quebec, Canada and holder of the Wyeth/UdeS Chair on Process Analytical Technologies. He earned his PhD from the NTU Polytechnic School Metsovion, Athens, Greece in 1989. He is

co-founder of Enerkem Technologies Inc. – a spin-off of the Université de Sherbrooke – a company that commercializes technologies in the field of energy from renewable resources.

A specialist in process engineering involving particulate systems in reactive and non-reactive environments, Dr Abatzoglou has focused his research activities during the last six years in the following areas:

- Studying water and dry reforming of methane, ethanol and biofuels for catalyst-supported SOFC application (recent US patent application).
- Developing cold biogas and hot biosyngas purification processes for H₂S, particulates and tar removal.
- Establishing an industry-university R&D collaborative program with pharmaceutical companies to study the mechanisms of particulate matter segregation and develop new prediction tools in order to improve the industrial processes.
- Developing technology for Carbon sequestration through CO₂ (dry) reforming (recent US patent application).

He represented Canada at the International Energy Agency (Gasification Task) from 1997 to 2001 and was the Secretary of the Board of Directors and the Executive Committee of the AQME (Association québécoise pour la maîtrise de l'énergie) from 1996 to 2000.

Two-time first-prize winner in environmental R&D at the Quebec Eastern Townships, Dr Abatzoglou also won the Bazinet award for best Chemical Engineering Professor five years running. His favored teaching fields are: reactor engineering, design of chemical processes, chemometrics and pharmaceutical process engineering.



Steve Boivin

Steve Boivin is a chemical engineer currently employed at Bio-Terre Systems Inc., a company specializing in the integration of anaerobic digestion processes into agricultural and agrifood operations. He graduated in Chemical Engineering at the Université de Sherbrooke in 2005 and he

is in the final year of his Master's studies on biogas purification through biological means. His work at Bio-Terre is mainly focused on research and development, with projects involving technical considerations pertaining to the transportation, conditioning and energy recovery of biogas. Notably, he was involved in the on-farm installation of a cogeneration unit, as well as the design and installation of heat-recovery systems for agricultural buildings.