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SOLUTIONS FOR THE TREATMENT OF HIGHLY SOUR GASES

PAPER PRESENTED AT THE 9TH INTERNATIONAL
SOGAT CONFERENCE

Abu Dhabi, March 24th – 28th, 2013



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EXTEND THE TREATMENT OF HIGHLY SOUR GASES TO NEW LIMITS

ABSTRACT

Natural gases contain variable amounts of H₂S and/or CO₂ that need to be removed before natural gas can be further processed and transported. The challenge of renewing the resources now brings Oil & Gas operators to look at reservoirs with high content of acid gas or even to reservoirs with ultra sour content, containing more than 40% mole CO₂, H₂S and sulfur contaminants. Amine based processes are the most common technology being used for such purpose. Both capital and operating costs significantly increase with the concentration of acid gases to be removed, mainly because of increased solvent circulation rate.

Solutions have been developed in order to mitigate these cost increases. With amine based processes, these solutions include: use of the most adapted solvent, improved/tailor made process configuration and high solvent loading. AdvAmine™ processes, amine based process technologies developed by Total, IFPEN and Prosernat, have experienced many of the possible solutions over the years. This paper illustrates through examples how an optimized design and/or an appropriate solvent help significantly reducing the capital and operating costs.

Nevertheless for the treatment of natural gases containing very high amounts of acid gases, several tens % by volume, amine processes touch their limit and alternative technologies are available. The Sprex® process is an illustration of such technology breakthrough. It was jointly developed by Total, IFPEN and Prosernat, and successfully tested at the Lacq sour gas plant. More recently a modified process configuration has extended the field of gas sources to gases containing high amounts of CO₂. Performance and economic studies presented in the paper show that the combined use of Sprex® and amine based processes can result in significant cost savings, when compared to amine based treatment only.

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INTRODUCTION

For decades to come, gas will be an energy source of choice to meet increasing energy demand. Oil and gas operators have always preferentially produced the gas from those reservoirs technically the easiest and the cheapest to develop, but they will have to develop fields with higher acid gas content in the future. Effectively, over forty per cent of the world's conventional gas resources currently identified as remaining reserves to be produced, representing over 2600 Trillion Cubic Feet (Tcf), are sour, with both H₂S and CO₂ present most of the time. Among these sour reserves, more than 350 Tcf contain H₂S in excess of 10%, and almost 700 Tcf contain over 10% CO₂ [1].

Middle East, Caspian Sea area, or China have gas reserves with high H₂S content, while large amounts of gases with high CO₂ content are encountered in South East Asia and, to some extent, in South America and North Africa.

Removing the undesired acid gases from highly sour gases is a costly operation. The size and cost of the acid gas separation units and of the acid gas handling facilities (transformation of the H₂S into sulfur and forming/shipping of the produced sulfur, or acid gas compression/pumping and re-injection facilities), increase with the amount of acid gases to separate. In the meantime, the sales gas exported volume decreases because of the reduced hydrocarbon content of the inlet raw gas, and because of the increased auto-consumption for the gas treatment. As a consequence, the technical cost per volume of exported sales gas is actually roughly doubled every 20-25% of additional acid gases present in the raw gas (Table 1).

*Orders of magnitude
for illustration purpose only*

<i>Production of pipeline gas, with AGI</i>		Sweet Gas	Highly Sour 20 % Acid Gas	Ultra Sour 40 % Acid Gas
Sales GAS	%of raw	98	75	52
CAPEX	MMUS\$	100 %	140 %	185 %
OPEX	MMUS\$/year	100 %	160 %	200 %
Technical Cost	\$/MMBTU	100 %	200%	400 %

Note: Acid Gas = H₂S+CO₂

Table 1: Relative technical cost of sour gas production versus acid gas content

To ensure an economic development of these fields, very efficient technologies are therefore necessary to separate the large amounts of acid gases at controlled costs. Prosernat implements several solutions within the AdvAmine™ series of processes, some of them developed in collaboration between Total and IFP Energies nouvelles/Prosernat. The paper presents some of the optimizations of the process scheme that give room to new developments at demonstrated and attractive economic duties.

Sulfur, the traditional sub-product from the treatment of gases containing high amounts of H₂S, formerly represented a substantial part of the revenues drawn from the production of such gases. It is no longer of economic interest to sell sulfur from several areas today, especially those locations far from the sea and the sulfur users: the world sulfur market is globally saturated as the supply of sulfur, mainly obtained from H₂S separated from sour natural gases or sour crude, has exceeded the demand, essentially coming from the fertilizer industry. Even though some companies have developed new sulfur uses such as sulfur asphalt in the 1970's, or more recently sulfur concrete, most experts consider that this situation is set to continue for several decades, at least in several parts of the world. The production of major oil or gas fields in the Middle East or in the Caspian Sea area could lead to the production of considerable quantities of additional sulfur in an already saturated market, while the storage of extra sulfur on the long term is also an issue that requests significant capital costs to be solved out. This is why new production methods give the green light to develop the ultra rich H₂S gas fields, in places where the economic interest does not rely on additional production of sulfur.

Companies willing to produce large gas fields with very high amounts of CO₂ have to face a different constraint, related to the essential need to reduce atmospheric emissions of greenhouse gases.

Economics may also be improved by the growing acceptance of the re-injection of separated H₂S and CO₂, for reutilization to enhance oil recovery (EOR). Separated acid gas re-injection into a depleted reservoir or an aquifer, as a feasible alternative to costly sulfur recovery to a diminishing sulfur market, or to limit atmospheric emissions of greenhouse gases, increases the number of highly sour gas fields that can be re-considered as exploitable to produce much needed natural gas.

These new constraints lead to the development of more energy efficient technologies for acid gas separation, adapted to these new production schemes. With this objective, in addition to the AdvAmine™ series of gas sweetening processes using amine based solvents, Total, IFP Energies nouvelles and Prosernat have developed the Sprex® and Sprex®CO₂ processes for the production of highly sour gas reserves with acid gas re-injection.

DISCUSSION

Optimization of amine processes for highly sour gas treatment

Amine processes (Figure 1) have been used for many years to remove acid gases from natural and associated gas streams. They are very versatile processes, which can be used to treat all types of sour gases, regardless of the H₂S and / or CO₂ content, down to the most severe specifications, such as those imposed by gas liquefaction plants.

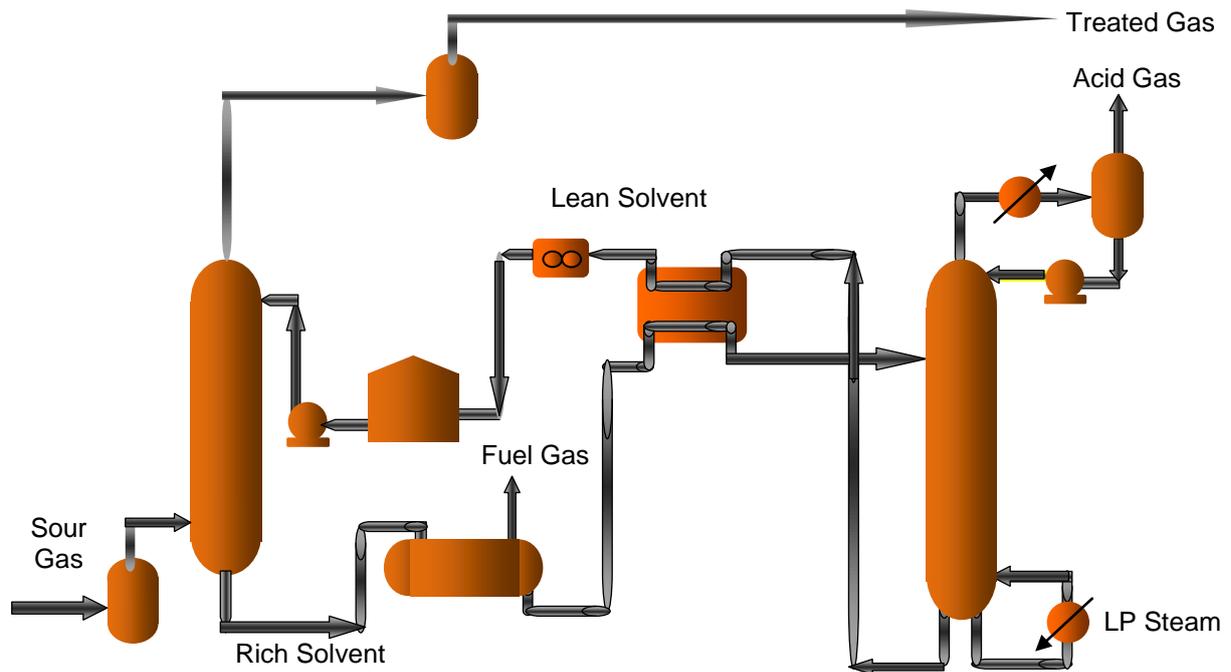


Figure 1: Acid Gas Removal Unit Design

But the cost of gas sweetening increases with the amount of acid gases to be separated, requiring larger amine solution flowrates and higher energy consumption for amine solution regeneration. On the other hand, amine processes, because of the variety of amines which can be used and the possibility to adapt and improve the process flow schemes, can be efficiently used for almost any type of gas sweetening application. Amine based technology can therefore actually be considered as the “workhorse” of the sour gas processing industry and as such still justifies continuous technological improvements to extend the economical limits of its applications. Issues like treatment costs, energy consumption are being addressed by such developments.

The designer shall be aware that treatment of such highly sour gas shall make him go far beyond the nice-to-have design practices he may have used during his first designs of acid gas removal unit. One of such criteria is the need to stick to moderate acid gas loading of the amine solution.

Perspective of CAPEX and OPEX savings cannot be met without an attractive solvent loading and deep thermal integration of the rich solvent regeneration section, based on the thankful self-regenerating properties of highly loaded solvent when they are moderately flashed or heated. The base use of highly loaded solvent at high temperature shall nevertheless be coupled with new recommendations for unit design, especially in terms of sizing criteria and metallurgy requirements.

The paper primarily discusses about the design perspectives to handle high contents of acid gas in feed load, and gives some of the improvements that can optimize the plant design in such conditions. It also describes how such references are now secured over long return period of operation by Total in their highly sour gas treatment plants.

The paper presents some of the solutions proposed by Prosernat for an efficient and economic treatment of gases with high acid gas content, either H₂S or CO₂. Among these solutions some are now widely proposed by several licensors, others have been developed through the joint R&D effort of Total, IFP Energies nouvelles and Prosernat.

The double split flow process configuration

Among the oldest process configurations, the double split flow design, sometimes called split flow design, has been used as an alternative flowsheet to minimize capital and operating costs in several sour gas processing plants. Generally used with primary or secondary amines, this design allows achieving very severe treated gas specifications for the same reboiler duty as in the conventional process flow scheme, and was documented, probably for the first time, by Estep, McBride and West in 1962 [2]. But the double split flow design also allows achieving the same treated gas specification as the conventional amine plant scheme with a much reduced reboiler duty when treating very sour gases. The conventional double split flow design is shown in Figure 2.

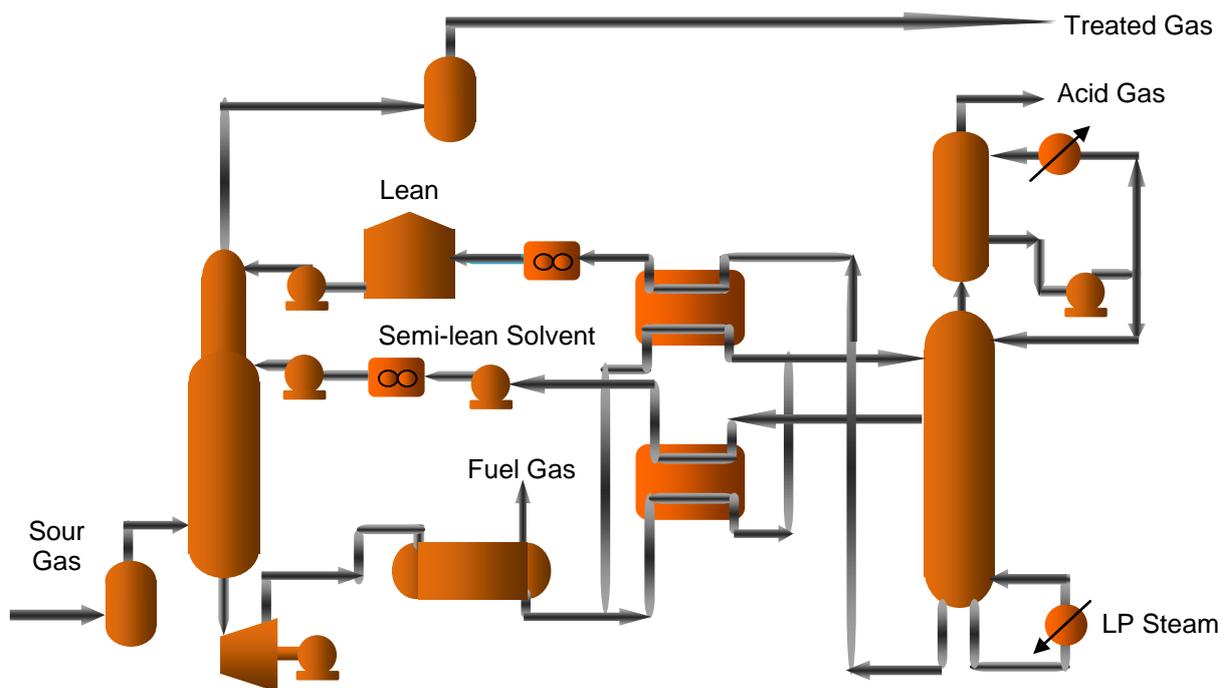


Figure 2: The conventional double split flow design

In this design, a part of the amine solution is withdrawn from the regenerator as a side stream, then cooled and pumped into the lower section of the absorber. The amine in the side draw is not fully regenerated and has a higher residual acid gas loading. However, as this semi-lean solution contacts the incoming sour gas, it can still pick-up the bulk of the acid gas. Because of the semi-lean amine side draw, the amine flow to the regenerator reboiler is reduced, and the duty of the reboiler can be decreased to achieve the same lean amine quality required on top of the absorber column to meet the treated gas specification.

The advantages of energized MDEA for the treatment of very sour gases

The main factors affecting a solvent's performance for acid gas absorption are its ease of regeneration, and acid gases solubility and reactivity.

Tertiary amines require less regeneration energy than primary and secondary amines. Being a tertiary amine, MDEA therefore requires less reboiling duty than DEA. It is however well known that MDEA reacts slowly with CO₂. This particularity, which is used to advantage for the selective H₂S and controlled CO₂ removal, becomes a handicap for the complete acid gas removal; especially when a substantial quantity of CO₂ has to be removed. To overcome this kinetic obstacle, energizers were sought among secondary amines having high speeds of reaction with CO₂ to blend into the otherwise desirable MDEA solvent. Several energizers were selected by Total from among those best suited to industrial conditions taking into account commercial availability, cost and impact on the environment [3].

While reactivity of CO₂ with MDEA is lower than the one with DEA, its solubility in MDEA is more strongly influenced by CO₂ partial pressure than by its solubility in DEA. This can be shown by the slopes of the equilibrium solubility curves (Figure 3).

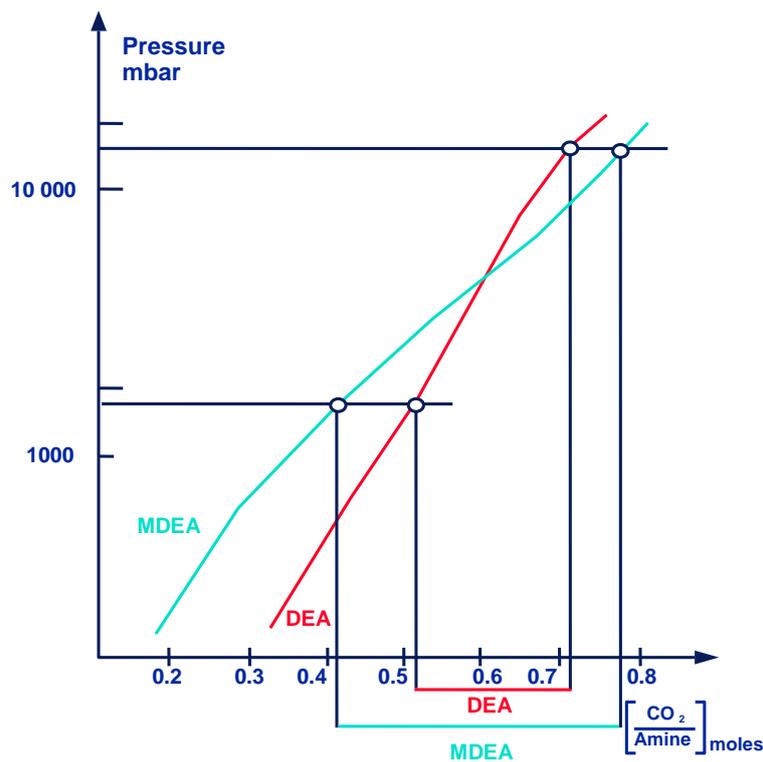


Figure 3: Equilibrium solubility of CO₂ in aqueous amine solutions

The basic concept for an efficient process for the removal of large quantities of acid gases consists in taking advantage of the slope of the equilibrium solubility curves of CO₂ in aqueous MDEA solutions to be able to liberate a maximum amount of the acid gas from the solution by simple physical pressure let-down flash and thus substantially reduce the thermal regeneration duty. For example, as shown in Figure 3, the MDEA solution releases almost

twice as much CO₂ as the DEA solution by a pressure letdown from 10 bars to 1 bar. In addition, the equilibrium solubility of H₂S in aqueous MDEA exhibits similar behavior to CO₂ allowing equivalent amount of H₂S liberation by pressure let-down. *energizedMDEA* approaches the equilibrium curve of MDEA at high pressure but behaves like DEA at low acid gas partial pressures. This is achieved thanks to the blend of an energizer with MDEA, generally a secondary amine [3] [5].

This particularity of *energizedMDEA* to release a substantial part of the absorbed acid gases in a low pressure flash can be combined with the introduction of a semi-lean solvent in the bottom part of the absorber, as in the double split flow design described above, as shown in Figure 4. The specificity of *energizedMDEA* is that it combines the characteristics of secondary and tertiary amines, based on the blend of various amine molecules. Given a certain concentration of secondary amine, it is possible to associate its performance at low acid gas partial pressures (the ones encountered in the upper section of the absorber), to the capacity of tertiary amines to load greater contents of acid gases at high acid gas partial pressures (the ones encountered in the lower section of absorber). This is especially valid for CO₂ because it does not react directly with MDEA but with secondary amines.

The rich amine solution after letdown through a hydraulic turbine is divested of co-absorbed light hydrocarbons in a first flash drum, as in the conventional process then further expanded to a low pressure in a second flash drum to partially liberate CO₂ and H₂S. The greater part of the rich amine thus partially regenerated is returned to an intermediate level of the absorber as a semi-lean solvent. This semi-lean solvent loop is particularly economic as it reduces the thermal regenerator load and consumes only pumping energy.

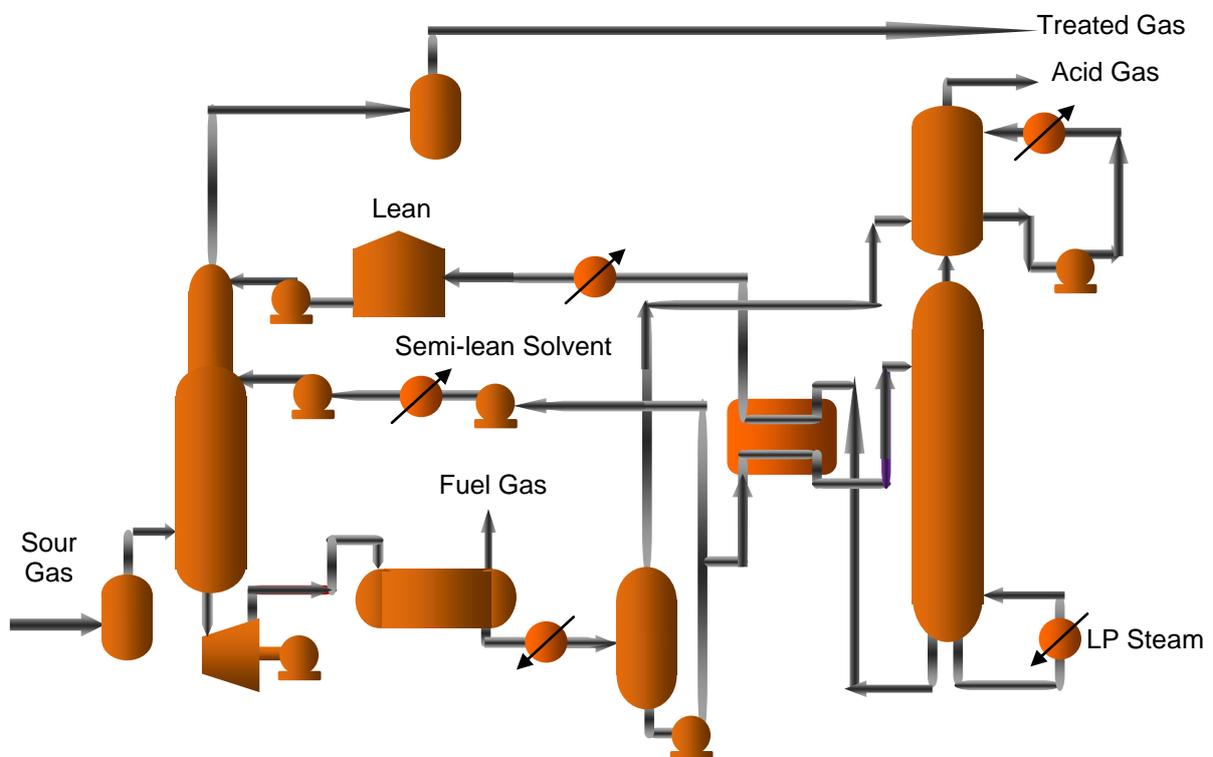


Figure 4: Split flow design with *energizedMDEA*

When H₂S is present and/or the treated gas specification calls for the removal of CO₂ below the 2 vol. % range, thoroughly regenerated, virtually H₂S and CO₂ free, amine is required. This is accomplished in a conventional thermal regenerator returning a small flow of the leanest amine to the top section of the absorber.

In 1990 the new solvent and regeneration system were tested on an existing DEA unit at the Lacq sour gas plant, South-West of France, which was then converted to the *energizedMDEA* process [4] [5]. This process was also used in several other locations such as offshore North Sea at Elgin Franklin for controlled CO₂ removal, in Venezuela, Egypt, Iran, and Yemen. Different energizers have been patented to suit each specific case of treatment: total, partial or controlled CO₂ removal, with or without H₂S.

The performance of the *energizedMDEA* process is closely related to site specific treatment conditions; notably feed gas composition and treated gas specifications. Below are some practical rules-of-thumb to highlight the general interest of regeneration by flash [6]:

- The greater the H₂S and/or CO₂ partial pressure in the feed gas, the greater is the efficiency of the flash. In the case of the Lacq sour gas plant, the acid gas partial pressure of the feed is approximately 15 bar in comparison to a total pressure of 2 bar in the second flash drum. This gives a ratio of 7.5/1 (acid gas partial pressure/flash pressure). In general the advantage of the flash procured regeneration starts above a ratio of 3.
- Targeting low H₂S content in the treated gas requests a thermal regenerator to clean-up the solvent down to low H₂S residual loading. The overall energy consumption of the *energizedMDEA* unit increases as the treated gas specification becomes more stringent, since the amount of lean totally regenerated amine from the thermal regeneration increases. In some bulk CO₂ removal cases with no H₂S, as mentioned, it may even be possible to completely eliminate the thermal regenerator.

As a consequence of the above attributes the *energizedMDEA* process is well adapted to the treatment of high pressure and very sour gases where the advantages of flash procured regeneration will be maximized to reduce the energy footprint of the sweetening.

High loading in amine sweetening

The effort towards moderating the solvent flowrate along with the reboiler duty quickly brought some process developers, and later on plant operators, to consider increasing the acid gas loading of the rich amine leaving the absorber [7]. The maximum achievable loading is controlled by the thermodynamic equilibrium between the sour gas entering the absorber and the rich amine and by the efficiency of the mass transfer in the absorber: the higher the acid gases partial pressure in the sour gas, the higher the amine loading at thermodynamic equilibrium. A high H₂S and CO₂ partial pressures will therefore invariably allow high amine loading at the benefit of an improved efficiency of process. Loadings higher than 0.8 (mole of acid gases per mole of amine) can theoretically be achieved when the acid gases partial pressure is above 15-20 bar, that is to say when treating a very sour gas at high pressure.

The pH of the rich amine solution decreases with its acid gas loading, in turn increasing the tendency of the amine solution to corrode carbon steel. This is the reason why some operators prefer to limit the loading at values below the 0.5 to 0.6 level. As a matter of fact, erosion/corrosion of carbon steel can be controlled and maintained under acceptable levels at high solvent loading under the operating conditions of an amine sweetening plant, provided that the design of the unit and the operating procedures are following basic rules [8], such as limiting the flow velocity in the rich amine lines. In some cases, for instance when treating gases with very high CO₂ content and little or no H₂S, the use of 316L stainless steel will be necessary in limited susceptible areas of the amine unit. It should be noted that using stainless steel piping lowers the bulk piping weight of the unit.

High amine loadings are well known by Total, which have operated plants for several decades, first of all the Lacq plant, with rich amine loadings above 0.6 and up to 0.85/0.90 without corrosion issues. Several AdvAmine™ units have also been licensed to other operators. Table 2 below gives examples of such amine units.

Amine Type	Feed Gas Pressure (bar)	Feed Gas H ₂ S (vol. %)	Feed Gas CO ₂ (vol. %)	Loading	Start-up year
HiLoadDEA	65	4.2	6.0	0.64	1984
MDEAmax	70	4.0	5.6	0.71	2001
<i>energized</i> MDEA	105	Traces	9.2	0.72	1996
HiLoadDEA	66	8.5	9.5	0.77	1980
HiLoadDEA	66	21.5	14.7	0.85	1987
HiLoadDEA	70	15.8	9.8	0.85	1957
HiLoadDEA	70	34.6	6.1	0.90	1972

Table 2: Some AdvAmine™ units operated with high acid gas loading

A case study on the use of *energized*MDEA for very sour gas sweetening

A noteworthy example of the use of the *energized*MDEA process is given below for the sweetening of a sour natural gas with very high H₂S content. The sour gas composition is given in Table 3 below.

Composition (vol%)	
H ₂ S	21.5
CO ₂	14.8
Nitrogen	2.8
Methane	57.0
Ethane	1.8
Propane	1.1
Butanes	0.4
Pentanes plus	0.5
Organic sulfur	0.1
Temperature (°C)	40
Pressure (bar)	70

Table 3: Case study: High H₂S content sour gas composition

This case study compares three different process configurations for the removal of H₂S and CO₂ down to a usual commercial gas specification, namely 4 ppm vol. H₂S and 2 vol. % CO₂:

- Single flow (conventional) process
- Double-split flow process, with thermal regenerator (conventional double-split flow design, as described in Figure 1 above)
- Split flow process, with flash supported regeneration to produce the semi-lean amine solution (as described in Figure 3 above)

Both split-flow process configurations entail a larger number of equipment than the single-flow process; this is due to the addition of a semi-lean amine circuit, which includes a rich / semi-lean amine exchanger or a rich amine preheater, a semi-lean amine cooler and pumps. In addition, the flash procured split flow scheme needs an amine heater and an additional flash drum at regenerator pressure. Both split-flow process configurations also need an absorber with a slightly increased height, compared to the conventional process configuration, to take into account the additional liquid feed. As only a fraction of the amine solution is fully regenerated, the total amine solution flowrate (lean + semi-lean) is also larger than that of the conventional process.

On the other hand, the reboiler duty is substantially decreased in both split flow configurations, and the whole regeneration section is considerably reduced in size in the flash procured split flow configuration; in large size plants necessitating multiple treatment trains, there may even be a reduced number of regenerator trains because of this reduced regenerator capacity.

Table 4 below gives the comparative energy consumptions for the treatment of the gas with the 3 schemes, as well as the relative capital costs of the corresponding units.

<i>energized</i> MDEA process scheme		Conventional single flow process	Double-split flow process	Split-flow process with flash supported regeneration
Acid gas loading (rich amine solution)	mol / mol	0.85	0.86	0.92
Rich amine solution concentration	g / l	458	461	458
Thermal energy: Reboiler	MW	77	67.5	39
Rich amine preheater				10
Power consumption	MW	2.7	2.7	3.6
Total energy demand *	MW	100.5 (base)	89.1 (88.7% of base)	69.6 (69.3% of base)
Capital cost	Arbitrary unit	100 (base)	113.7	123.1

* Steam boiler efficiency 83%, power generation efficiency 33%

Table 4: Case study: Energy consumption and capital cost comparison

Increasing further the loading of amine solutions

The loading of the rich amine solution is limited by the thermodynamic equilibrium at absorber bottom and by the approach to this equilibrium. The thermodynamic equilibrium is a function of the acid gases partial pressures in the feed sour gas, and high loadings are favored by low temperature, as shown in Figure 5 below. Lowering the rich amine solution temperature on the lower part of the absorber is therefore a mean to increase the loading of the rich amine solution leaving the absorber.

It is generally not practical to reduce the temperature of the feed sour gas. This would require an expensive high pressure gas cooler and the use of a refrigeration loop in many fields, and in any case the cooling would be limited by the hydrate formation temperature of the gas. In addition, the gas cooler needs additional pressure drop on the gas route that is detrimental to the efficiency of downstream units. Eventually, the low temperature of solvent at absorber top slows down the reaction rate of CO₂ with amines, requiring additional transfer height to achieve tight CO₂ specification for some cases.

The solution to lower the absorber bottom temperature without cooling the feed gas and without decreasing the top trays temperature consists in the installation of a liquid intercooler, which will remove some heat from the amine solution from an intermediate tray, or section of packing, in the absorber column where the temperature of the gas and of the liquid is the highest because of the exothermicity of the acid gases absorption. In this process configuration, the semi-lean amine solution is withdrawn from a chimney tray, pumped through a cooler, and re-injected to the tray just below the withdrawal tray.

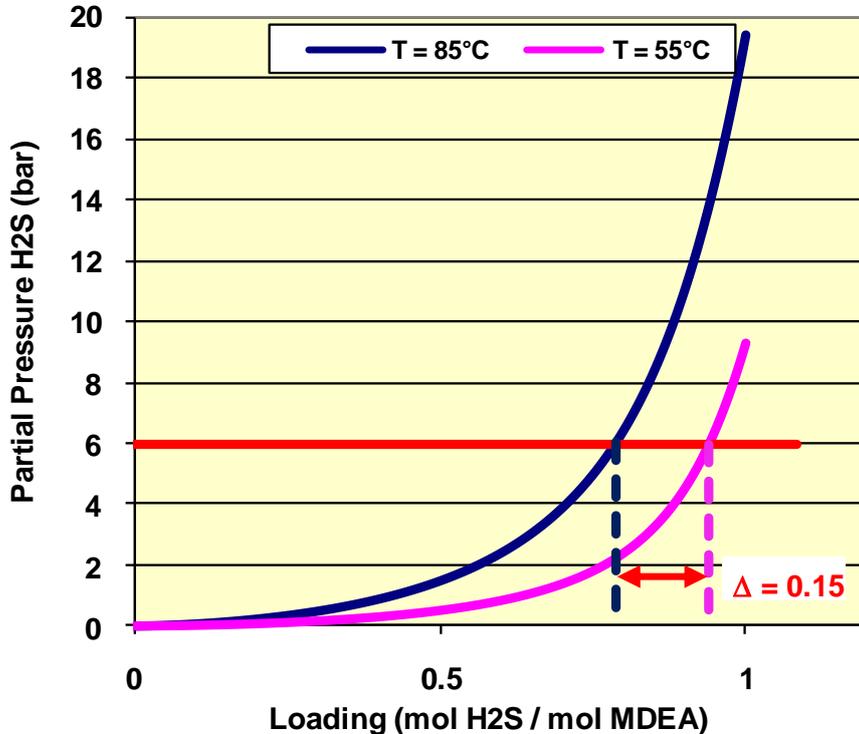


Figure 5: Rich amine loading as a function of temperature

The example below demonstrates the incidence of the absorber intercooler in the case of the sweetening of a very sour gas with the composition given in Table 5.

Composition (vol %) H ₂ S	11
CO ₂	11
Hydrocarbons	Balance
Gas Flowrate (10 ⁶ Sm ³ /d)	5.1
Temperature (°C)	50
Pressure (bar)	66

Table 5: Case study: Sour gas composition

The amine solution temperature is decreased to 55 °C in the intercooler. As a consequence, the absorber bottom temperature is reduced from 85.2 °C to 71.2 °C, and the rich amine loading can be increased from 0.60 to 0.71 (Figure 6).

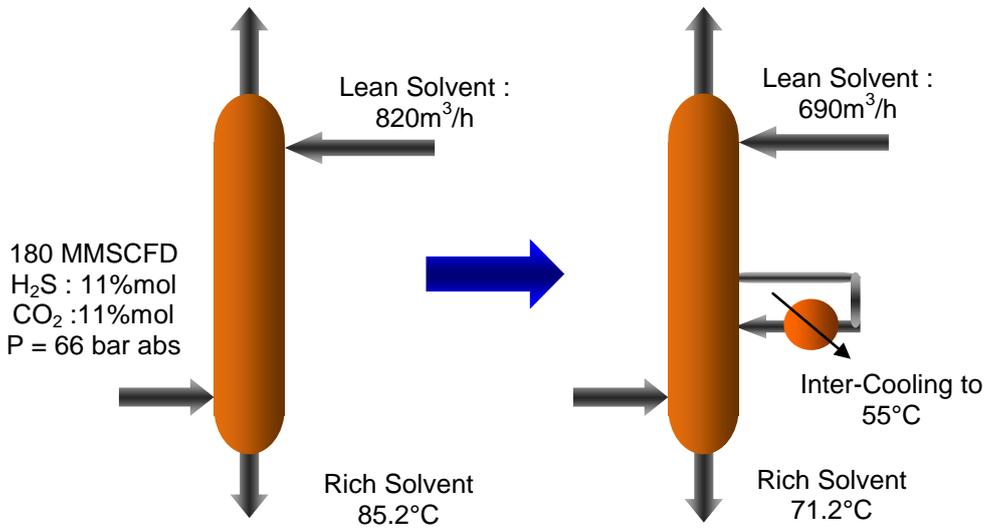


Figure 6: Incidence of the intercooler on absorber operating conditions

Table 6 below gives the comparative energy consumptions for the treatment of the gas with the 2 schemes, as well as the relative capital costs of the corresponding units

<i>energized</i> MDEA process scheme		Conventional absorber No intercooler	Absorber with intercooler
Absorber bottom temperature	°C	85.2	71.2
Acid gas loading (rich amine solution)	mol / mol	0.60	0.71
Amine solution flowrate	m ³ /hr	820	690
Thermal energy: Reboiler	MW	67.0	59.5
Power consumption	MW	2.40	2.05
Total energy demand *	MW	87.6 (base)	77.6 (88.5% of base)
Capital cost	Arbitrary unit	100 (base)	96.4

* Steam boiler efficiency 83%, power generation efficiency 33%

Table 6: Energy consumption and capital cost comparison

Addressing all aspects of the problem: the side question of mercaptans removal in highly sour gas

Gases with H₂S also contain variable amounts of organic sulfur compounds, such as mercaptans, often because of the equilibrium conditions with high concentrations of sulfur compounds in the reservoir. The presence of high concentration of mercaptans becomes an issue, as the capability of amine solvents to remove mercaptans may not be sufficient to meet current stringent commercial gas specifications with regards to organic sulfur species.

Amine solvents feature good capabilities for the removal of mercaptans with however some limitations:

- As weak acidic species (at least compared to H₂S and CO₂), mercaptans compete with H₂S and CO₂ for absorption by alkaline amine based solvent. The disadvantageous acidic strength in comparison with the ones of H₂S or CO₂ makes them be absorbed slower than H₂S and CO₂.
- At highest solvent loadings, the reduced pH of the solution in the bottom section of the absorber evenly reduces the solvent strength to further absorb mercaptans.
- Looking at the problem more precisely, it has been demonstrated for some years now that the solubility of mercaptans in highly loaded solvent is much lower than the one in lean solvent of the upper part of absorber [13]. In some cases, high solvent loadings and high temperatures in the bottom part of the absorber even stop any form of absorption of mercaptans. This results in slippage of sulfur species in treated gas and in increased difficulties to target the requested sulfur specification.

When significant mercaptans removal is looked at, the solution given to the plant designer consists in increasing the solvent flow and more marginally in reducing the solvent temperature. This approach reduces the solvent loading. As such the increase of solvent flow has a significant impact on the economics of the plant, because of increased equipment size, and increased energy consumption. This is why the hybrid solvents have been developed for such applications.

Hybrid solvent processes for enhanced mercaptan removal

Hybrid solvent processes, such as the recently developed HySWEET[®] from Total [9][10], may be considered as they show a greater affinity for mercaptans.

The drawback of hybrid solvent processes is their limited selectivity towards hydrocarbons, and their use should be limited to the sweetening of natural gases with low heavy hydrocarbons content. This is why, when developing the HySWEET[®] technology, Total has focused on the selection of an hybrid solvent composition having a very limited hydrocarbon absorption capability.

Thus heavy hydrocarbons co-absorption is maintained within acceptable limits in the HySWEET[®] process. The process has been commercially used at Lacq since 2008 treating feed gas with more than 20% mol H₂S + CO₂, and a second unit is under construction for another operator in France, designed by Prosernat.

The process scheme of HySWEET[®] is versatile, and it is possible to adapt any of the process optimizations listed above in a HySWEET[®] based process scheme.

Cryogenic distillation for the sweetening of super sour gases

Some gas fields contain very high amounts of H₂S (more than 30 vol. %) or CO₂ (up to 70 vol. %) in natural or associated gases. Even though amine processes can be optimized to treat very sour gases as documented here above, the high cost associated to sweetening may make the production of these super sour gases uneconomic under certain gas price conditions.

Permeation membranes have been commercially used since the 1980s for the bulk removal of CO₂ from gases with very high CO₂ content down to levered CO₂ content generally between 5 to 10%. With the current status of this technology, permeation membranes can only be used to treat gases with very limited H₂S content, as they are very sensitive to this chemical. Membrane units are relatively simple and use very little energy, however permeation membranes are not selective and one must accept large methane losses with the separated acid gases, even with dual stage membrane units with inter-stage re-compression. Provided that an adequate preconditioning of the gas is performed, membrane life is considered as acceptable to limit the cost of replacement. However, the preconditioning unit is generally fairly large, which substantially increases the cost of the sweetening. The process further needs post treatment with an amine solvent to reach tight CO₂ specification.

Cryogenic distillation processes offer many advantages when the separated acid gases need to be reinjected, to limit undesired sulfur production or to minimize green house gases emissions to the atmosphere: they are very selective towards light hydrocarbons, and the separated acid gases (H₂S and/or CO₂) are recovered in the liquid state under pressure. Producing the acid gases as a high pressure liquid saves expensive and energy-consuming compression requirements because the pumping duty is much lower.

It is possible to produce pipeline quality gas with cryogenic distillation. Such technologies require dehydration of the sour gas prior to entering the cryogenic separation. Separating CO₂ or H₂S down to commercial specification requires a very low temperature in the reflux drum, corresponding to a very significant refrigeration requirement. Furthermore, CO₂ separation down to commercial levels suffers from the limitation due to CO₂ freezing conditions in the top section of the cryogenic distillation column. Some processes address this limitation by adding for example a suitable hydrocarbon solvent to the top section of the demethanizer to stay outside the CO₂ freezing conditions, or by using a column with a specific frozen CO₂ remelting zone.

The Sprex[®] and Sprex[®]CO₂ processes, jointly developed by Total and IFP Energies nouvelles/Prosernat, are bulk fractionation processes. The Sprex[®] process for bulk H₂S removal does not require upstream dehydration of the gas. The refrigeration requirements of Sprex[®] and Sprex[®]CO₂ are limited compared to those of other cryogenic processes, and, as the temperature in the Sprex[®]CO₂ is not as low, the operating conditions are far away from the CO₂ freezing region, therefore avoiding the need for an additive fractionation and recycle or for a remelting zone.

When pipeline or LNG specification is required, the Sprex[®] or Sprex[®]CO₂ unit is easily and economically combined with a solvent based acid gas removal unit.

Bulk H₂S removal with the Sprex[®] process

The Sprex[®] process was jointly developed by Total and IFP Energies nouvelles /Prosernat, based on an initial patent filed in 1994 by IFP Energies nouvelles, to improve the economics of the production of ultra sour gas with high H₂S content when the separated H₂S is reinjected. The process was improved and several other patents were filed in the 2000's [11]. Figures 7 and 8 show the principles and process flow diagram of the staged acid gas separation from a very sour natural or associated gas, using Sprex[®] followed by a conventional solvent sweetening plant.

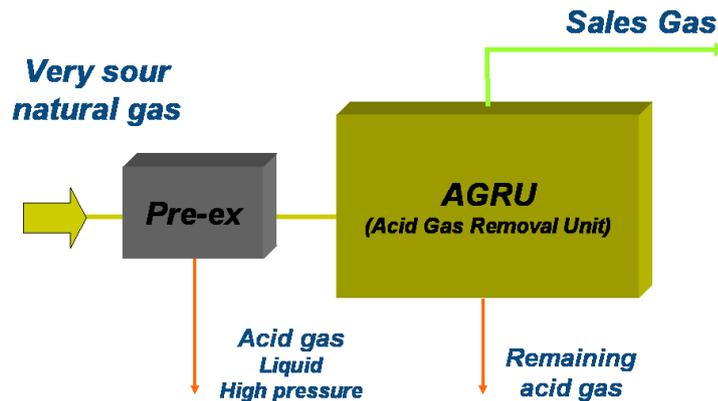


Figure 7: Staged acid gas separation with the Sprex[®] process

The process has the following advantages [6]:

- It reduces the H₂S content in the gas by producing a partially sweetened gas which can then be processed by a smaller size conventional amine sweetening unit, capable of meeting the most severe H₂S and CO₂ gas specifications (pipeline gas or feed for a LNG plant),
- It produces a high-pressure liquid H₂S soup (50 to 65 bar) that can be easily reinjected into a geological reservoir.

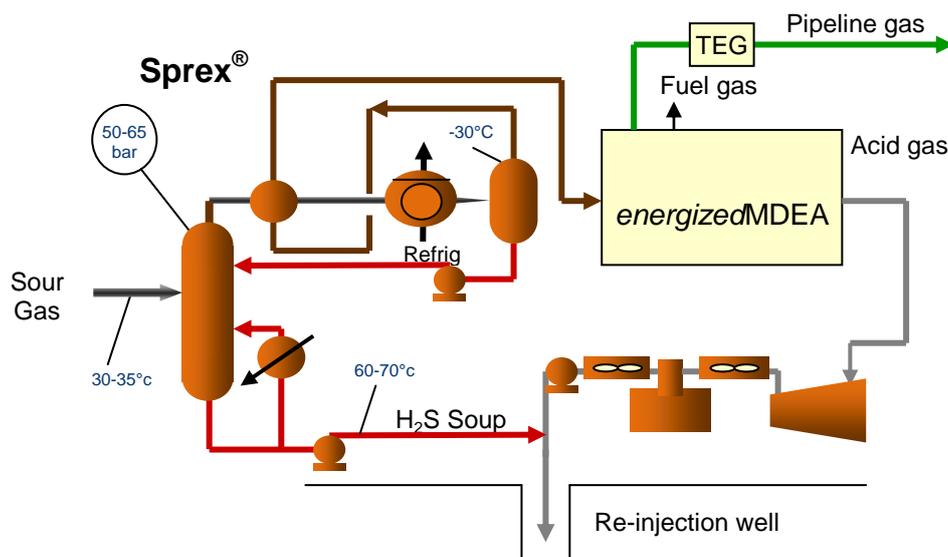


Figure 8: Sprex[®] simplified process flow diagram

In this basic version of the process, which has been demonstrated in an industrial context at the Lacq plant [12], South West of France (Figure 9), the H₂S content in the gas leaving the Sprex[®] unit is about 10-12%. The reflux, consisting in cold dry H₂S, dehydrates to some extent the incoming gas in the upper zone of the Sprex[®] column. The minimum temperature reached in the Sprex[®] unit low temperature reflux drum is limited to about -30°C, so as to remain outside the hydrate zone at all points of the unit. This rules out the necessity of installing a dehydration unit upstream of the Sprex[®] column.



Figure 9: The Sprex[®] demonstration plant at Lacq (France)

The H₂S separated out in the Sprex[®] process is produced in a high-pressure liquid phase, requiring considerably less energy for re-injection into an underground reservoir, as the large multistage acid gas compressors can be replaced by injection pumps.

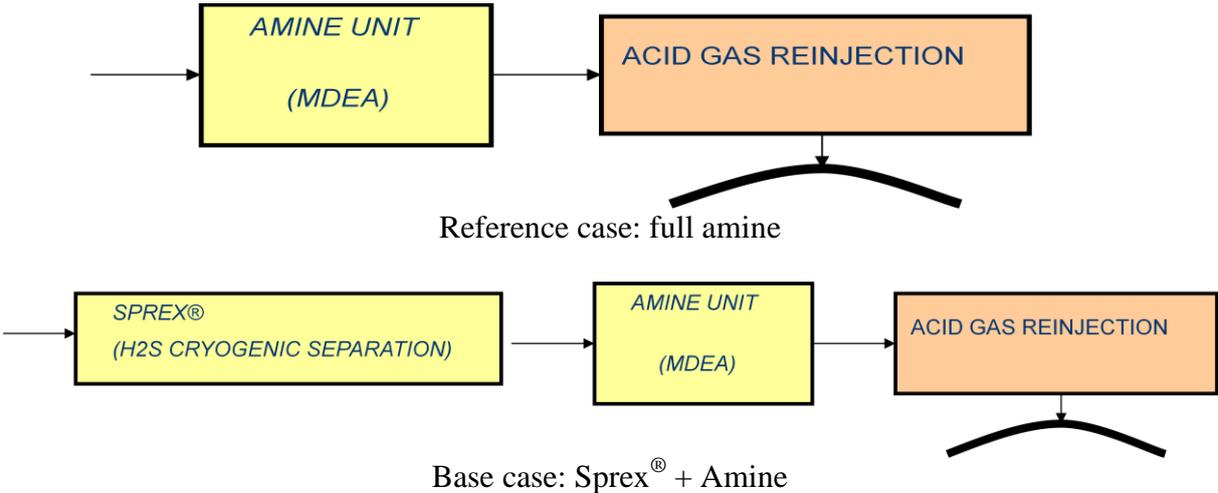


Figure 10: Sprex[®] economic evaluation: considered cases

Now that the amine sweetening unit located downstream has less H₂S to separate, the amine solvent circulation rate can be substantially decreased, as can the size of the equipment. This drastically reduces both the investment cost and energy consumption.

To illustrate the benefits of using the Sprex[®] technology, the two schemes shown in Figure 10 have been compared: a reference case using amine unit and a base case using Sprex[®] for bulk removal and amine unit as finishing unit.

The comparison has been made for a sour gas containing 33 mol % H₂S and 10 mol % CO₂ at 70 bar. The sales gas specification has been considered at 4 ppm mol of H₂S and less than 2 mol % CO₂. The acid gas containing H₂S and CO₂ is re-injected at 200 bar. Comparison of the utilities consumption of the two schemes shows that the compression power is much lower for the base case than for the reference case (Figure 11).

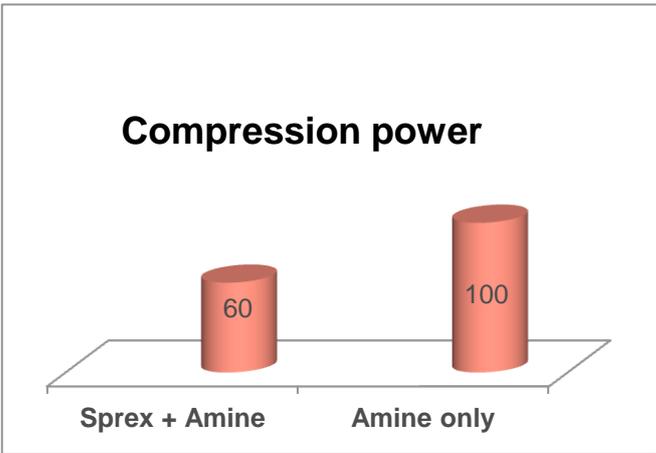


Figure 11: Sprex[®] economic evaluation: acid gas compression power

As far as the steam consumption is concerned, the decrease linked to the use of the Sprex[®] technology is more than 30% compared to the full amine scheme (Figure 12). This leads to a saving in energy consumption of 23% for the Sprex[®] +Amine scheme compared to the Amine scheme.

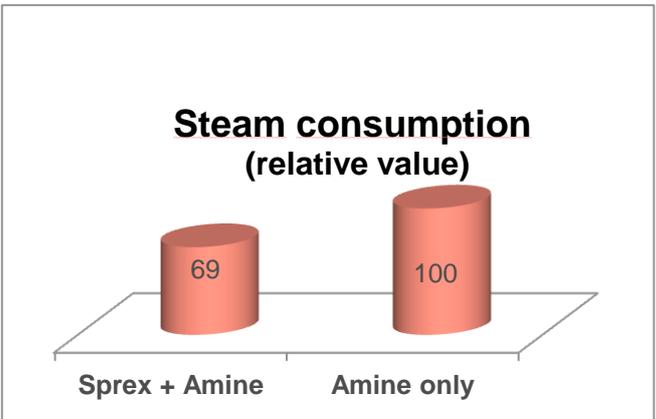


Figure 12: Sprex[®] economic evaluation: steam consumption

Moreover, the comparison of the two schemes has shown that overall CAPEX is decreased using the Sprex[®]. Depending of the overall flowrate to be treated, the Sprex[®] can also lead to a reduction of the number of trains, further reducing the CAPEX, the overall plant foot print and thus reducing the toxic risk.

When considering the possible H₂S increase with time, due to H₂S reinjection in the producing reservoir, the Sprex[®] design is less sensitive than the amine unit design. This reduces the cost of the necessary oversizing of the treatment capacity to handle such H₂S concentration increase.

When the sour gas contains mercaptans, the Sprex[®] condenses those sulfur species and allows meeting the sales gas specification, which greatly simplifies the downstream treatment.

Finally, in case of a distant finishing treatment (downstream amine unit located in a different location), the pretreated gas stream from Sprex[®] (bulk removal) is dry and monophasic, which allows easy transfer line design and operation.

A brief review of Sprex[®] development history and validation process

From the first patent filed in 1994 to the formal qualification of the process for the sweetening of super sour gases with acid gas reinjection, a long pass had to be cleared to meet the challenges imposed by the Sprex[®] innovative concept. Below are the main steps of this work:

- Develop and validate a liquid/liquid/vapor thermodynamic model within the range of compositions and operating conditions of the process: the GASWEET model was calibrated from literature and specifically acquired isotherms, for fluid compositions including light and heavy hydrocarbons, H₂S, CO₂, Nitrogen, water, aromatics, mercaptans, COS, CS₂, methanol, in a wide range of temperature/pressure conditions, from -85°C to 150°C and up to 150 bar.

Figure 13 shows that the developed thermodynamic model well predicts the vapor –liquid equilibrium and the liquid-liquid-vapor equilibrium of such complex systems.

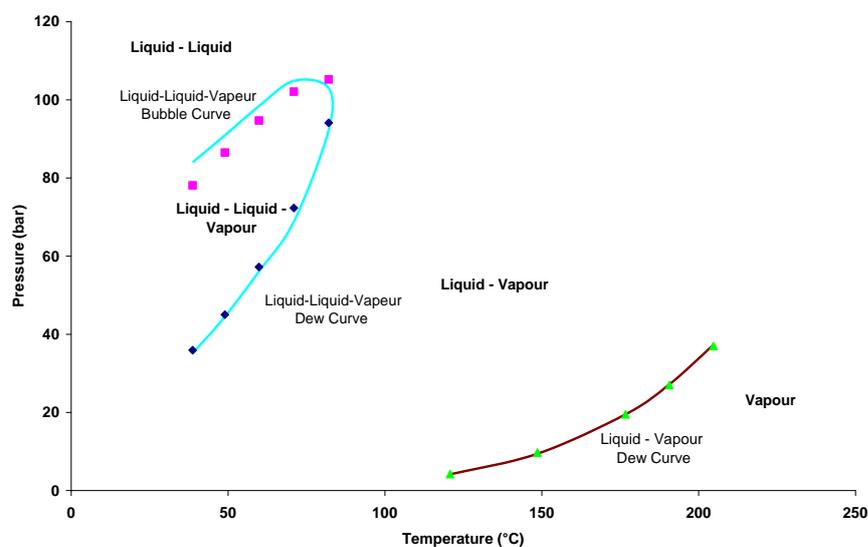


Figure 13: Phase diagram of H₂O/H₂S/CH₄/CO₂ system. Comparison between experimental data and the GASWEET Model

- Select and validate a liquid/vapor/solid model, able to predict hydrate formation conditions with very low water contents. As very limited data were found in the literature, hydrate dissociation temperatures were measured at high pressure for hydrocarbon/acid gases mixtures containing up to 80% H₂S and with low water contents. The model which was eventually selected, as giving the best results, was an in-house model (Figure 14).

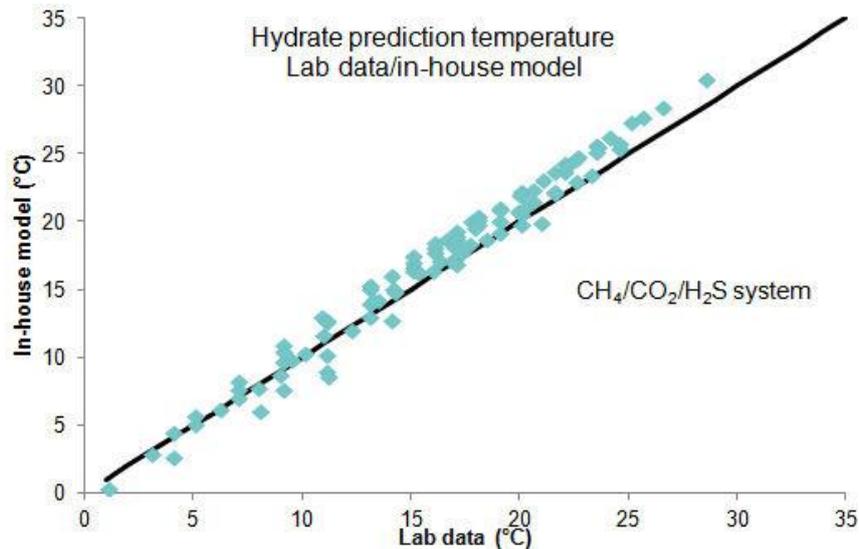


Figure 14: Hydrate prediction temperature with very low water contents - In house model

- Develop and optimize the Sprex[®] process scheme: the original scheme, patented in 1994, has evolved and matured to the current scheme, including a distillation column where the sour gas is dehydrated with cold liquid H₂S in the upper zone and light hydrocarbons and CO₂ are stripped from the H₂S soup in the lower section.
- Run the necessary testing to determine the corrosivity of super sour gas mixtures towards carbon and stainless steel under the operating conditions of the Sprex[®] unit and acid gas injection pipelines and wells, to allow the safe selection of the materials of construction.
- Develop adequate risk management studies and mitigation measures to manage the risk involved in handling dense phase H₂S-rich mixtures in large processing units
- Select and qualify specific pieces of equipment, such as liquid H₂S pumps

The decision was made to build and operate an industrial demonstration plant, to validate the Sprex[®] concept, unit design parameters, metallurgical recommendations, process control system, normal and emergency operating procedures, and verify the robustness of the process.

The pilot unit was installed and integrated in a large size commercial sour gas plant located South-West France in a populated area (Figure 9), with all its constraints, such as variations of raw gas flow, conditions and quality, production upsets, etc...[11]. The unit processed sour gas of variable H₂S content (from 18 to 40%), operated by normal plant personnel, from beginning of 2005 to 2006.

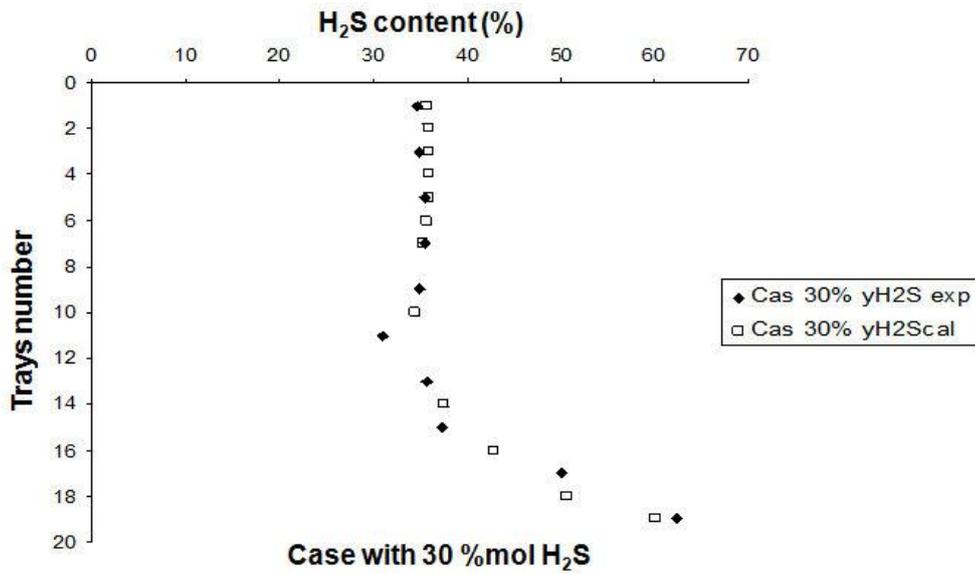


Figure 15: H₂S concentration profile: pilot results vs. GASWEET model

Operation has demonstrated the excellent adequacy between the thermodynamic models (L/V equilibriums (Figure 15), and hydrates formation conditions), measured the actual efficiency of the trays used in the column, validated the process and safety engineering studies, validated the adequacy of the choice of materials of construction for large scale units using corrosion coupons installed in selected places of the pilot unit (Figures 16, 17).

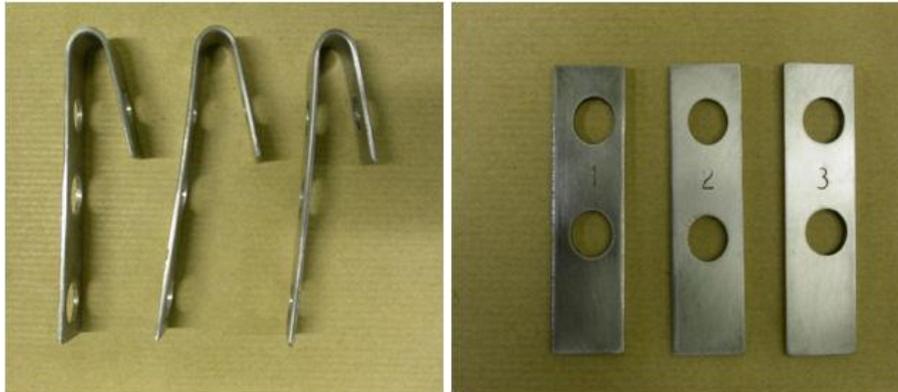


Figure 16: SS and CS Corrosion coupons used in the Sprex[®] pilot



Figure 17: Corrosion coupons installed in the Sprex[®] pilot piping

Operating procedures have been optimized and validated [12]. The stability and robustness of the process was demonstrated through long continuous operation runs. Behaviour of plant was also tested under start-up and shutdown, including emergency shutdown procedures. Hydrate formation and melting in the unit was tested, and the column has proven to easily to recover stable operation by quickly melting the hydrates through adequate adjustments in the operating conditions and methanol injection (Figure 18).

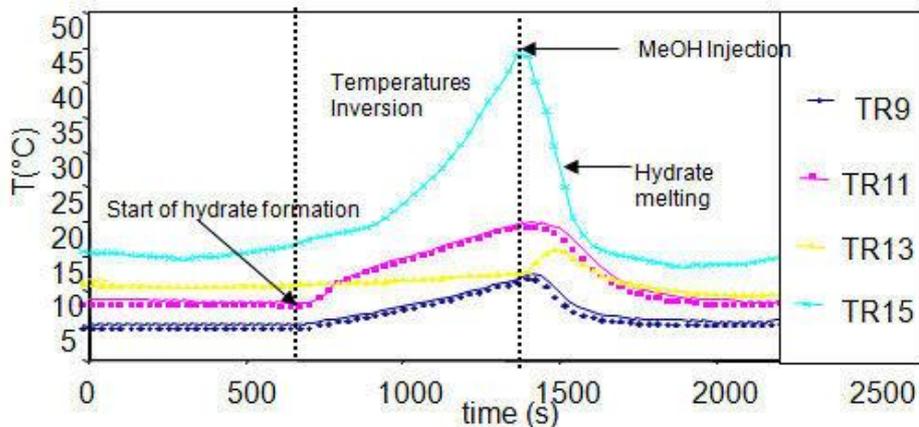


Figure 18: Forming and melting an hydrate in Sprex[®] pilot. Temperatures on selected trays

The process was eventually formally qualified by Total for implementation in the development of large super sour gas fields, using their formal internal qualification procedure for innovative processes.

Cryogenic bulk removal of CO₂ with the Sprex[®] CO₂ process

Yet, with a dehydration unit upstream of the cryogenic fractionation column, the gases can be cooled to well below the -30°C of the basic version of the Sprex[®] process, which improves the efficiency of the H₂S separation process and allows separation of CO₂ from the gas. However, the limit then becomes the temperature at which CO₂ crystallizes. The enhanced

version of the Sprex[®] process, called Sprex[®]CO₂, allows bulk removal of CO₂ from gases containing very high CO₂ content ($\geq 40\%$ or so) possibly together with high concentrations of H₂S.

The Sprex[®]CO₂ process is based on an optimized CO₂ distillation which is performed at conditions outside the CO₂ crystallization domain. The parameters and limits to avoid crystallization are illustrated in the distillation chart based on the main binary mixture (CO₂/CH₄). Fig.19 shows a typical gas specification achievable in the distillation outlet, i.e. around 20% CO₂ mol, at 30/40 bar.

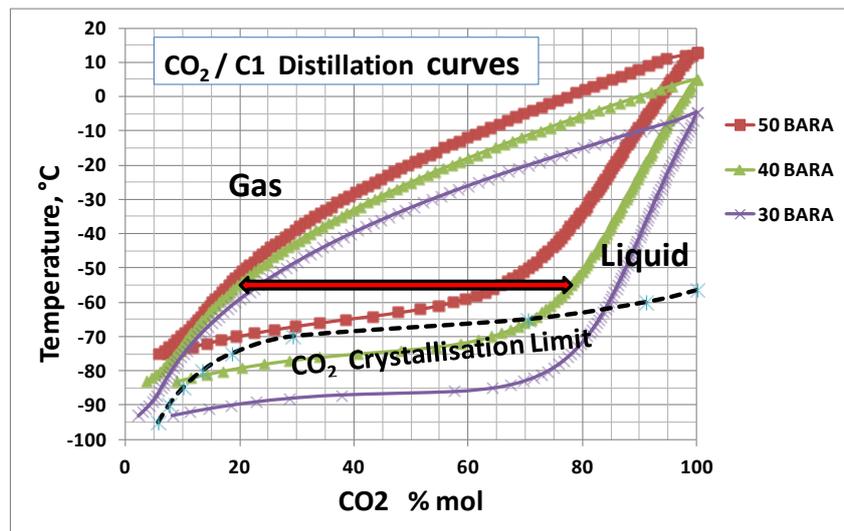


Figure 19: CO₂/ C₁ distillation chart

The Sprex[®]CO₂ process is competitive in comparison with conventional CO₂ separation processes (amines) or other hybrid solutions (membranes + amines) when CO₂ concentrations are higher than 40% and CO₂ reinjection is required for EOR (Enhanced Oil Recovery) and/or carbon sequestration. Carbon dioxide being recovered in liquid “soup” phase, injection is realized by pumps instead of multi-stage compressors, with considerable energy savings.

In order to match final gas export specifications (pipeline or LNG plant feedstock), the Sprex[®]CO₂ unit can be associated to a finishing AdvAmine[™] unit.

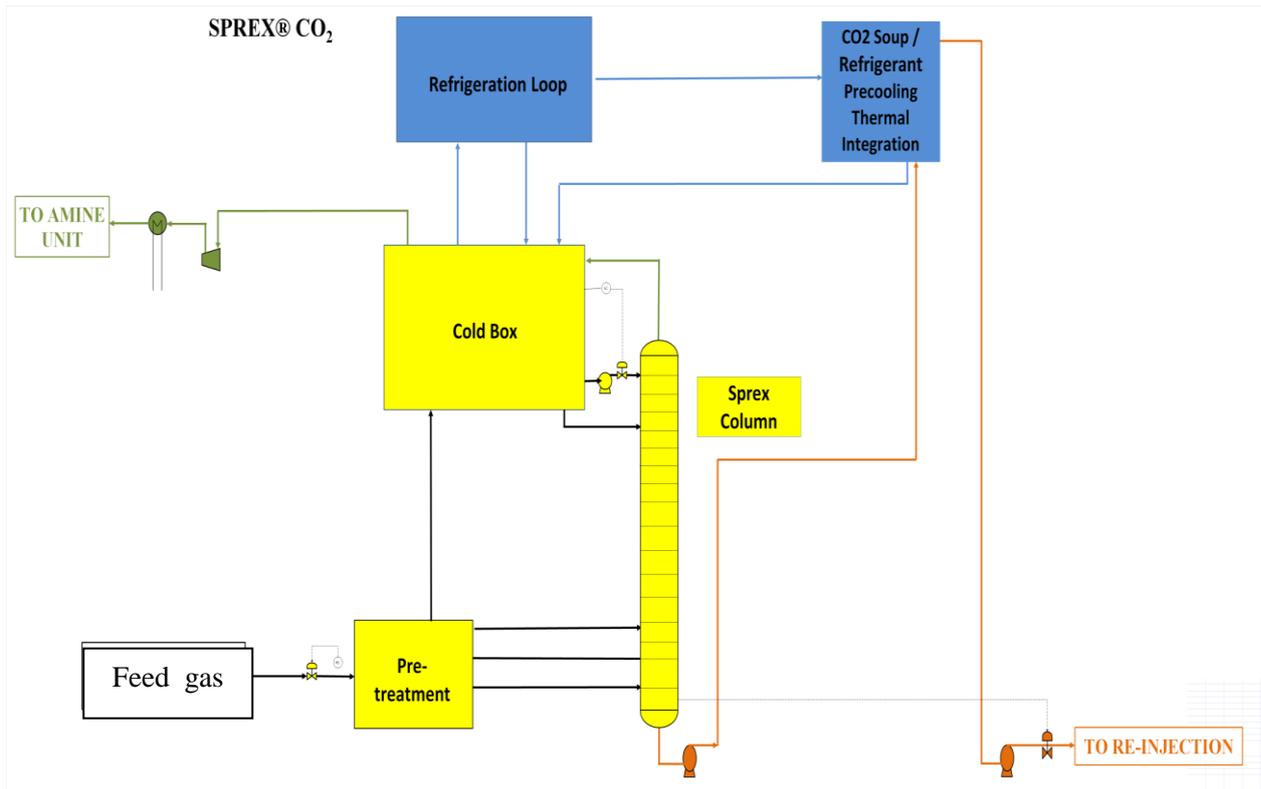


Figure 20: Sprex® CO2 simplified process scheme

A simplified Sprex® CO2 scheme, including upstream pre-conditioning units and downstream CO2 boosting and transfer/injection pumps is shown in Figure 20.

The scheme in Figure 20, given for illustration purpose, is typical: some process scheme alternatives are achievable depending on the raw gas conditions and final specifications required for export gas (pipeline, LNG feed or other uses...).

An example of the use of the Sprex® CO2 technology is presented below. The case study compares the 'Sprex® CO2 + amine' combination and the 'membranes + amine' combination. The range of methane and CO2 in the raw gas composition is given in Table 8 below.

	Mol %
Methane	24-27%
CO ₂	68-71%

Table 8: Fluid composition

The gas contains a few percents of C₂₊ and inerts as well.

The base case for natural gas sweetening includes the Sprex® CO2 technology for bulk removal of CO₂ and a finishing gas treatment based on AdvAmine™ technology

(energized MDEA). The ‘membranes + amine’ combination has been evaluated as an alternative, using commercial membranes vendors’ design data.

Removing CO₂ from 70% to 20% (our reference case) represents more than 90% removal of the CO₂ from the feed gas. Subsequent amine units, using the AdvAmine™ technology, remove all the remaining CO₂, down to the gas specification as required.

The better performances of the Sprex® CO₂ option, compared to those of the membrane alternative, are illustrated in Figure 21 and Figure 22.

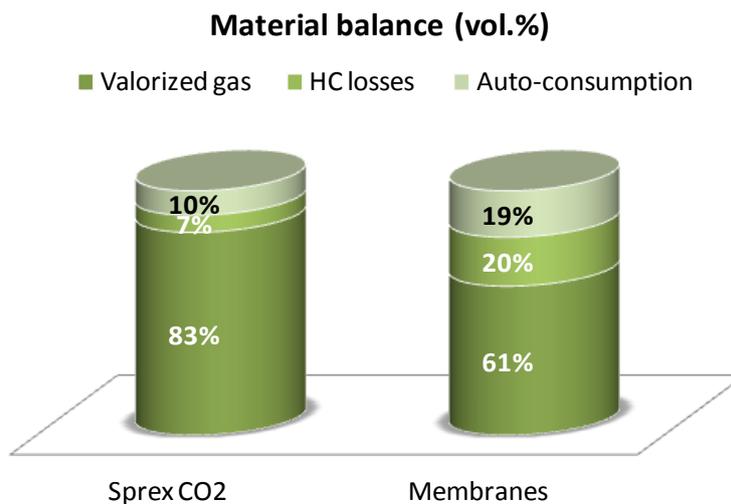


Figure 21: Overall performances comparison: ‘Sprex® CO₂ + amine’ vs. ‘membranes + amine’

Sprex® CO₂ maximizes the gas valorization by halving the overall auto-consumption needs and significantly reducing the overall hydrocarbon losses with the separated CO₂.

As shown in Figure 20, there is roughly an order of magnitude difference in power required for CO₂ recompression. From an energetic point of view, one of the interests of the Sprex® CO₂ is indeed that the CO₂ is recovered in liquid phase, thus not necessitating a compression step.

The case study also demonstrates that the two processes, Sprex® CO₂ and AdvAmine™, are energetically paired, with utmost benefits in terms of waste heat recovery optimization.

Acid gas compression system - Power consumption ratio (Relative value)

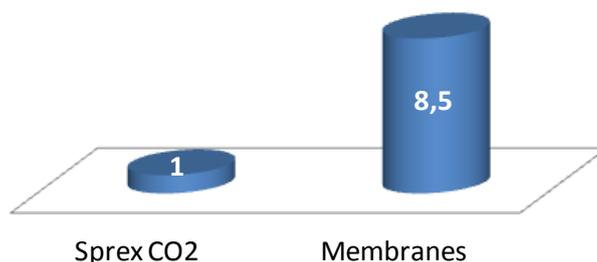


Figure 22: Power consumption dedicated to CO₂ recompression: ‘Sprex[®]CO₂ + amine’ vs. ‘membranes + amine’

One of the advantages of the proposed CO₂ separation scheme is the possibility to increase process flexibility to a certain extent by means of bulk and finishing separation units in series, in order to cope with fluctuations in feed gas composition or temporary off-set conditions.

The level of complexity of the proposed CO₂ separation scheme remains moderate: no prototype equipment is required, minimum acid gas compression system is required (only for the acid gas separated in the amine unit) and spare capacity considered is adequate to achieve availability levels typical of AGR (Acid Gas Removal) units.

In terms of capital investment, the estimation made in the case study shows an overall reduction in the range 17 to 20% by using the Sprex[®]CO₂ bulk separation instead of membranes.

CONCLUSIONS

Technologies to treat sour natural or associated gas are numerous on the market, but none has shown to be as versatile and economic as those using amine based solvents.

Amine processes can be optimized to efficiently and economically treat any type of highly sour gas. The historical and current R&D involvement as well as the operating experience of Total coupled with resources of IFP Energies nouvelles and Prosernat, allow the AdvAmine[™] series of processes to be credited with one of the most significant know-how back-up technology base on the market today.

To be truly competitive, the removal of acid gas components H₂S and CO₂ from highly or super sour gases requires the optimum choice of process. Within the AdvAmine[™] series of processes, the *energized*MDEA process can be optimized to reduce energy requirements, taking advantage of the ability of MDEA to release a substantial part of the absorbed acid gases in a low pressure flash to produce the semi-lean stream in a split-flow process configuration. The acid gas loading of amine solutions needs to be maximized to reduce the required amine solution flowrate. Operating amine plants at high loadings has been proven by Total through an extensive operating experience, and a liquid side cooler scheme on the acid gas absorber was developed to further increase this loading and reduce the cost of highly sour gas sweetening.

When the mercaptans content of highly sour gas becomes an issue to meet a stringent total sulfur commercial gas specification, the HySWEET[®] process from Total may be considered.

Even though amine based sweetening has proven to be a very efficient technology, cryogenic bulk removal of H₂S or CO₂ offers an economic advantage when the separated acid gases from super sour gas are reinjected. The Sprex[®] and Sprex[®]CO₂ processes, jointly developed by Total, IFPE and Prosernat, can be combined with an amine unit to reduce the cost of the production of gases containing more than 25-30% H₂S or over 40-45% CO₂. They provide an economic and easy to operate alternative to amines, to membranes and to other more complex cryogenic fractionation processes for the treatment of such highly sour gases. The Sprex[®] series of processes was demonstrated in a unit installed at the Lacq sour gas plant and the technology is now ready to be implemented at industrial scale.

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