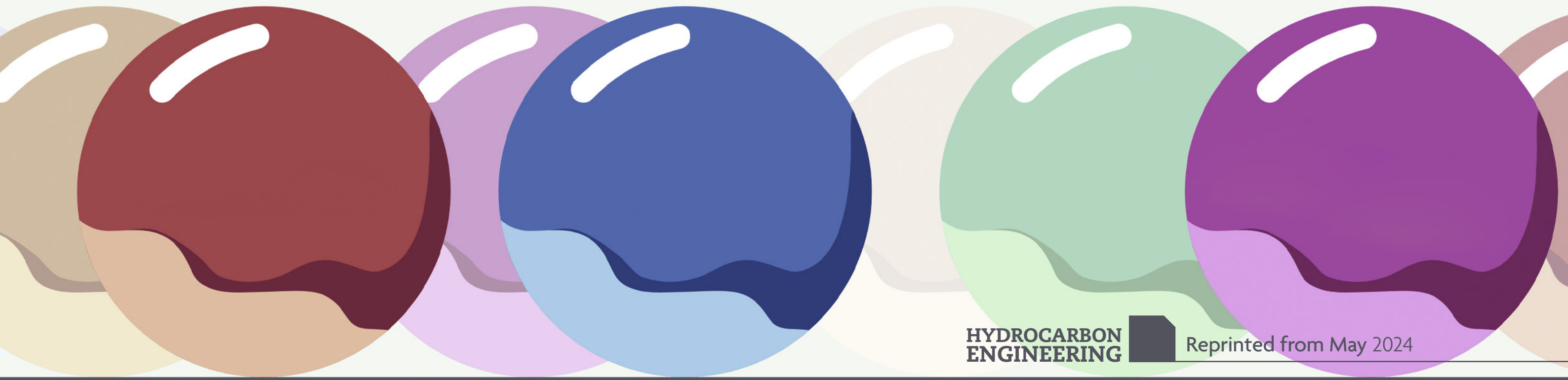
SPECIALISED SOLVENT SELECTION

Ashraf Abufaris, BASF Middle East Chemicals LLC and Blake Morell, BASF Corp., USA, consider how use of a highly H_2S selective solvent can help to optimise capital investment and reduce operating costs.

Selective removal of hydrogen sulfide (H_2S) has become an important topic over the last two decades. Selective designs are tailored either on maximum or controlled H_2S selectivity depending on the application. This article will focus on highly selective designs in low-pressure tail gas treating units (TGTUs) using BASF's OASE® yellow technology in comparison to generic based methyldiethanolamine (MDEA) solutions.

The reaction equilibrium prevents the complete conversion of the sulfur species in the feed gas to elemental sulfur in



sulfur recovery units (SRU or Claus section) to elemental sulfur. Typically, an SRU with two to three Claus reactors is only able to achieve 93 - 98% sulfur recovery efficiency. However, higher recoveries of 99.8% and above are achievable if the remaining sulfur compounds in the SRU tail gas are hydrogenated to H_2S, which is then consequently removed in a selective amine unit (TGTU).

The selection of the proper amine technology for the TGTU is essential to make these projects economically and environmentally viable. Use of a highly H_2S selective solvent, such as OASE yellow, can provide benefits by optimising the capital investment or reducing the operating cost.

During the design phase there are various parameters to influence the H_2S selectivity (and consequently the CO_2 slip) in TGTUs, such as: absorber height, amine circulation rate and absorber internals in the mass transfer zone. However, one of the most effective levers is the amine temperature itself. The H_2S selectivity of generic solvents rapidly deteriorates once the amine temperature exceeds 45°C. A key benefit of the OASE yellow selective solvent is a maintained H_2S selectivity, even in high ambient temperature environments and subsequent high lean amine temperatures of up to 50°C. This avoids installing/operating costly chillers for solvent cooling and makes the design reliable, robust, and flexible for various operational scenarios.

This article will discuss the key parameters for these selective designs followed by real operational start-up data from OASE yellow solvent swaps.

Design options to influence H_2S selectivity

There are a number of factors that influence H_2S removal in the presence of CO_2. Adjusting these parameters plays a critical role in unit optimisation throughout the design, commissioning, start-up, and operation phases.

Type of amine

Historically, MDEA has been widely used in H_2S selective applications in the industry. However, recent stricter SO_2 emission targets that meet the World Bank standard of 150 mg/Nm^3 often require additional chemistry to further boost the performance of MDEA and other amines to achieve tight treated gas H_2S specifications. Besides the performance related characteristics, properties such as volatility, stability, acid gas loading capacity and commercial aspects are important selection criteria.

Lean amine temperature

Selective treatment with amine-based solvents generally takes advantage of the rapid reaction of H_2S compared to the kinetically hindered reaction of CO_2: CO_2 first must react with water to form carbonic acid before the solvent can absorb the CO_2. Thus, tertiary amines such as MDEA are often used for selective applications as they are not able to form carbamates (the only fast reaction with CO_2).

The following reactions of tertiary amines take place in aqueous solutions:

Reaction of water and amine (fast):
$R1R2R3N + H_2O \rightleftarrows R1R2R3NH^+ + OH^-$
$2\ H_2O \rightleftarrows H3O^+ + OH^-$

H_2S reaction (fast):
$H_2S + H_2O \rightleftarrows HS^- + H_3O+$

CO_2 reactions (overall reaction: slow):
$CO_2 + 2H_2O \rightleftarrows HCO_3^- + H_3O^+$ (slow)
$HCO_3^- + OH^- \rightleftarrows H_2O + CO_3^{2-}$ (fast)

In this reaction system, the CO_2 co-absorption and, therefore, H_2S selectivity is heavily influenced by reaction conditions. This means higher pressure and temperature, as well as a higher CO_2/H_2S ratio in the feed gas, favours the CO_2 co-absorption and lowers the H_2S selectivity. Especially at lean amine temperatures above 50°C, which are typical for the Middle East region, the CO_2 reaction accelerates and strongly competes with the H_2S reaction. As a result, a cooling system/chiller is often part of the design in these climates to achieve H_2S selectivity with a MDEA/acidified MDEA solution.

Mass transfer

Besides lean amine temperature and feed gas pressure (partial pressure), the absorber internals, the column height and the liquid/gas (solvent/feed gas) ratio all strongly affect the total mass transfer of the individual components from the gas into the liquid phase. While the mass transfer of H_2S is predominantly gas phase driven, the CO_2 reaction kinetics are mostly related to resistance in the liquid phase. The absorber height and mass transfer surface determine vapour/liquid contact, which directly impacts the reaction selectivity. The liquid/gas (solvent/feed gas) ratio itself not only impacts the mass transfer, but also influences the temperature profile within the absorber impacting reaction kinetics.

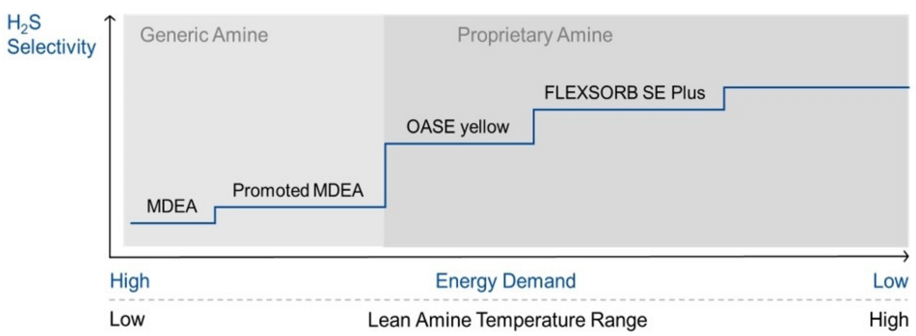


Figure 1. Selective solvent performance comparison.

Selecting the right solvent

While designing a TGTU, one of the most important decisions is selecting the type of amine. A typical gas sweetening amine unit with primary or secondary amines such as MEA or DEA would require a very high amine circulation rate, as these solvents absorb both H_2S and CO_2 almost without any selectivity towards H_2S. For this reason, a more H_2S selective amine must be considered to reduce solvent circulation/inventory, the amount of CO_2 recycled to the SRU, and reboiler duty.

Figure 1 illustrates a comparison between generic amines such as MDEA and acidified MDEA against proprietary amines offered by BASF Gas Treating (OASE yellow and FLEXSORB^{TM} SE PLUS).

OASE yellow was developed to enable the selective removal of H_2S in both high (natural gas) and low-pressure applications (acid gas enrichment or tail gas treatment). The proprietary combination of several amines and a promoter system provides higher acid gas capture capacity and enables lower achievable treated gas H_2S specifications.

FLEXSORB SE Plus is a proprietary gas treating agent that was developed by ExxonMobil Research and Engineering Co., specifically for selective H_2S removal. The FLEXSORB technology is well known in the industry for its high performance, even at high ambient temperatures. The selectivity advantage allows the unit to achieve H_2S removal at lower solvent circulation rates, resulting in lower energy consumption compared to conventional processes. The reliable and simple to operate process is characterised by low corrosion and lower foaming compared to conventional gas treating solvents.

Both OASE yellow and FLEXSORB SE PLUS can achieve high treated gas purity to meet the stricter SO_2 emission targets of the World Bank Standard. In addition, both solvents can maintain H_2S selectivity at high lean amine temperatures (+50°C), which makes designs without an expensive chiller unit possible. On the contrary, generic amines would require high energy demand and lower lean amine temperature to achieve the required H_2S selectivity which increases the unit's costs significantly.

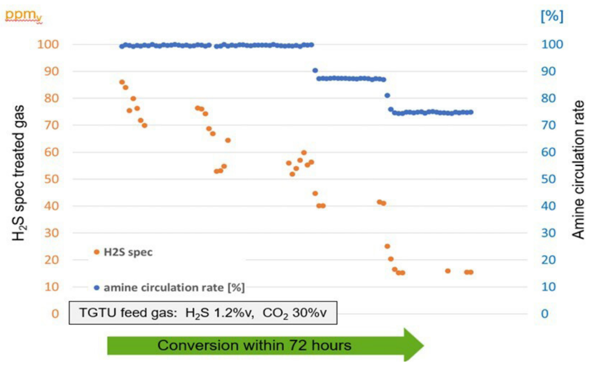


Figure 2. Case study 1: OASE yellow conversion results.

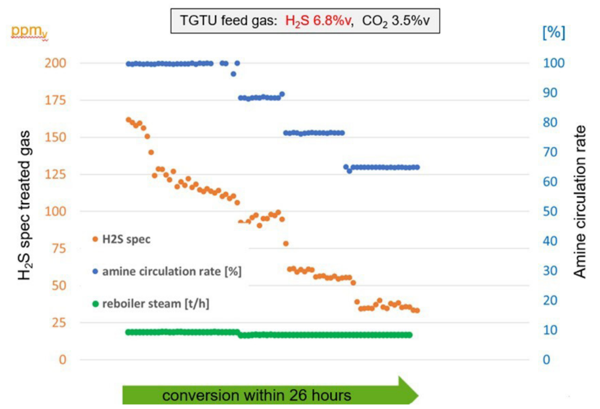


Figure 3. Case study 2: OASE yellow conversion results.

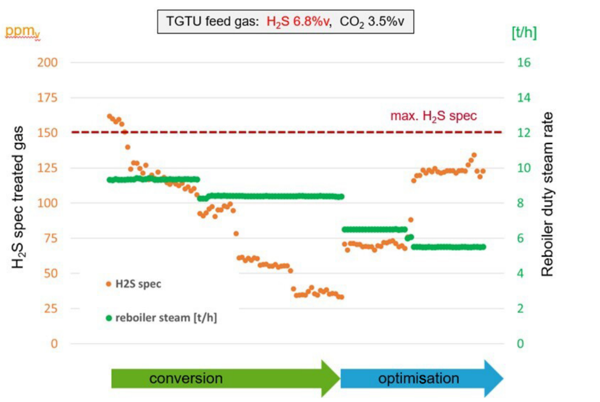


Figure 4. Case study 2: optimisation.

Case study 1

In this case study, a refinery located in Germany operated a TGTU with generic MDEA solvent which often limited the refinery operations. The feed gas to this unit includes 1.2 mol% H_2S and 30 mol% CO_2. The constraint encountered at the TGTU is the environmental permit limit for SO_2 emissions from the thermal oxidiser. This environmental constraint typically occurred in the summer months due to an increase in the lean amine temperatures in the tail gas unit. As the lean amine temperature approached 37.8°C, the amount of H_2S that slipped to the thermal oxidiser increased significantly, resulting in increased SO_2 emissions. To mitigate increased emissions during the summer, the overall SRU capacity needed to be limited even with the use of rented chillers.

These factors warranted a review of alternative technologies and a solvent changeover. However, the refinery already passed the turnaround period, and the operation team had a challenge to changeover the solvent while the unit operated 'on the fly'.

As part of this evaluation, BASF was requested to analyse the possibility of utilising OASE yellow in this unit to reduce the treated gas H_2S content during the summer from 90 ppmv to 35 ppmv. OASE connect, an in-house rate-based model simulator, was used to assess the possibility to meet this target without any mechanical modifications to the existing equipment.

Based on the simulation results, it was concluded that with the addition of OASE yellow enhancer system to the existing MDEA inventory, it was not only possible to meet the H_2S target, but the unit could also reduce the solvent circulation rate to approximately 65% of the current operating level.

The switch increased the refinery's annual average sulfur capacity, which allowed it to run additional sour crude. It was also no longer necessary to rent chillers to cool the lean amine, leading to considerable operating cost savings.

Figure 2 illustrates the actual performance test results collected from the unit during the 72 hour swap process. A noticeable decrease of the H_2S at the outlet of the unit absorber (orange dots) was observed. The solvent circulation rate was able to be reduced at the same time, resulting in operational cost savings for the unit.

Case study 2

In this case study, a refinery located in South Korea operated a TGTU with acidified MDEA. The feed gas to this unit includes a higher H_2S content compared to case study 1 with 6.8 mol% H_2S and a lower CO_2 content of 3.5 mol%. The objective of this study was to reduce the steam consumption while maintaining the environmental permit limit for SO_2 emissions from the thermal oxidiser.

Similar to the previous unit, the changeover from acidified MDEA to OASE yellow had to be carried out during the unit operation without shutting down the process.

BASF completed a study considering the unit mechanical details and concluded that it was possible to reduce the H_2S content from 150 ppmv to 25 ppmv, maintaining the current steam consumption to the unit. In turn, the steam consumption could be reduced by 35% while still meeting the unit's environmental limits.

Figure 3 illustrates the first step of the conversion with the actual performance test results collected from the unit during the 26 hour swap process. As the OASE yellow enhancer system was added to the system, the treated gas H_2S content decreased, even as the circulation rate was reduced by 25%.

In the second step, the steam consumption was reduced by 35%, allowing the H_2S concentration to increase to the acceptable limit of 150 ppmv. This steam rate reduction resulted in an annual OPEX saving of approximately US$1 million for the unit.

Conclusion

The selective removal of H_2S has become an important topic over the last 20 years. With dwindling sweet gas reserves, H_2S selective gas treatment at low pressure (AGE, TGTU, or combinations of the two) has become a necessity to produce a high-quality Claus gas, enabling sulfur removal and monetisation of these gas fields.

Savings in energy and circulation rate (OPEX), as well as a reduction in equipment sizing (CAPEX) are the obvious benefits of enhanced H_2S selective treatment. Many of the newest projects also require a high degree of operational flexibility combined with a robust operation in warm locations enabled by these technologies.

Capacity, operational flexibility, reliability, and the ability to achieve specifications are all considered during BASF's technology selection process utilising the in-house simulation tool, OASE connect.

OASE yellow technology utilising the most common selective base amine, MDEA, allowed for smooth swaps from generic solutions to meet the stricter emission limits as well as optimise the unit operational costs. The technology can also be utilised in grassroots designs to achieve further savings on the capital investment of these projects, making them more economically attractive and feasible.