

BIOLOGICAL PROCESS FOR H₂S REMOVAL FROM GAS STREAMS THE SHELL-PAQUES/THIOPAQ™ GAS DESULFURIZATION PROCESS

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1. ABSTRACT



On 12 September 2002 natural gas containing H₂S was introduced to the first high-pressure Shell-Paques unit at Bantry, east of Calgary in Canada. H₂S in the sweet gas is guaranteed to be 4 ppmv, while the total design amount of sulfur to be removed per day is approximately 1 ton. The start up was organized in such a way that the specification on H₂S in the sweet gas was met immediately and occurred virtually without flaring. Sulfur concentrations were typically 4 ppmv H₂S or lower in the treated gas and the H₂S removal efficiency was always above 99.5%

The Shell-Paques/THIOPAQ™ process has been developed by Paques B.V., Shell Global Solutions International BV, and UOP and is a biological process for removing H₂S from (high-pressure) natural gas, synthesis gas and refinery gas streams.

In this process, which has been used successfully in biogas (atmospheric mixture of CH₄, CO₂ and H₂S) sweetening since 1993, essentially complete removal of H₂S can be achieved by selective biological conversion of H₂S into elemental sulfur.

A long-duration test, of in total six months, in a large pilot-plant used for treating high-pressure natural gas has demonstrated the very smooth operation of the process, and shown the high potential of this breakthrough technology for gas desulfurization.

For the past four years, the process has been marketed as a very attractive alternative to traditional gas treating and sulfur recovery technologies. This resulted in the start-up of the first commercial unit in September 2002. The start-up of the second and third units, both refinery applications, is planned for August and December 2003.

In comparison with conventional liquid redox processes significant savings in capital and especially operating costs can be achieved. In addition, economic savings can be delivered compared to conventional Amine + Claus + SCOT technology for loadings of up to 50 ton sulfur/day; this upper limit increases continuously due to optimization of the process.

The sulfur produced has a hydrophilic nature, which significantly reduces the chance of equipment fouling or blocking. Moreover, this characteristic makes the product suitable for agricultural use as fertilizer. Alternatively, the sulfur can be melted to yield a high purity product which meets international Claus sulfur specifications.

This paper focuses on the successful start-up and the operational experience of the EnCana Bantry North Shell-Paques unit. It explains the underlying working-principle of the Shell-Paques/THIOPAQ™ technology. It also gives some details of two refinery projects and information on the special and potentially very valuable characteristics of the THIOPAQ™ sulfur.

2. INTRODUCTION

Currently, H₂S removal from natural gas with subsequent sulfur recovery is mainly performed in Amine and Claus plants. These processes are, in general, most economical for larger quantities of sulfur (> 50 ton/day). If H₂S removal from smaller gas fields is required, the gas is generally treated by liquid redox processes, or, alternatively, by amine treatment followed by incineration or re-injection of the acid gas in an empty well.

All these gas-processing options have their strengths and weaknesses. Moreover, it is expected that more of the smaller gas fields with a relatively high H₂S concentration will be explored in the near future. As a result, the search for alternative H₂S removal technologies, that are safe, cost-effective and easy to operate, continues.

Shell-Paques/THIOPAQTM¹ is a biotechnological process for removing H₂S from gaseous streams by absorption into a mild alkaline solution followed by the oxidation of the absorbed sulfide to elemental sulfur by naturally occurring microorganisms.

The Shell-Paques/THIOPAQTM process offers:

- ⇒ Replacement for liquid redox processes or amine treating, Claus recovery and tail gas treatment.
- ⇒ Minimal chemical consumption.
- ⇒ High turndown ratio.
- ⇒ Gas treatment as well as sulfur recovery.
- ⇒ H₂S removal to below 4 ppmv can be guaranteed.
- ⇒ Essentially 100% conversion of sulfide in the bioreactor with 95-98% selectivity to S⁰.
- ⇒ No replacement of the biocatalyst needed. Applies to H₂S concentrations of 100 ppmv to 100 vol.% and pressures from 1-75 bar(g). Therefore, direct treatment of either the sour gas or the amine off-gas is possible.

In comparison to traditional removal processes such as the Amine/Claus process the following advantages are recognized:

- There is practically no free H₂S available anywhere downstream of the scrubber inlet; therefore the unit is very safe and easy to operate.
- Very simple line-up, therefore little control and supervision required.
- There are no complex control loops.
- A relatively large volume of (cheap) solvent is used; therefore changes in solvent composition and performance of the unit are very slow and the process becomes more robust.

¹ Shell-Paques process is the name of the technology licensed by Shell and Paques for applications in (1) Natural Gas, (2) Synthesis Gas and (3) Claus Tail Gas treatment. THIOPAQTM is the name for the same process licensed by Shell, Paques and UOP for refinery gas and other applications. The THIOPAQTM trademark name is owned by Paques BV.

The first THIOPAQ™ installation, for removing H₂S from biogas (CH₄=80 vol.%, CO₂=18 vol.%, H₂S=2 vol.% @ 30 mbarg) and landfill gas (CH₄=60 vol.%, CO₂=40 vol.%, H₂S=5000 ppmv, @ - 50 mbarg), began in 1993. Since then, 25 similar units have been installed in Germany, U.K., Denmark, France, Spain, Italy, India, Chili and the U.S.A. Generally, the H₂S content in these gases is reduced from about 2.0 vol.% down to a level of 100 to 10 ppmv, although desulfurization down to a few ppmv can also be achieved as demonstrated in the Bantry plant data.

The Shell-Paques/THIOPAQ™ process has been further developed together with UOP LLC and Shell Global Solutions International BV for the desulfurization of natural gases containing H₂S as well as for gas streams in the refining industry. The THIOPAQ™ process has been commercialized for sulfur removal applications in several industries including the pulp and paper, chemical and mining industries.

3. PROCESS PRINCIPLE

A simplified flow scheme of the Shell-Paques/THIOPAQ™ process is presented in Figure 1.

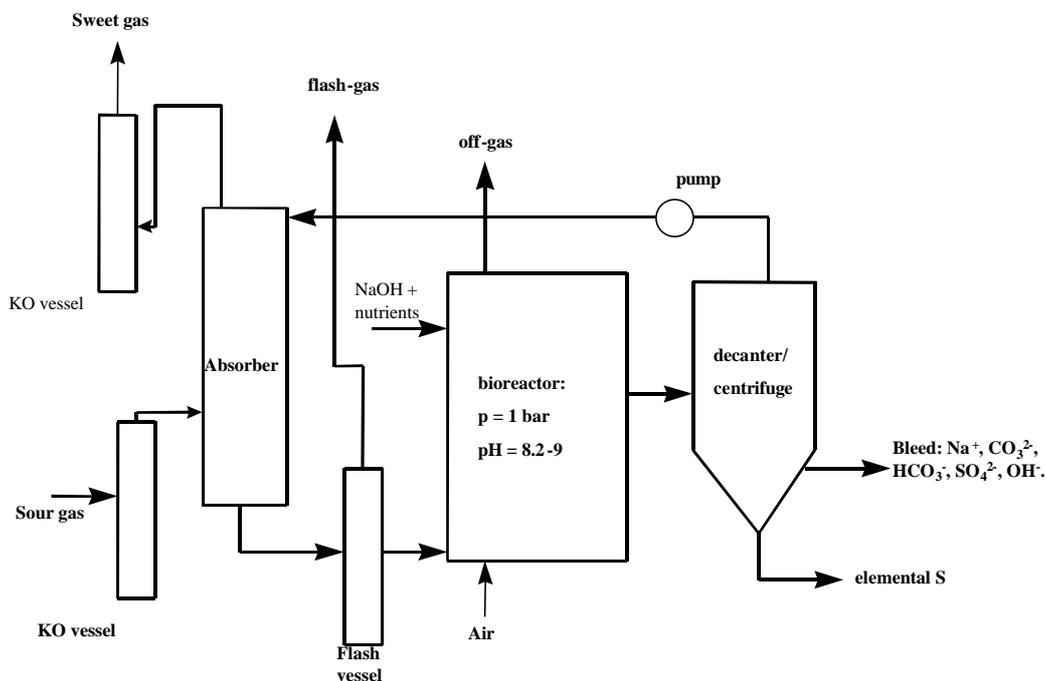


Figure 1: Simplified process flow scheme of the Shell-Paques/THIOPAQ™ process.

In the Shell-Paques/THIOPAQ™ process, H₂S-containing gas is absorbed in a mildly alkaline solution under full pressure (up to 75 barg). For hydrocarbon-containing gases, a trayed or packed column is the preferred gas/liquid contactor but gases at low pressures and without hydrocarbons can be directed immediately to the bioreactor. The dissolved sulfide is subsequently oxidized into elemental sulfur in the THIOPAQ™ reactor:

Main Reactions in the Absorber (at feed gas pressure):

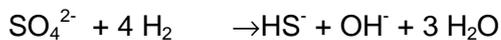
| | | |
|--------------------------------|--|-----------------------------|
| 1. H ₂ S absorption | $\text{H}_2\text{S} + \text{OH}^- \rightarrow \text{HS}^- + \text{H}_2\text{O}$ | OH ⁻ consumption |
| 2. H ₂ S absorption | $\text{H}_2\text{S} + \text{CO}_3^{2-} \rightarrow \text{HS}^- + \text{HCO}_3^-$ | |
| 3. CO ₂ absorption | $\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-$ | OH ⁻ consumption |
| 4. Carbonate formation | $\text{HCO}_3^- + \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$ | OH ⁻ consumption |

Main Reactions in the Bioreactor (at atmospheric pressure):

| | | |
|------------------------------|---|-----------------------------|
| 5. Sulfur production | $\text{HS}^- + \frac{1}{2} \text{O}_2 \rightarrow \frac{1}{8} \text{S}_8 + \text{OH}^-$ | OH ⁻ production |
| 6. Sulfate production | $\text{HS}^- + 2\text{O}_2 + \text{OH}^- \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O}$ | OH ⁻ consumption |
| 7. Carbonate decomposition | $\text{CO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{OH}^-$ | OH ⁻ production |
| 8. Bicarbonate decomposition | $\text{HCO}_3^- \rightarrow \text{CO}_2 + \text{OH}^-$ | OH ⁻ production |

From the reactions shown above, it follows that the caustic used to absorb H₂S-gas, is regenerated during the production of elemental sulfur. Normally, less than 3.5% of the sulfide is completely oxidized to sulfate. In order to avoid accumulation of sulfate ions, a continuous bleed stream from the bioreactor is required and make-up water with some caustic is needed.

For installations located in dry and/or remote areas, the discharge of sulfate-containing aqueous streams into the environment may be undesirable. This bleed stream can be reduced by using membrane filtration or by a biological hydrogenation step. The membrane-filter separates the bivalent sulfate ions from the monovalent bicarbonate ions, leading to a concentrated sulfate effluent stream. To avoid the production of any bleed stream at all, a part of the bioreactor content can be continuously recycled over a sulfate-reducing stage where sulfate is converted to hydrogen sulfide:



The sulfide thus formed is subsequently recycled to the sulfur-producing THIOPAQ™ reactor.

In 1999, the first full-scale installation for the daily production of 4 tons of H₂S from a spent H₂SO₄ stream came into operation with H₂ gas as the reducing agent.

A key feature of the Shell-Paques/THIOPAQ™ process is its proprietary bioreactor design. Depending on the capacity required, either a bubble tank or gas-lift-loop system is used. The gas-lift-loop reactors for sulfide oxidation and sulfate reduction are proprietary Paques' designs.

4. FIRST HIGH-PRESSURE SHELL-PAQUES UNIT

4.1. Bantry Project Background

The Bantry Shell-Paques unit is located near the town of Brooks east of Calgary, in Canada and is owned and operated by EnCana Resources, a major Canadian and global gas producer. The natural gas is extracted from well sites that are on, or adjacent to the properties of over forty Canadian landowners around the Bantry North facility.

New Paradigm Gas Processing Ltd. (New Paradigm), a subsidiary of the Canadian technology company (CCR) Technologies Ltd. and the authorized licensor of the Shell-Paques process in Canada, constructed the unit under license.

The Shell-Paques biological technology was selected because it was the best available technology for this application. The alternative was acid gas re-injection, which was too expensive and therefore not attractive.

4.2. Project Schedule

The license agreement between EnCana Resources and New Paradigm was signed in the last week of November 2001.

Basic engineering started directly in December and detailed engineering was completed by April 2002, i.e. five months after signing the agreement. Late April the constructor, International Fabrication Contractors was selected, with Equinox Engineering Ltd. being responsible for all engineering and procurement activities, and start was made with the construction of the facility on two skids. These skids were transported to site at the end of July. The construction and the tie-ins to the existing Bantry North infrastructure were done in August.

The unit was handed over to the start-up team on 11 September and taken on stream on 12 September 2002.

4.3. Project Investment Costs

The actual total investment was within 10 % of the original estimate on which the investment decision was based.

4.4. Design Basis

The Bantry Shell-Paques unit is designed to remove H₂S and recover it as sulfur from nine natural gas fields. The various operating modes resulted in a large matrix, which could be further reduced to two design cases.

Table 1: The two design cases for the Bantry Shell-Paques unit.

| | Units | Low Pressure, winter case | High Pressure, summer case |
|------------------------|--------------------------------------|------------------------------|-------------------------------|
| Gas Flow | 10 ³ Nm ³ /day | 321.5 | 321.5 |
| | MMSCFD | 12.0 | 12.0 |
| Pressure | Barg | 5.9 | 13.8 |
| | Psig | 85 | 200 |
| Temperature | °C | 4 | 10 |
| | F | 39 | 50 |
| Gas Composition | | | |
| H ₂ | % vol. | 0.005 | 0.005 |
| He | % vol. | 0.061 | 0.061 |
| N ₂ | % vol. | 4.112 | 4.112 |
| CO ₂ | % vol. | 2.506 | 2.506 |
| H ₂ S | % vol. | 0.202 | 0.202 |
| C1 | % vol. | 84.429 | 84.429 |
| C2 | % vol. | 4.348 | 4.348 |
| C3 | % vol. | 2.041 | 2.041 |
| i-C4 | % vol. | 0.496 | 0.496 |
| n-C4 | % vol. | 0.862 | 0.862 |
| i-C5 | % vol. | 0.330 | 0.330 |
| n-C5 | % vol. | 0.281 | 0.281 |
| C6 | % vol. | 0.211 | 0.211 |
| C7-plus | % vol. | 0.117 | 0.117 |

4.5. Process Description

A simplified process flow scheme of the Bantry Shell-Paques unit is included on the next page.

Sour natural gas is routed via a feed gas knockout vessel and a glycol heater to the absorber. Even though the Shell-Paques process is an exothermic process, the latent heat content of the feed gas was so low that heating duty needed to be supplied for this project rather than cooling duty. Application of the heater on the feed gas flow has one major advantage; it allowed the feed gas temperature to be controlled in relation to the solvent temperature, i.e. hydrocarbon condensation control was achieved.

The sour natural gas is washed in the absorber counter-currently. This absorber has three packed beds with 2-inch Pall rings. A total draw-off tray combined with a liquid redistribution tray in-between the packed beds ensures proper liquid redistribution. Treated natural gas leaves the top of the absorber and is routed to the sales gas grid via a knockout drum.

The loaded THIOPAQ™ solvent is routed from the absorber to the horizontal flash vessel. The flash gas, which contains some H₂S, is washed in the small column on top of the flash vessel. The treated flash gas is routed to flare at the Bantry unit.

Flashed, loaded THIOPAQ™ solvent is then sent to the bioreactor. A blower supplies air to a distributor in the bottom section of this tank. Part of the oxygen is consumed in reactions with sulfide and sulfur (see section 3, reactions 5 and 6). The distribution of air also ensures that the content of the bioreactor is continuously mixed.

Regenerated THIOPAQ™ solvent is recycled to the main absorber, the flash absorber, the solids separator and to the top of the bioreactor. The last feature is mainly as a pro-active measure to prevent foaming.

The bacteria catalyze the regeneration reactions 5 and 6, the reaction of sulfide with oxygen to give either elemental sulfur or sulfate. The reaction that gives elemental sulfur is very much preferred because:

- It produces a hydroxyl molecule, which can capture a molecule of H₂S in the absorber.
- It produces elemental sulfur, which can be separated fairly easily from the solvent.

We have to accept a small percentage of over-oxidation however since we need to convert all sulfides in the bioreactor.

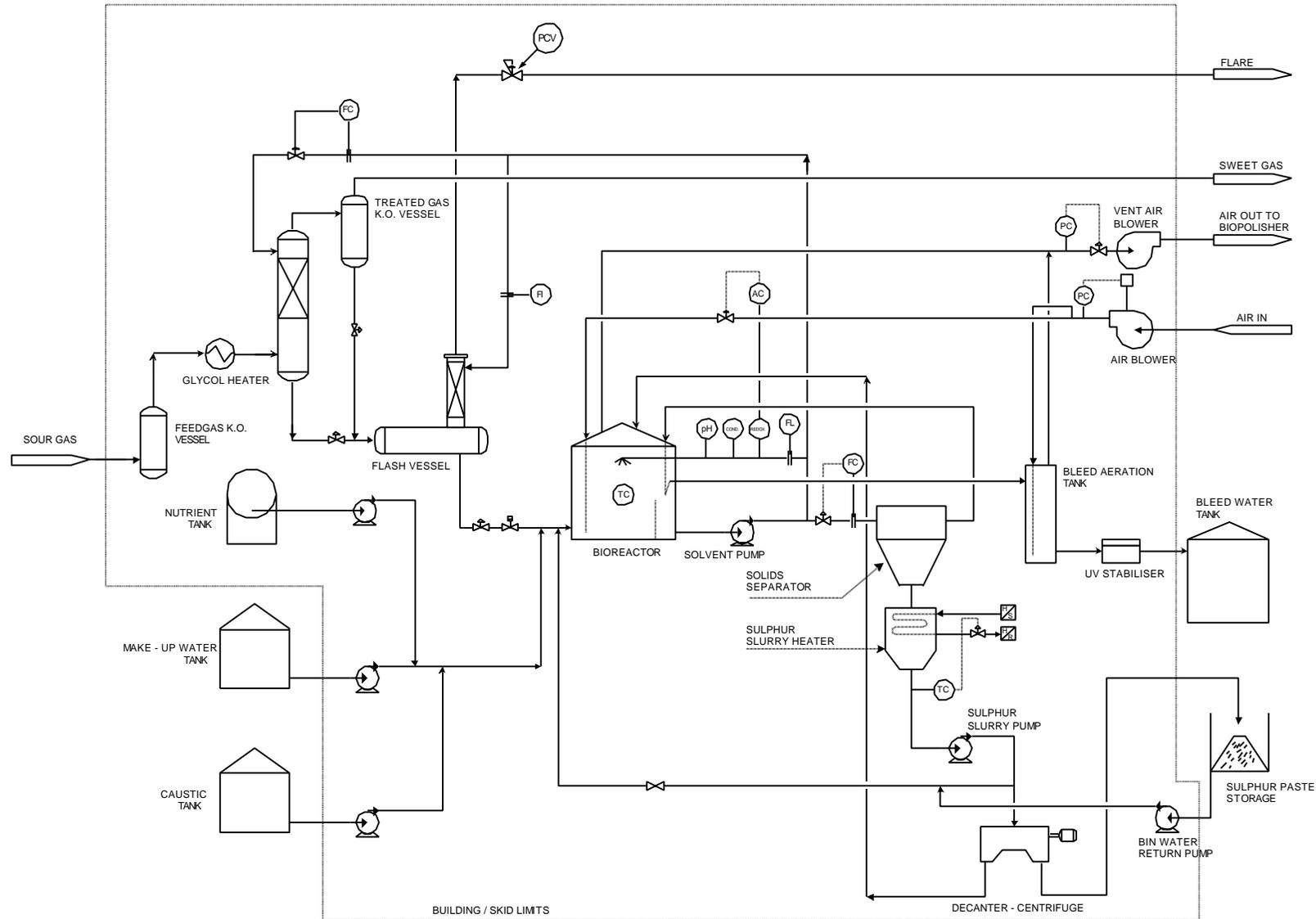
The sulfate production necessitates a continuous bleed from the unit. The bleed stream is taken from a separate calm section of the bioreactor, to minimize the sulfur content. The clarified bleed stream is subsequently aerated. Some bacteria will still be present, they will ensure that all sulfur and sulfide is completely oxidized to sulfate for which the biological oxygen demand is zero. Local legislation required sterilization of the bleed stream; therefore a UV source has been installed after the aeration tank. Bleed water is collected and transported by truck to a nearby water treating facility.

The vent air leaving the bioreactor can contain a little H₂S (typically less than 1 ppmv) and is therefore routed to a bio-polisher. This bio-polisher is a tank with a layer of compost; the vent air contains sufficient water vapor to keep this compost filter humid. The vent air is discharged directly into atmosphere.

The regenerated solvent leaving the bioreactor typically contains 10 kg sulfur per cubic meter, or roughly one weight percent. The solvent is concentrated into sulfur slurry with around 10 % wt. sulfur content in the solids separator, the clarified water phase is returned to the bioreactor.

This sulfur slurry is further concentrated into a sulfur paste, with around 65 % wt sulfur content, in a decanter-centrifuge. The sulfur paste produced at the Bantry Shell-Paques unit is routed to landfill.

Figure 2: Simplified PFS of the Bantry Shell-Paques unit.



4.6. Process Control

The main operating parameters of the Shell-Paques process are:

- Redox potential, which reflects the sulfide concentrations, controls directly the amount of regeneration air via the frequency of the air blower.
- Conductivity or total salt concentration, controls the make-up water flow to the bioreactor. The bleed flow is an overflow of the bioreactor. If, for example, the conductivity is too high, then more make-up is added which increases the bleed flow and thereby reduces the salt concentration.
- The solution pH or alkalinity, controls directly the addition of caustic (50 % wt NaOH solution in the Bantry case).

4.7. Product Specifications

The Shell-Paques unit is designed to meet a H₂S specification of 4 ppm volume on the treated natural gas.

4.8. Start up of the unit

Customers require a start up period that is as short as possible, for this particular unit an additional demand was that start up was to be without flaring i.e. the unit had to be on specification immediately.

An existing Dutch THIOPAQ™ unit provided the biomass, which is attached to the sulfur particles, for the Bantry Shell-Paques unit. A large enough volume of sulfur slurry was arranged, such that the total sulfur content was 50 % higher than the design sulfur content of the THIOPAQ™ solvent. The import and registration of the Dutch biomass was in line with the relevant Canadian Environmental Protection Act (CEPA), 1999 guidelines.

At handover to the start-up team the unit was; pressure and leak tested, the safeguarding functionality was tested, all process control was on automatic (except for the conductivity, pH and the redox analyzers), make-up water was added to the unit, liquid circulation was established and the regeneration air blower was on stream, etc.

The next phases of the start-up preparations were split into the following steps;

1. The amount of sodium bicarbonate and caustic in the bioreactor was adjusted to the same values as in the seed material
2. The compost filter in the bio-polisher was inoculated using several jerry cans of the clear liquid of the sulfur slurry.
3. Sulfur slurry was mixed and circulated for several hours to bring all the sulfur particles into suspension. This suspension was then transferred to the bioreactor some hours before feed gas was introduced.
4. Solvent was circulated to the absorber, flash gas absorber and bioreactor according to the design value. Redox, pH and conductivity probes were put on automatic control.
5. Sour natural gas was routed to the absorber whilst manually analyzing H₂S and CO₂ content in the feed gas. The sour gas flow was 150,000 Nm³/day (47 vol. % of the design flow rate) with 475 ppmv H₂S or 0.1 t/d sulfur load (11 weight % of design sulfur load).

The H₂S in the treated gas was analyzed on-stream, and the QMI reported values of the order of 0.1 to 0.2 ppmv H₂S (confirmed by Dräger tubes). The first high pressure Shell-Paques unit was successfully brought on-stream and directly met sales gas specifications!

4.9. Actual Operation

4.9.1. Sulfur Harvesting

Sulfur is produced on a continuous basis in a Shell-Paques/THIOPAQ™ unit whenever the unit is processing H₂S. The sulfur concentration in the THIOPAQ™ solvent is initially allowed to increase to roughly double the normal operating value before the decanter-centrifuge is put into service to run off the sulfur as product. The sulfur dispersed into the THIOPAQ™ solvent provides a substantial part of the total solvent loading capacity and its concentration is therefore important in meeting the H₂S specification on the treated gas.

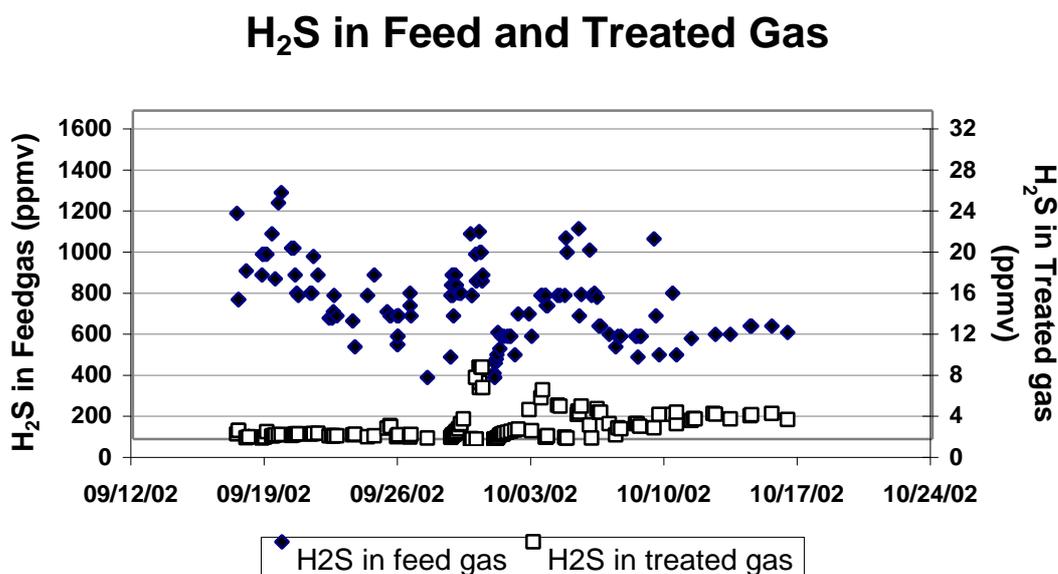
The sulfur concentration in the Bantry solvent was at a high enough level on 24 September, so the decanter-centrifuge was used to harvest the very first sulfur produced in a high-pressure Shell-Paques unit.

The decanter-centrifuge was initially operated in a batch mode mainly because the sulfur load was relatively low but more importantly because the physical presence of operators was desired until operational familiarity was achieved. It currently is operating in a continuous mode with the feed to the solids separation being adjusted based on solution solids content of the THIOPAQ™ solvent.

4.9.2. Some operating trends

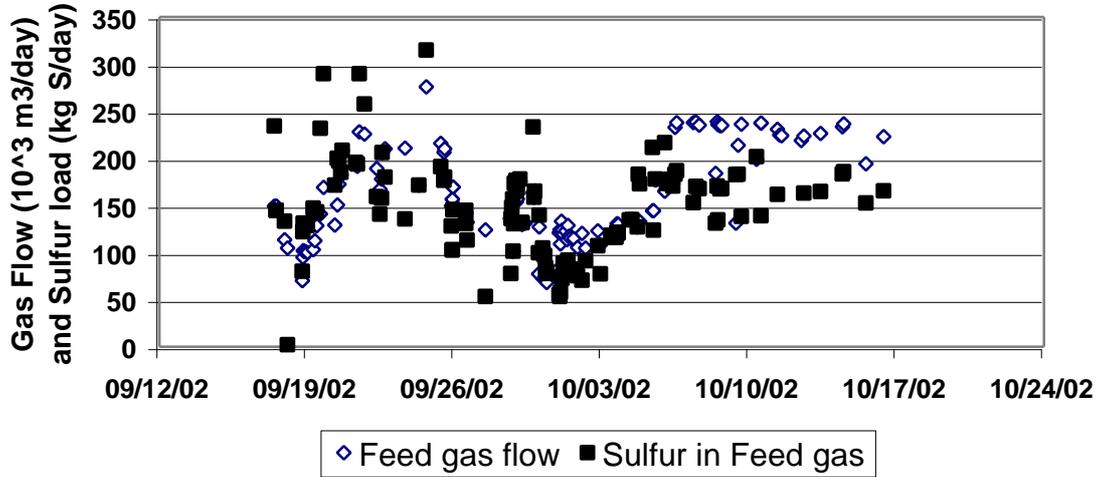
Monitoring of the unit provided a wealth of information from which we have prepared some graphs to show the most important parameters, such as:

1. H₂S content in the treated gas as a function of the H₂S content in the feed gas:



2. Variations in feed gas flows

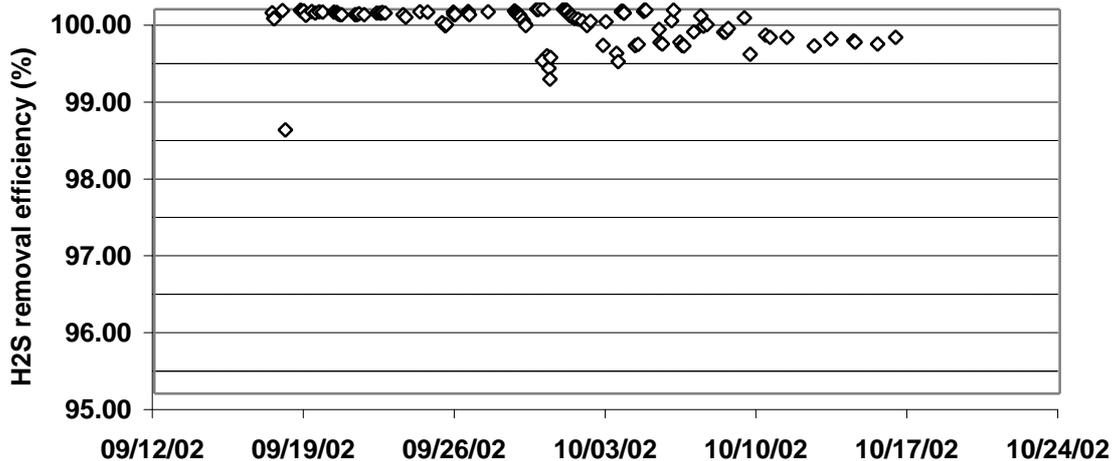
Variations in Feed gas flow and Sulphur load



The two graphs shown above illustrate the robustness and the flexibility of the Shell-Paques process. The H_2S specification on the treated gas is met independently of the H_2S concentration in the feed gas and independently of the feed gas flow and is not influenced by strong fluctuations in sulfur load.

3. H_2S removal efficiency:

H_2S removal efficiency



The H_2S removal efficiency of the Shell-Paques/THIOPAQ™ process is consistently very high and equivalent to what traditionally only can be achieved by three separate units; an Amine + Claus + SCOT unit. The H_2S removal efficiency is expected to increase further once higher H_2S content feed gas will become available.

During late September there was one period when we did not meet the 4 ppm vol. H₂S specification on the sales gas. The incident was directly after the first sulfur harvesting which had been slightly too long, lowering the sulfur concentration in the THIOPAQ™ solvent.

During this phase of rebuilding the sulfur content, the unit could be kept into operation since the treated gas exiting the Shell-Paques unit is mixed with sweet Natural Gas well and this mixture was still meeting Sales Gas H₂S specifications.

The slightly increased H₂S concentrations in early October were, in hindsight, due to incorrect analysis results. The H₂S analyzer in the treated gas reported too high H₂S concentrations, this was confirmed by several Dräger tube analysis. The reason was that slightly sour condensate had collected in the sample line. Equipment sample loop reconfiguration has eliminated this problem.

5. STATUS OF THE LICENSED PROJECTS IN THE OIL & GAS INDUSTRY

So far, two refinery THIOPAQ™ units are in the EPC phase. A short description of these is given in the section below.

5.1. AMOC project

In October 1999, UOP licensed a new THIOPAQ™ unit to Alexandria Mineral Oils Company (AMOC) in Alexandria, Egypt. This unit will be used to remove and recover sulfur from several streams within the AMOC grassroots dewaxing complex. It is expected to start up in Q3 of 2003.

5.1.1. Design Basis: Feed, Effluent and Sulfur Product Compositions

The AMOC THIOPAQ™ unit is designed to remove and recover hydrogen sulfide from three streams simultaneously, an off-gas, an acid gas and a spent caustic stream. The THIOPAQ™ unit is designed to treat these streams with the following throughput capacity and composition.

Table 2: Feed Rate and Composition Specifications

| | Flow (m ³ /hr) | Sulfur concentrations (% wt) |
|----------------------|------------------------------|---------------------------------|
| Sour Off gas | 437 | 3.09 % H ₂ S |
| Acid Gas | 290r | 93.0 % H ₂ S |
| Spent Caustic | 0.0075 | 3.09 % HS ⁻ |

The sour off-gas stream is scrubbed to remove H₂S with the spent scrubbing liquid being regenerated in the bioreactor and recycled to the scrubber. However, the acid gas stream and the spent caustic stream do not require scrubbing and can be admitted directly to the bioreactor for conversion of sulfide to sulfur.

The H₂S specification on the treated off gas is 3 ppm vol. H₂S, the vent gas leaving the compost filter will contain less than 6 ppb vol. H₂S.

5.2. THIOPAQ™ unit at CPRL Cyprus

In November 2001, Shell Global Solutions International BV licensed a new THIOPAQ™ unit to Cyprus Petroleum Refining Ltd (CPRL) in Larnaca, Cyprus. This unit will be used to remove and recover sulfur from several streams of the existing and the extension of the CPRL refinery. It is expected to start up in Q4 of 2003.

5.2.1. Feed gas specifications

The THIOPAQ™ is designed to treat two fuel gas streams and two off gas streams. The first fuel gas stream originates from an existing kero-minus HDT and the existing platformer. This stream is called the refinery fuel gas. The second fuel gas stream originates from the new GO HDS, and will be called fuel gas ex GOHDS. The two off-gas streams originate from the existing high vacuum unit and the existing amine regenerator, respectively. The total amount of H₂S to be treated is 14.7 ton per day.

Table 3: Feed Rate and Composition Specifications

| | Flow (t/d) | Concentration H₂S (% wt) |
|-------------------------|-----------------------|--|
| Fuel gas existing units | 14.4 | 2.7 |
| Fuel gas new GO HDS | 31.0 | 41.1 |
| Acid gas | 1.3 | 96.9 |
| HVU off-gas | 1.0 | 32.1 |

5.2.2. Product specifications

The general H₂S specification on the bulk fuel gas streams is 50 ppm vol. maximum. The actual guarantee given for this THIOPAQ™ unit is however lower, maximum 10 ppm vol. H₂S.

The vent gas leaving the compost filter will contain less than 1 ppm vol. H₂S.

6. OTHER OPERATIONAL EXPERIENCE WITH THIOPAQ™ TECHNOLOGY, OUTSIDE THE OIL & GAS INDUSTRY

In 1993 the first THIOPAQ™ unit was started up, treating 7200 Nm³/day of biogas (2.5 vol. % H₂S, 20% CO₂, 78% CH₄) from an anaerobic wastewater treating facility at the Industriewater Eerbeek in the Netherlands. At the end of 2002, 32 THIOPAQ™ units treating biogas and one treating vent-air have been licensed; most of them have been started up.

In addition, Shell Global Solutions Int. B.V. and Paques B.V. carried out an extensive pilot-plant testing program at the BEB's gas plant Großenkneten (Germany), where the process was tested for treatment of high-pressure natural gas under a variety of conditions.

7. CAPITAL AND OPERATIONAL COSTS

In a previous paper [3] the economics (capital investment and operational costs) of the Shell-Paques process were compared with liquid redox processes for natural gas and synthesis gas applications. The capital investment costs were comparable for both technologies (there was some variation depending on gas stream properties) but the operational costs for the Shell-Paques process were 2.5 to 5 times lower, mainly due to the lower chemical costs.

We benchmarked the THIOPAQ™ process with a traditional Amine + Claus + SCOT line-up in a refinery where a gas stream containing 38.5 tons/day of sulfur needed desulfurization. The results are summarized in **Table 4**.

In this study we assumed for the traditional Amine/Claus/SCOT line-up that:

- The amine unit has one low-pressure absorber column treating one fuel gas stream to a specification of 50 ppm vol. H₂S.
- The Claus unit is designed to treat the amine regenerator acid gas and a sour water stripper off-gas.
- The liquid sulfur is stripped using the Shell Sulfur Degassing Process and the stripped sulfur is further processed in a sulfur pelletizer, investment costs for both the degassing unit and the pelletizer are included in the total CAPEX numbers of **Table 4**.
- The SCOT unit will be integrated with the Amine unit.
- The Claus tail gas or the SCOT off gas is incinerated in a dedicated thermal incinerator.

For the THIOPAQ™ layout it was assumed that:

- The THIOPAQ™ unit has one low-pressure absorber column treating one fuel gas stream to a specification of 10 ppm vol. H₂S.
- The THIOPAQ™ unit will not treat the sour water stripper off-gas, it is assumed that this stream will be routed to an incinerator.
- The sulfur slurry product of the THIOPAQ™ unit is purified by melting leaving a > 99.9% pure sulfur product which is processed in the same pelletizer as for the traditional line-up, investment costs for both the melter and the pelletizer are included in the total CAPEX number of **Table 4**.
- The THIOPAQ™ unit includes a sulfate reduction step, biological, on the bleed stream.

Table 4: The capital investment and operational costs for treatment of low-pressure gas containing 38.5 tons/day of sulfur.

| Configuration | THIOPAQ™ | Amine + Claus | Amine + Claus + SCOT |
|---|----------|---------------|----------------------|
| Capital investment + 10 year Operational costs (MMUS\$) ^{NOTE} | 16.6 | 17.7 | 22.2 |
| Operators costs | Low | High | High |
| Maintenance costs | Low | High | High |
| Sulfur removal (based on SO ₂ emitted) | > 99.95 | > 95.0 | > 99.9 |
| Sulfur recovery (based on S ⁰ produced) | 96.5 | 95.0 | 99.9 |

Notes:

- Capital investment includes all equipment, instrumentation, design & engineering and installation and is a factored $\pm 35\%$ estimate based on Dutch conditions and climate.
- Operational costs includes steam, electricity and, for THIOPAQ™ caustic, and nutrients for the bacteria too. Electricity is assumed to cost 0.05 US\$/kWh.
- The operating costs have been discounted against a 15 % interest rate.

Note that costs for operators and maintenance were not included since such figures may vary from location to location. In general, costs for operators (0.5 hr/shift) and maintenance (low number of equipment) are low for the Shell-Paques/THIOPAQ™ process whereas these costs are significantly higher for the amine + Claus (+ SCOT) combination.

The data in **Table 4** demonstrate that:

1. The sulfur removal efficiency of the THIOPAQ™ unit is far superior and the present value expenditure is lower compared to the combination of the amine and Claus units.
2. The combination of amine, Claus and SCOT units result in similar sulfur removal efficiency as the THIOPAQ™ unit but against a far higher present value expenditure.

This benchmarking study proved that for sulfur loads in the order of 50 tons/day the Shell-Paques/THIOPAQ™ process is also very competitive compared to conventional technology.

At smaller sizes the THIOPAQ™ approach becomes even more economical as this process requires much less instrumentation and the equipment size can be significantly reduced, particularly the size of the regeneration reactor.

8. SULFUR HANDLING OPTIONS

In many situations the Shell-Paques/THIOPAQ™ process can be used for sulfur removal and recovery. When sulfur recovery is desired, the elemental sulfur produced in the aerobic bioreactor will be separated from the aqueous effluent in a separator inside the reactor as a slurry with 10 % w/w solids content.

There are three options for handling this slurry.

1. The sulfur slurry can be dewatered using a continuous decanter centrifuge. This results in a sulfur cake with 60 - 65% dry solids content. The water is returned to the bioreactor as process make-up. The sulfur purity of the filtered dry mass is ~ 95-98%. The remaining 2-5% is organic material and trace salts, especially sodium

bicarbonate and sodium sulfate. This sulfur cake can be safely sent to landfill as a non-hazardous refinery waste or used in sulfuric acid manufacture.

2. The same decanter centrifuge step described above can be used with the addition of a reslurry vessel to remove dissolved salts attached to the sulfur particles. Then a second separator and centrifuge produces a sulfur cake, again of 60 – 65% dry solids content, but of 99% sulfur purity. The wash water can be returned to THIOPAQ™ as process make-up water. This sulfur is suitable for addition to the refinery sulfur pit, or for use in sulfuric acid manufacture.
3. The sulfur paste from the decanter centrifuge can be processed in a drier to produce a product with a dry weight content of more than 90 wt.%. Options 1 and 2 can be followed by a drying step where a powder is produced that normally can be applied as a fungicide or miticide. Excellent results on the application of biosulfur as a fertilizer were produced by the Alberta Agricultural Research Institute and repeated by the University of Alexandria.

An alternative to options 1 and 2 is for the sulfur slurry to be directed to a sulfur smelter where molten sulfur with a purity exceeding 99.9% is produced for sale. The water is returned to THIOPAQ™ as process make-up and the solid impurities are land filled.

9. USE OF SHELL-PAQUES/THIOPAQ™ BIO-SULFUR AS FERTILIZER.

Sulfur is a major nutrient which ranks fifth or sixth in quantity of macronutrients taken up by plants; this is comparable to the demand for phosphorus. Plant leaves can take up sulfur from the atmosphere as very reduced (COS, CS₂ and H₂S) up to highly oxidized compounds (SO₂). However, most of the sulfur is taken up by plant roots as water-soluble sulfate.² Because of the adoption of pollution control measures in industrial countries the decrease in SO₂ emissions between 1980 and 1987 varied from 22% in Poland to 64% in France. Several countries switched from coal-fired to gas-fired industries at the end of the 1960's.² The improvement in air quality was beneficial to natural ecosystems, but from the late 1980's onwards, the decreased sulfur supply resulted in a widespread S deficiency in the soils used for cultivation of several highly S-demanding crops, such as oilseed rape and cereals in Denmark, England, F.R.G. and Scotland.² It is clear that in those circumstances additional sulfur feeding is required.

The hydrophilic properties of the bio-sulfur and its small particle size (less than 100 µm) should offer agronomic advantages for short season climates affected by sulfur deficiency. In greenhouse experiments the applicability of Shell-Paques/THIOPAQ™ bio-sulfur as a soil fertilizer was evaluated by the Alberta Agricultural Research Institute (AARI), University of Edmonton.

For this purpose, the effect of biologically produced sulfur on the Canola yield was compared with the effects of several commercially available sulfur fertilizers in both greenhouse and field tests. The first year results looked very good for the biologically produced sulfur. Compared with the reference test (without any sulfur added) the growth stimulation due to biosulfur addition is very significant as a yield increase of 50% is observed⁴. This result places the biosulfur among the best of the presently produced sulfur fertilizers.

After the successful greenhouse tests on Canola, extensive field tests in western Canada have been performed under the supervision of AARI to compare the performance of various commercial fertilizers, K_2SO_4 , Claus sulfur and bio-sulfur (both in paste as in powder form). For these field tests, the effect of the fertilizers was determined for several types of soil and various types of crops (canola, forage, wheat).

Below, a typical result for canola is shown:

Table 5: Breton Canola Trial; 4 replicates: 15 kg of sulfur product per hectare applied

| Sulfur source | Grain yield (kg/ha) |
|-------------------|---------------------|
| None | 1460 |
| K_2SO_4 | 1590 |
| Commercial 1 | 1740 |
| Commercial 2 | 1800 |
| Claus sulfur | 1710 |
| Bio-sulfur paste | 2230 |
| Bio-sulfur powder | 1980 |

From these results it is clear that the grain yield is about 50% higher using bio-sulfur as fertilizer than in the reference test without sulfur fertilizer. Moreover, the superior performance of the bio-sulfur compared to the commercially available products at present is more pronounced than was observed in the greenhouse tests.

10. CONCLUDING REMARKS

The following experience with Shell-Paques/THIOPAQ™ has been achieved:

- Successful start-up of the first high pressure Shell-Paques unit on Sour Natural Gas, whilst directly meeting Sales gas H_2S specifications.
- Projects have been developed with H_2S loads ranging from 50–13000 kg/day. Benchmarking studies show that Shell-Paques/THIOPAQ™ is cost effective up to 50 tons per day.
- H_2S concentration in sour gas ranging from 50 ppm(v) up to 100 vol.%.
- H_2S concentration in sweet gas 1 ppm(v)
- Pressures of the sour gas up to 75 bar(g)
- Reactors ranging from 5 – 2500 m³.
- Highly flexible in responding to H_2S peak loads.
- Significantly simpler to operate than a conventional Amine/Claus/Tail gas combination.
- Intrinsically safe process with practically no free H_2S present downstream of the absorber.
- Formation of hydrophilic sulfur. So far plugging problems have not been encountered and little operator attendance is needed.
- THIOPAQ™ Sulfur is a valuable product, rather than a waste stream, and can be re-used for the production of sulfuric acid, hydrogen sulfide, and agricultural applications.

11. LITERATURE REFERENCES

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