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SUCCESSFUL OPERATION OF SELECTIVE AMINE UNIT AT LOW GAS TURNDOWN

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Successful Operation of Selective Amine Unit at low gas turndown

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Abstract:

When natural gas contains H_2S and CO_2, selective amine sweetening technology allows achieving stringent H_2S specification and partial CO_2 removal.

Total designed a few years ago a selective amine unit for natural gas treatment, to eliminate the H_2S content while keeping the CO_2 within a range of 1.5 to 1.7 mol%. The design combined the use of formulated MDEA, multiple injections of amine and a mix of trays and structured packing bed in the absorber.

Lately, operators had to manage low turndown conditions (gas flow rate at 20% of design and lower inlet CO_2 content) with the same treated gas specifications. Several options and parameters outside of conventional amine operating practices were studied using an in-house amine unit simulator named Desulfo to determine the new optimum operating conditions.

The proposed solution considered a less concentrated amine and optimized injection of amine. The unit has been successfully operated under the new operating conditions determined through simulation demonstrating how flexible, robust and accurate Desulfo is.

This paper shows how the study was conducted and how the optimized operating parameters were selected. It also demonstrates how accurate and robust simulations are compared to operational data.

1. FACILITIES DESCRIPTION - ORIGINAL DESIGN

Most of the time sour gas treatment consists in H_2S and CO_2 removal followed by dehydration and dew pointing unit, to be able to deliver sales gas at specifications. The design of the facility described in this paper consists in an Acid Gas Removal Unit (AGRU), a glycol gas dehydration unit, a NGL splitter for condensates recovery, an export gas compression unit and associated utilities.

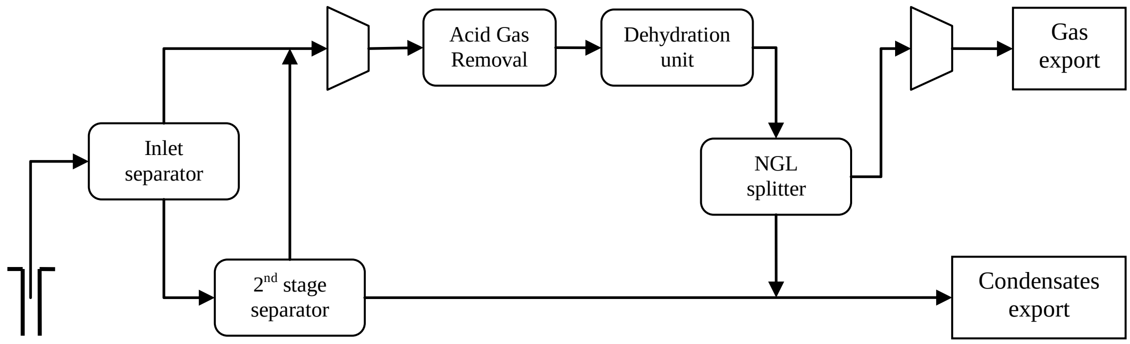

Figure 1: Process simplified bloc flow diagram

The gas treatment units, and especially the AGRU, had to overcome two challenges. The first challenge was the wide range of composition and flowrate of the sour gas to be treated, which required a very flexible design. The sour gas contains about 40 ppm H_2S with CO_2 content varying from 2.2% mol to 4.1% mol. Gas flowrate varies from 30% to 100% of design flowrate.

The second challenge was the sales gas specification, which required a very well controlled Wobbe index between 48.3 and 51.2 MJ/Sm^3.

Several options were studied to achieve this specification. C3+ removal was not sufficient to meet the specification and C2 removal was not economical. Another option consisted in nitrogen injection in sales gas which was not retained because of excessive complexity and high cost.

Eventually the selected solution consisted in leaving a controlled quantity, between 1.5 and 1.7%, of CO_2 in the gas from the AGRU, using an amine based solvent removing H_2S down to the severe 3 ppm vol. specification.

The design of such an acid gas removal unit required specific arrangements in order to get the desired CO_2 slippage within the large range of gas flowrate:

- The solvent used was a formulated MDEA and the energizer was selected among the family of industrial energizers available in the Advamine™ technology from TOTAL. Figure 2 indicates how solvent formulation, and selection of energizer can be adjusted to control the CO_2 removal performance. Whilst the target for CO_2 removal was above the one achievable with pure MDEA, only a weak activation was needed. As the concentration of the energizer in the solution had to remain sufficiently high to allow a reliable dosing and control in operation, the selected energizer presented a moderate reaction rate with CO_2.

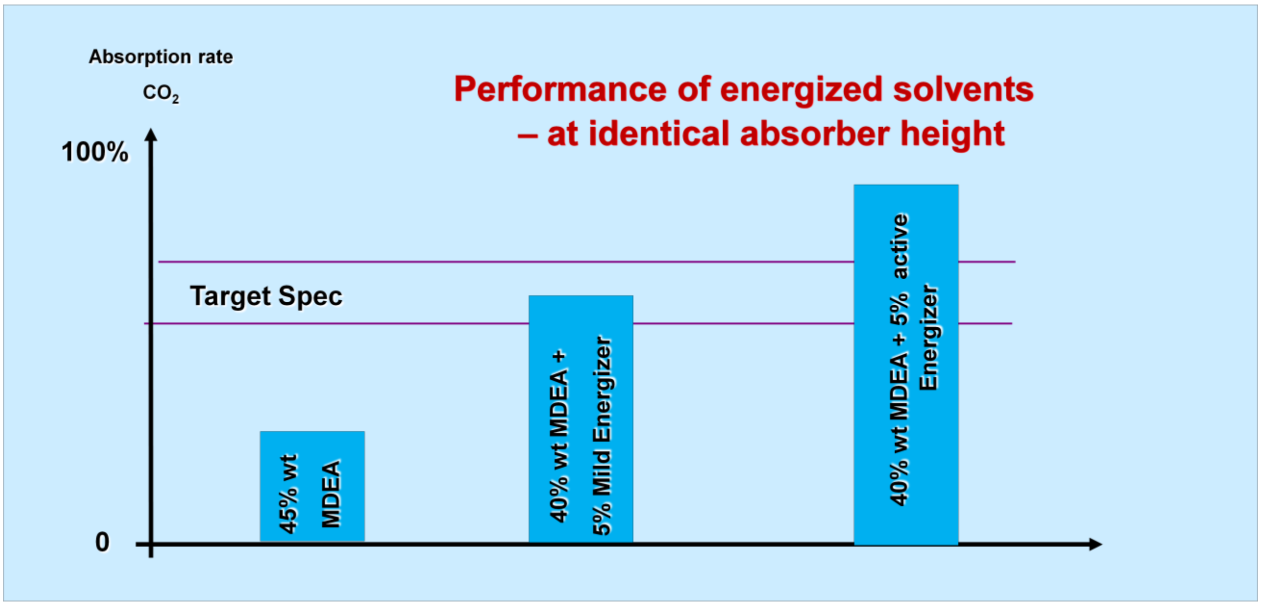

Figure 2: Selection of energizer influences the CO2 absorption rate

- The amine absorber was specifically tailored to provide the required ability to control the CO_2 co-absorption within the entire range of operating conditions, including low turndown with variable sour gas CO_2 content. A mixed column was designed with valve trays in the upper part and structured packing in the lower part. Use of trays enables to install multiple solvent feed locations on the upper part of the column to adjust CO_2 slippage for different gas flows and compositions. The lower CO_2 absorption capability of the structured packing installed in the bottom section of the column provides the required very high selectivity at low gas flowrate when CO_2 concentration is close to the minimum.

- As shown on Figure 3, the process scheme, except for the design of the absorber, is quite conventional. Lean solvent is contacting the sour gas in the absorber where all the H_2S and a controlled amount of CO_2 are removed. The rich solvent is then flashed and heated by use of amine/amine exchanger before feeding the regenerator. The rich solvent is regenerated by stripping, to the quality required to meet the H_2S specification at overhead of the absorber. The lean solvent is then cooled down and recycled back to the absorber. It is also possible to send part of the lean amine solution directly to the flash drum, bypassing the absorber, so that the regeneration section can be operated above turndown conditions when solvent feed to absorber is minimal. This configuration offers additional flexibility on the amine solution flowrate to the absorber, which is particularly important for transiant phases such as unit start-up and turndown conditions.

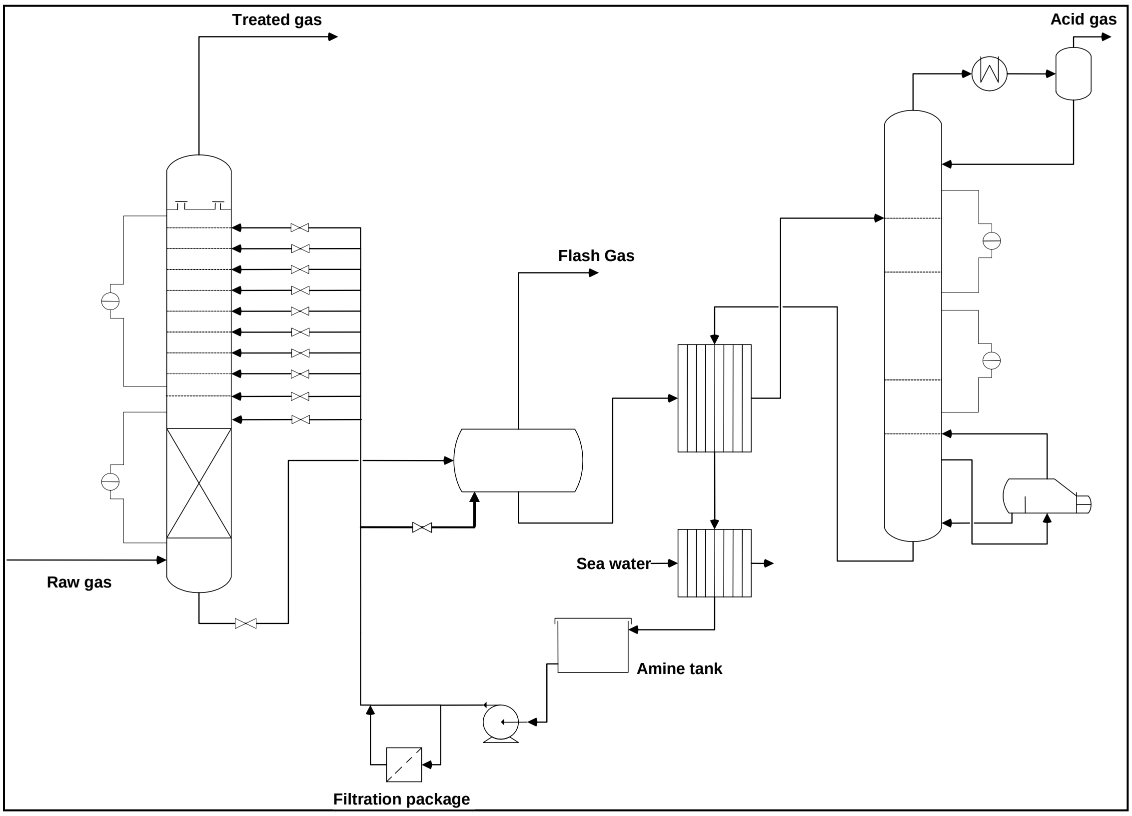

Figure 3 : Acid Gas Removal Unit simplified diagram

2. START-UP CONDITIONS AT VERY LOW TURNDOWN

The amine unit has performed according to expectations, for some fifteen years. More recently, some problems encountered in the field lead to shut down gas production for a while. The operator then wanted to restart the gas treating facilities to restore production. However, it was foreseen that the gas flowrate would be reduced due to wells limitations.

The future start-up conditions were found to be particularly difficult, as the gas flowrate was going to be well below the minimum flow the unit was designed and built for. Some modifications to the operating procedure and possibly to the equipment needed to be implemented to ensure a safe start-up with minimum impact to the environment. The time provided by the shut-down allowed to perform the necessary assessments and to study the new start-up conditions, which are explained below.

2.1 - **Overview of the challenging new start-up conditions**

Low turndown condition

Only a very limited number of wells was expected to be available for the start-up. Cumulated with the depletion of gas field, the estimated maximum raw gas flowrate was around 20% of the unit design capacity, well below the minimum turn-down of 30% for which the unit had been originally designed.

A process study was therefore undertaken, to define the new operating conditions, with a special emphasis on the start-up conditions at very low turn-down, and verify whether modifications of some pieces of equipment were necessary or could be avoided.

Stringent treated gas specifications

In this plant, the H_2S and Wobbe Index specifications required for gas to be exported are the following:

	Specification
H_2S	3 ppmv
Wobbe Index	48.3 < WI < 51.2 MJ/Sm^3

Table 1: Export gas specifications

In order to meet the export WI specification, it is essential that CO_2 content is kept within a range of 1.5 % to 1.7% mol at the outlet of amine absorber.

Wells composition uncertainties

Two different reservoirs are gathered from this field. The raw gas composition is fairly different especially for CO_2 content which can vary from 2.4% to 4.0%. During the start-up phase, operators will have to face different cases with low or high CO_2 content or the combination of them according to the number of wells in production. This wide range of inlet CO_2 content is very challenging for the amine unit. The inlet gas CO_2 content was however expected to be in the lower part of the range, i.e. 2.4-2.9% mol.

Meanwhile, the H_2S content in the raw gas was expected to be identical for the two reservoirs; however it was still possible to encounter an H_2S content change due to long well shutdown.

The defined start-up conditions had to be as robust and flexible as possible to cover all these uncertainties.

Environmental issues: limited flaring allowance during start-up phase

During the start-up phase, the out of spec gas must be sent to the flare. Many efforts needed to be made to ensure a smooth, safe start-up with limited flaring time, in order to limit the environmental impact. It means that the good performance of AGRU had to be reached quite quickly, by relying on accurate results given by the process study.

CO_2 specification not met according to preliminary simulations

As previously explained, the gas flowrate to be treated in the Absorption Tower was expected to be very low compared to design flowrate (circa 20% of design flowrate) and in the low part of the range in terms of CO_2 content, i.e. 2.4-2.9% mol.

A preliminary simulation of the Absorption Tower at this gas flowrate with the original *Energized***MDEA** solvent containing 45.5%wt MDEA gave a CO_2 content in the treated gas below the required specification when contacted with the minimum possible solvent flowrate of 40 m^3/hr injected into the absorber at the lowest injection point, i.e. top of the packing bed. The study also evidenced the risk of unstability of H_2S and CO_2 content in the treated gas due to the low liquid feed flow to absorber. The first simulation of the unit performance based on the same formulation of solvent as the original composition demonstrated that the CO_2 content in treated gas would be far below the target specification. Even if the solvent flow rate is reduced at the minimum liquid flow acceptable by the liquid distributor to the packing bed, it is not possible to increase the CO_2 content in treated gas to the required specification.

As a consequence, it was necessary to look for innovative operational modifications, and determine new conditions that would allow the amine unit to absorb less CO_2 in order to meet the required Wobbe Index specification of the export gas, without modifications of the existing amine unit.

2.2 – **Simulation tool: Overview on model theory and acquired expertise**

The process design of Advamine™ units relies on the use of a proprietary software named Desulfo. The Desulfo simulator includes mass transfer rate-based models for acid gas reactions with liquids which have been validated against more than 50 years experience of plant operation and consolidated by operating data from running gas sweetening units.

Below is a brief description of this proprietary simulation tool developed by TOTAL, IFP Energies nouvelles and PROSERNAT for amine units.

Indeed, the need to be able to design acid gas absorption units, and to understand the complexity of mass transfer and chemical reaction mechanisms that are unique to them, required the development of accurate models to calculate the acid gas absorption rate with different types of amines with an absorption tower fitted with different types of packings or trays. While a detailed description of these models and the long R&D effort made is not the purpose of this paper, in order to have a better picture of what is at stake here, it is necessary to introduce the rudiments of the chemical absorption mass transfer theory.

As shown in Figure 4, the acid gas absorption rate depends on many factors such as:

1. Hydraulic conditions,
2. Thermodynamics,
3. Mass transfer coefficient on gas side
4. Mass transfer coefficient on liquid side
5. Kinetics of the reaction between acid gas and amines.

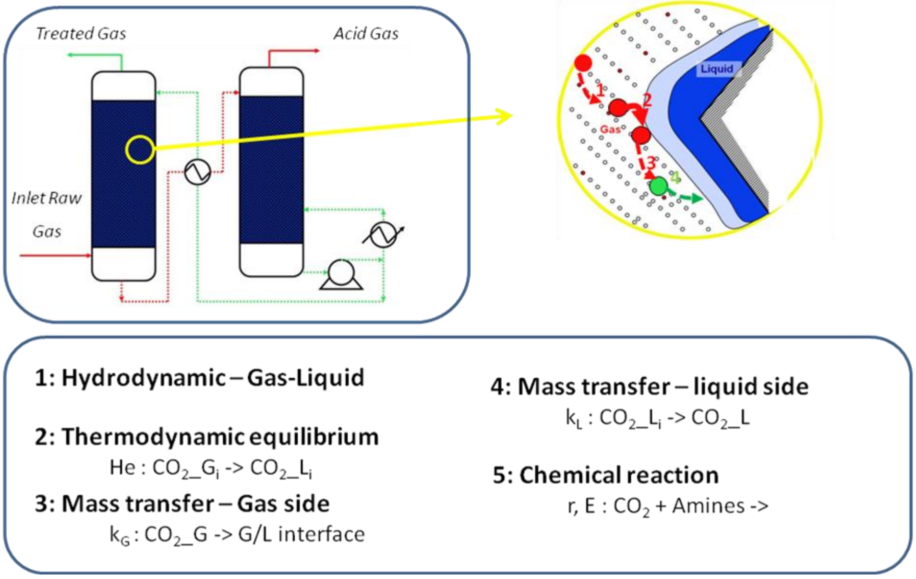

Figure 4: Mass Transfer – Principle of Reactive Absorption

The knowledge of the incidence of all these parameters was acquired through extensive laboratory and pilot plant experimentations on thermodynamics, kinetics, and through characterisation of several contactor internals (trays, random packing or structured packing). The mass transfer equation can be summarized in a basic equation of the flux of acid gas from the bulk of gas to the bulk of liquid. The illustration given below is taken from the well-known theory of double film [1]. It is presented in Figure 4 and is available in many rate-based simulators used to compute the performance of an amine unit to establish their design. The equation which determines the flux of acid gas transferred from gas phase into liquid phase shows the interactions between all the parameters.

If the chemical engineering models listed above are individually precise, the absorption of acid gas is calculated accurately based on the given operating conditions, for the selected tower design (diameter) equipped with an actual height of a specific packing or with an actual number of specific trays, thanks to specialized simulators. The in-house proprietary simulator Desulfo integrates a sophisticated mass transfer model for the calculation of amine systems and absorption of acid gas by amine solvents. With a rate-based simulator like Desulfo, the calculation of acid gas absorption is not performed on the basis of a theoretical stage approach including a correction with a mass transfer efficiency coefficient. Rather, Desulfo calculates the absorption of acid gas stage after stage along the column, based on the type and arrangement of the selected internals for the design. Desulfo provides a clear picture of the absorption profile within the tower and gives an accurate understanding of the absorption behavior for any new application of acid gas removal unit. After each development step based on R&D studies, the simulator is validated and continuously upgraded based on the feedback recovered from the operating and design experience aggregated over the last 50 years on Advamine™ H_2S and CO_2 removal units, operated by TOTAL or licensees.

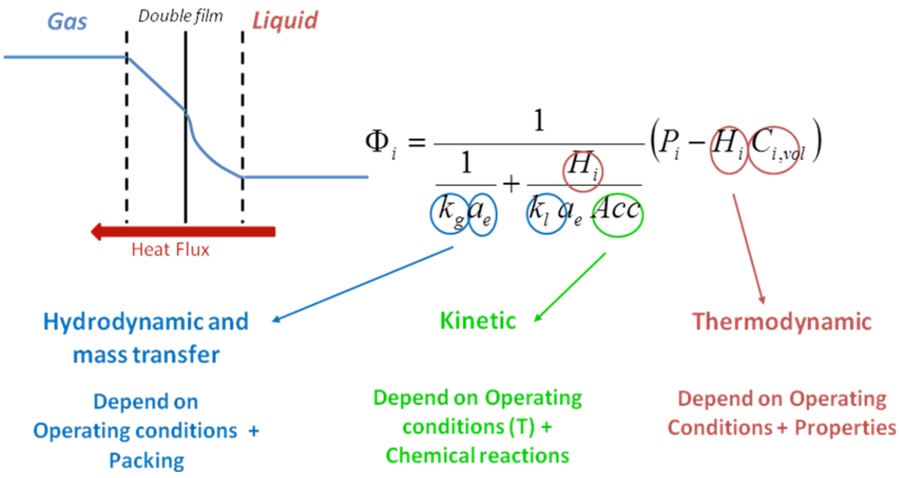

Figure 5: Calculation of the gas to liquid flux with chemical reaction

2.3 – **Simulation limits due to unusual hydraulic conditions**

Desulfo was used to perform the investigation on the operating parameters and the unit configuration to determine the ability of the amine unit to perform the required duty or if other solutions needed to be investigated to allow the AGRU to restart in such degraded conditions.

Before turning to simulation results, the expected hydraulic conditions in the absorber for restart-up conditions are identified and discussed here-after:

- Gas turndown 20%
- Gas velocity and kinetic factor on packed bed lower than 0.3 (Note 1)
- Liquid load on packed bed below 3 $m^3/hr.m^2$ based on preliminary simulation with original *Energized***MDEA** solvent

<u>Note 1</u>: The kinetic factor is an expression of the gas velocity taking into account the gas pressure: $Fc = Gas\ velocity \times \sqrt{Gas\ density}$ [2]

Both kinetic factor and liquid load are outside the usual ranges expected in running absorbers. The top section of the absorber is equipped with trays. It is well known that trays experience weeping at low loading, and that their efficiency is greatly affected at gas turndown at 20%. Indeed the gas is likely to follow preferential flow paths through the active area of the trays and it is difficult to assess about the extension of the phenomenon. Some special tray design can allow adequate performances to be achieved at such gas turndown but the trays installed in the column are not specially designed for that purpose. As a consequence, even though some industrial feed-back could support an optimistic view of the the good performance of the absorber towards H_2S removal, mainly because of the quick reaction of H_2S with amine solvent, it was far more difficult to conclude that trays can perform a selective and slow absorption of CO_2.

Regarding the packed bed section, provided it is fed with an adequate liquid distributor, it is generally less limited than trays in terms of hydraulics and it can accept much lower turndown rates without loosing efficiency. But, the efficiency of structured packing will start to be greatly affected at low kinetic factor. In addition, it is also impacted by low liquid load.

Based on previous references [3], it is well established that the active area developed by the packing and on which depends, among other parameters, the actual absorption of CO_2 by amine solvent, decreases drastically at low gas flowrate and low liquid load. This is shown on Figure 6.

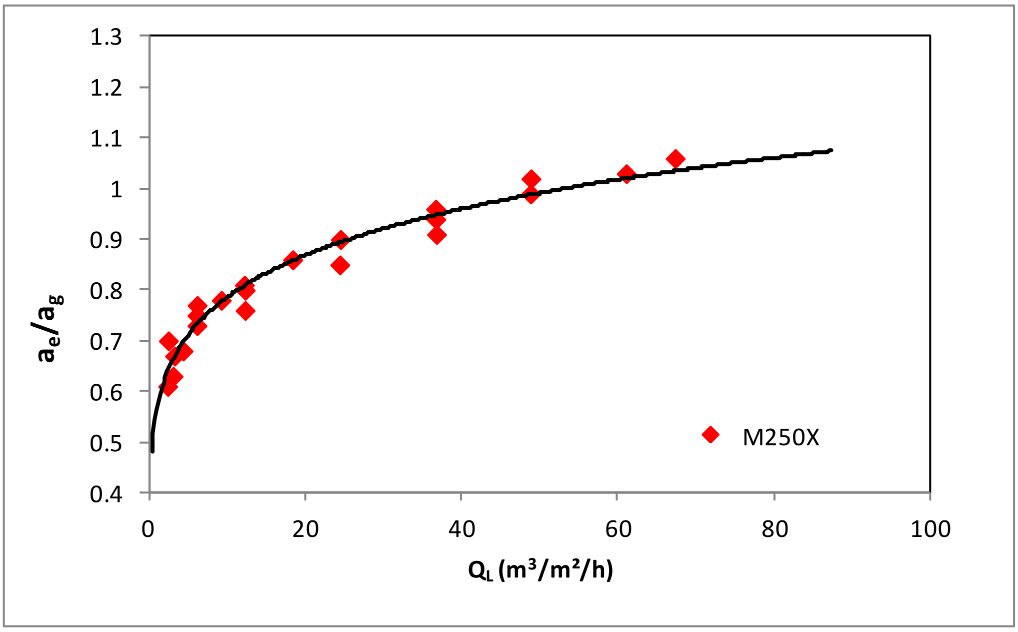

Figure 6: Active area developed by packed bed at different hydraulic conditions - Experimental results

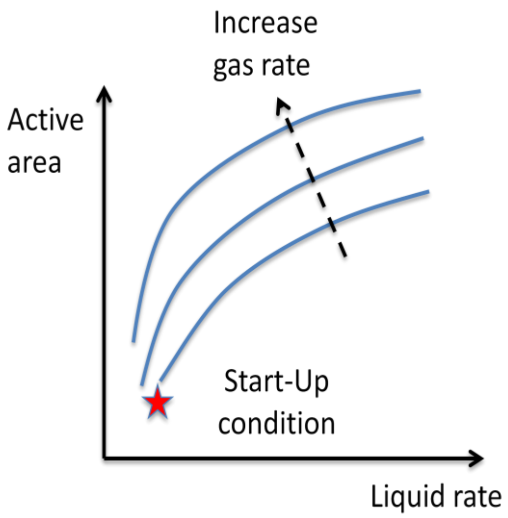

Figure 7: Active area developed by packed bed at different hydraulic conditions.

In amine AGRU, the gas kinetic factor and liquid load are generally respectively greater than 0.4 and 10 $m^3/hr.m^2$ for amine unit. The hydraulic conditions experienced by the packing bed at restart would then be far below usual conditions in amine absorbers.

As a reminder, the hydraulic conditions of the absorber at design conditions are:

- Kinetic factor 1.5
- Liquid load 30 $m^3/hr.m^2$

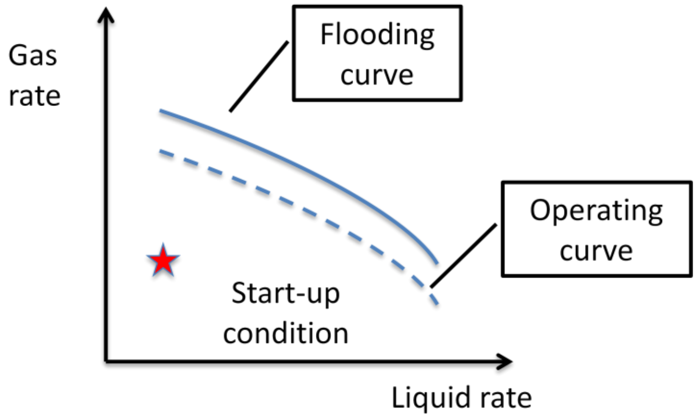

Figure 8: Start-up conditions versus normal operating hydraulic conditions

Generally, the accuracy of the correlations developed in mass transfer rated-base simulator for amine units provide a poor prediction under these low hydraulic conditions, as they are far from the usual design point of acid gas absorption towers with amine. In addition, few experimental data are available in such hydraulic conditions especially for low feed gas flow. Industrial feed-back is also limited, generally due to the fact that plants close to their end of life, providing marginal economic returns because of low feed gas flowrates, are considered as not much attractive for process knowledge capitalization studies. Indeed, the diameter of the absorption tower is generally minimized as it represents an important part of the cost of the amine unit and removal of acid gases generally requests significant amount of amine. This result in high kinetic factors associated to high liquid loads.

On the liquid side, a loss of efficiency of the packing due to very low liquid feed flow is possible but not validated by industrial experience. Indeed, the type of structured packing installed in the AGRU absorber is widely used in gas dehydration plant operating with glycols. Ratios of glycol liquid flowrate to gas flowrate are commonly extremely low compared to the ones experienced in AGRU plants, resulting in extremely low liquid loads to packing bed, and glycol plants have never reported a noticeable loss of efficiency of structured packing bed.

2.4 - **Determination of optimized operating conditions**

Total conducted the re-start-up preparation study with the support of PROSERNAT, Licensor of Advamine^{TM} technologies. As mentioned above, a preliminary simulation of the absorption tower at minimum acceptable gas flowrate with original *Energized***MDEA** solvent at 45.5%wt MDEA gave a CO_2 content in the treated gas below the requested specification. The gas is treated with 40 m^3/hr of solvent injected at top of packing bed. The lowest amine injection point is at the top of the packing bed and 40 m^3/hr is the minimum liquid flowrate that the liquid distributor installed there can handle.

As a consequence, it was required to determine new conditions, if any, that would allow the amine unit to absorb less CO_2 while removing all the H_2S, in order to meet the required specification on Wobbe Index and H_2S to be able to export the gas.

It is worth noting that, due to the project constraints, physical modifications of the absorption tower were not desired. An investigation of the operating conditions of the amine unit was performed using the mass transfer simulator Desulfo, bearing in mind all the above constraints.

The following parameters were studied in order to identify the appropriate operating conditions to perform the required CO_2 specifications if at all possible:

- Solvent injection point
- Concentration of energizer and of MDEA to control CO_2 absorption
- Solvent flowrate

In order to limit the absorption of CO_2, it was decided to inject the amine at the lowest possible injection point in the column in order to limit the contact time between amine and CO_2. The amine solvent is therefore injected at top of the packing bed section fitted with a liquid distributor which runs at a minimum flow of 40 m^3/hr.

The energizer selected in the original design was chosen among the list of available energizers for its relatively low reactivity towards CO_2. It allowed the solvent to increase slightly its CO_2 absorption capacity to give even more flexibility to the amine unit.

After trial calculations with the simulator to solve the constraints posed by the new operating conditions, it was decided to remove the energizer from the solvent and to use a MDEA solvent to limit CO_2 absorption at its minimum.

In this configuration, several simulations were run to evaluate H_2S removal and the absorption of CO_2 with MDEA solvent injected at the top of the packing bed section of the column. The following steps further moderated the activity of the solvent by a reduction of its strength. Different concentrations of MDEA in the solvent were simulated from 45.5%wt down to 20%wt in water.

Figure 9 shows the calculated CO_2 concentration profile in the gas phase along the packing bed at different concentrations of MDEA in water, considering the same flowrate given by Desulfo.

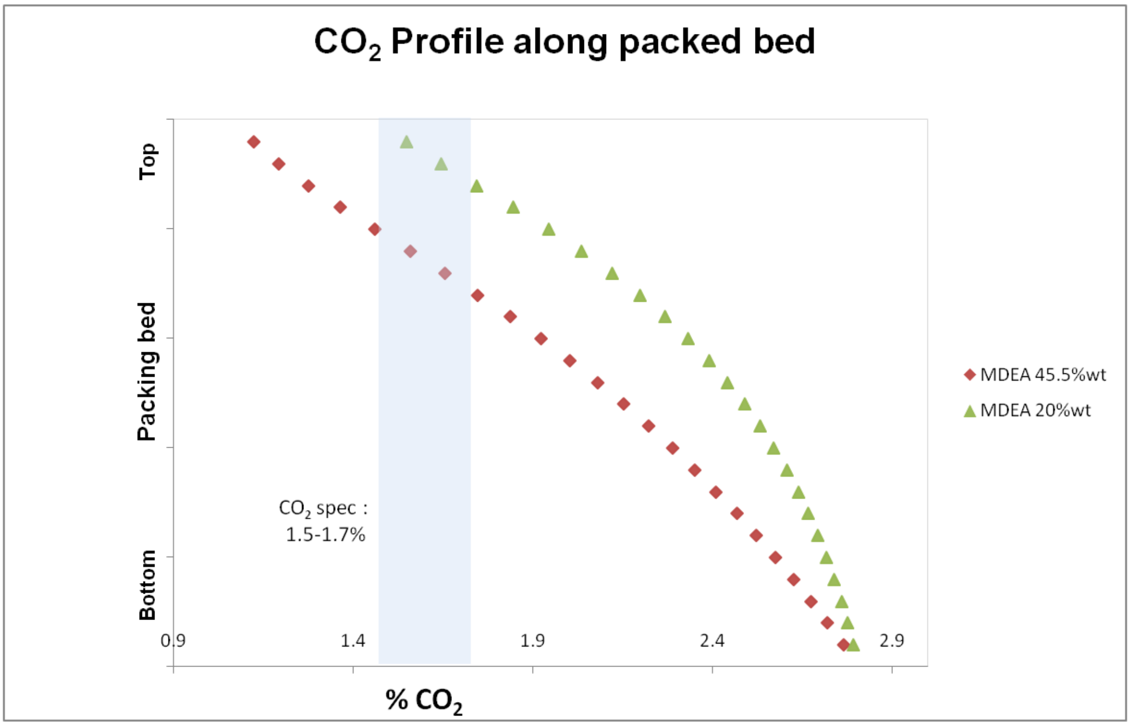

Figure 9: CO_2 concentration profile in the gas phase along the packed bed.

The figure shows that MDEA concentration must be decreased to 20%wt to limit CO_2 absorption as low as possible and thereby achieve the required CO_2 content in the treated gas. Performance towards H_2S was still established for all those strengths of solvent, for a solvent flow of 40 m^3/hr.

The recommendations at the end of the simulation study were hence the following:

1. Inject the solvent at the lowest injection point, top of packing bed section
2. Replace the *Energized*MDEA solvent by MDEA.
3. Decrease the concentration of MDEA down to 20%wt
4. Maintain the solvent at the minimum rate acceptable by the liquid distributor e.g. 40 m3/hr or above.
5. The excessive solvent from high pressure solvent pump has to be eventually diverted to MP flash vessel, using the line installed for that purpose at the design stage.

These recommendations were followed by TOTAL operation team prior to restart-up of the platform.

3. INDUSTRIAL RESULTS

3.1 - **Start-up history**

Once the recommendations that came out from the simulation study had been fully implemented in the amine unit, the start-up was initiated. Three different wells were available for production. They were started successively by operators.

The full history of the start-up is depicted in Figure 10, illustrated through the key parameters which are: raw gas production, circulated lean amine flowrate, H_2S content in the outlet gas and CO_2 content in the inlet and outlet gas.

Note that H_2S content in the inlet gas was not monitored as no in-line measurement device was in service during the start-up.

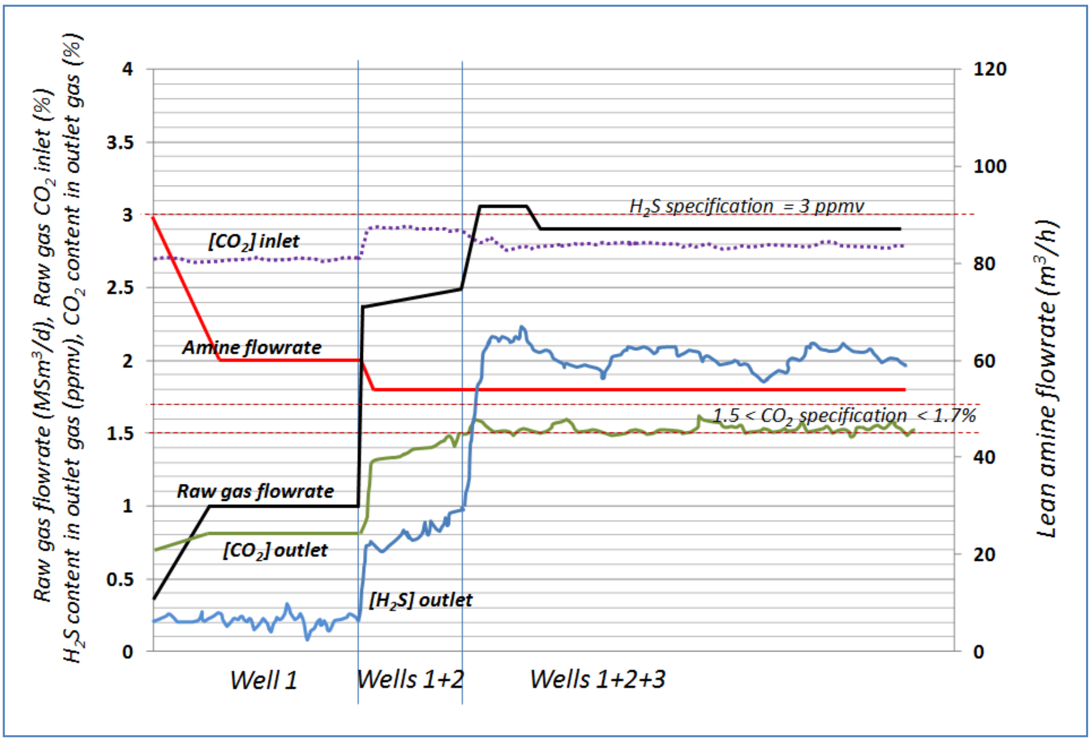

Figure 10: History of start-up through key parameters

Start-up of first well

The first well was put in production alone. Gas production initiated at around 0.4 MSm^3/d while lean amine flowrate was set at 90 m^3/h nominal flow. First measurements established that H_2S content in the outlet gas was around 0.2 ppm, far below the 3 ppm specification value. On the other hand, CO_2 content in outlet gas was about 0.7% mol, i.e. less than half of the targeted specification range (1.5 - 1.7% mol).

During few hours, gas production ramped-up progressively to 1 MSm^3/d. In parallel to this, amine flowrate was progressively decreased to 60 m^3/h in order to help CO_2 content increase in outlet gas. However, no major effect was observed. CO_2 content in treated gas gained only 0.1 %, whereas H_2S content remained stable.

Start-up of second well

When the second production well was put under production, gas production flowrate jumped to 2.3 MSm^3/d. The second well being richer in CO_2, CO_2 content in the inlet gas gained 0.2 points to 2.9%. At the same time, the amine solution flowrate was further decreased, to 55 m3/hr.

The combination of three effects: raw gas flowrate increase, lean amine flowrate decrease , and inlet CO_2 content increase led to substantial increase of H_2S and CO_2 in the outlet gas: H_2S content jumping to 0.7 ppmv, still below 3 ppmv upper limit, and CO_2 in the outlet gas growed up to 1.3%, close but still below the minimum limit of the specification range, at 1.5% mol.

Then, the production ramped-up to 2.5 MSm^3/d, which improved the CO_2 content in the outlet gas, eventually reaching 1.5%, while H_2S content remained below 1 ppmv.

Hence, the objective was achieved with 2 wells put in service, producing below 20% of the nominal capacity of the plant.

Start-up of third well

When the third well started, gas production rose up to above 3 MSm^3/d and lean amine flowrate was maintained at 55 m^3/hr. CO_2 content in the inlet gas remained stable at around 2.8%.

Due to the gas production increase, H_2S content in outlet gas increased to an average value of 2.2 ppmv, staying below the 3 ppmv limit, while outlet CO_2 stabilized at 1.5%.

Despite the fact that amine flowrate could be further decreased to 40 m^3/hr, pushing the unit to its performance limits, operators preferred to stick to 55 m^3/hr, as the outlet gas became compliant to export specifications. The liquid load at 55 m3/hr is only 4.1 $m^3/hr/m^2$. This figure is still below the figure considered for industrial design of AGRU that starts above 10 $m^3/hr/m^2$.

3.2 - **Industrial results versus simulation**

The absorption performances of the Amine Unit were monitored during the start-up phase and compared with the simulation results. The results of this comparison are given in Figure 11.

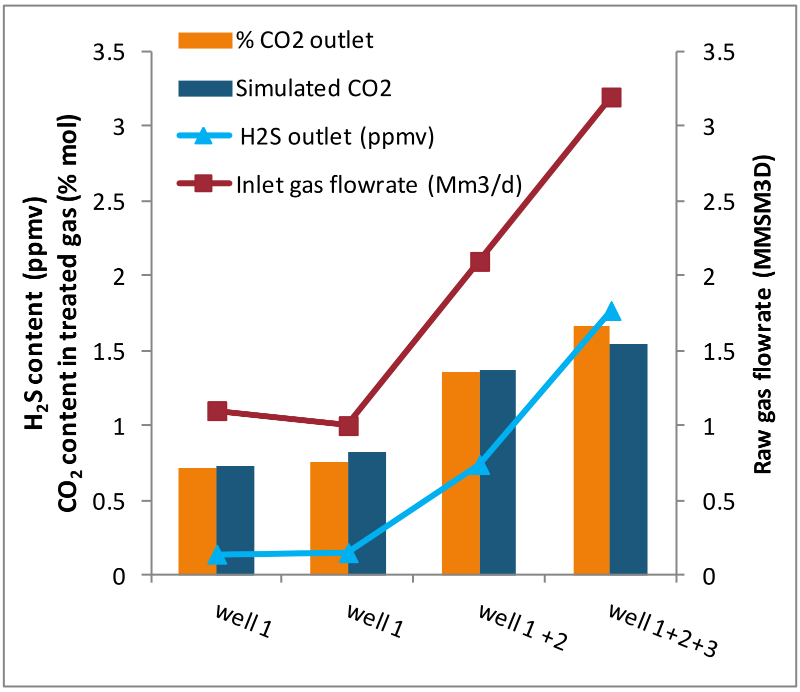

Figure 11: Comparison of simulation results with actual absorption performances during start-up.

The results are given for four cases that correspond to different times of the start-up sequence taken during gas flowrate ramping-up through the Amine Unit.

It can be noticed that gas flowrates recorded for the three first cases are well below the minimum gas flowrate considered in the initial design of the unit. Despite the fact that outlet CO_2 content is below the requested specification and varies between 0.7 and 1.4%, these points are remarkably reproduced by Desulfo.

Finally, when the gas flowrate reached a substantial value (Case 4), the outlet CO_2 content met the required specification, between 1.5 and 1.7% mol, as forecasted by Desulfo.

H_2S performance has never been an issue in operation, this was in line and fairly depicted by simulations.

4. CONCLUSIONS

Start-up conditions can be simulated by industrial amine simulators to predict and support the operations on site. Even for conditions far from the initial design, the simulation determines how the plant shall be tuned to secure the process performances on specs.

The amine units simulator "Desulfo" that Total, IFP Energies nouvelles and PROSERNAT have developed for many years includes mass transfer rate-based models for acid gas reactions with liquids which have been validated against more than 50 years experience of plant operation and consolidated by operating data from running gas sweetening units.

The results presented in this paper, show how flexible, accurate and robust the Desulfo simulator is, as it can accurately predict the performance of an absorption column, even in a degraded mode characterized by low gas flowrates and low liquid loads. It can also precisely simulate the behavior of the solvent at different concentrations.

Thanks to Desulfo, it was possible to overcome several uncertainties related to the very unusual hydraulic conditions imposed to an amine unit, and made possible to propose innovative operational modifications that led to a successful start-up.

In this specific application, the dilution of the solvent strength, and the removal of the activator, allowed operating the liquid flow above the minimum limit imposed by the mechanical design of the distributor to packing bed.

In terms of performances, the structured packing used in the absorber of this unit operated nicely even fed with a very low flow of gas and a minimum liquid load. Those parameters were found far below the typical hydraulic values of conventional AGRU's normally designed to handle high velocities of gas at maximized liquid load, in order to minimize the diameter of the absorber. For the encountered start-up condition, the treated gas was on specs and flaring could be avoided.

5. REFERENCES :

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