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Innovation in Materials Development for LNG Dehydration

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Effective dehydration of natural gas to cryogenic specification is a critical stage of the pretreatment train for LNG production. Zeolitic molecular sieves are the only class of adsorbents capable of meeting the required dewpoint for liquefaction. Failure to reach the required dewpoint or inability to maintain the necessary gas flow to the liquefaction section can constrain or shutdown the production of valuable LNG cargo.

The existence of physical effects such as hydrothermal damage and retrograde condensation in the dehydrator vessels during regeneration and adsorption are well understood. These effects are known to lead to degradation of the molecular sieve adsorbent by leaching of the clay binder and loss of adsorption capacity. The resulting increase in pressure drop and mal-distribution of the adsorption and/or the regeneration flow may ultimately require premature adsorbent replacement. Improving resistance to refluxing has focused mainly on improvements to the molecular sieve binder system, whereas reduction of the tendency for refluxing may be mitigated by better management of regeneration.

This paper presents an innovative approach to the refluxing problem based on materials development. This innovation is supported by many years of successful and highly durable installations in cryogenic applications. The paper describes the first retrofit installation of this new development in dehydration of gas for LNG production. It will also discuss potential benefits for new installations such as reduced vessel size and operational security in addition to extended bed lifetimes which could be achieved for existing units.

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Background and History

Increasing demand for LNG - Geopolitical issues stall new projects

The global demand for natural gas continues to grow – consumption growth rates between 2 and 5% p.a. are frequently cited. However, the gap between production and consumption continues to be the primary barrier. As one of the common forms of transportation, LNG offers flexibility and security impossible to offer with hard pipelines. However, one difficulty lies in the requirement that gas for LNG production must be processed to a much lower level of contaminants (e.g., water, heavy hydrocarbons, sulfur, CO_2) than the equivalent volume of gas transported by pipeline. Additionally, the scale of LNG production (notwithstanding the impact of mini- and micro-LNG plants such as peak shavers) means that project cost and approval is dependent more than most on a strong link between gas price and demand. Lastly, geopolitical impacts, such as tariffs, can change project economics in very short timeframes, leading to project FIDs being repeatedly delayed or postponed completely.

The implications are clear; many of the currently proposed projects will not see the light of day in the next 5-10 years. But the demand for LNG will not abate. Thus, incremental upgrades and debottlenecking of existing plants become critical tools for owners and customers alike.

Existing plants look to debottleneck and expand

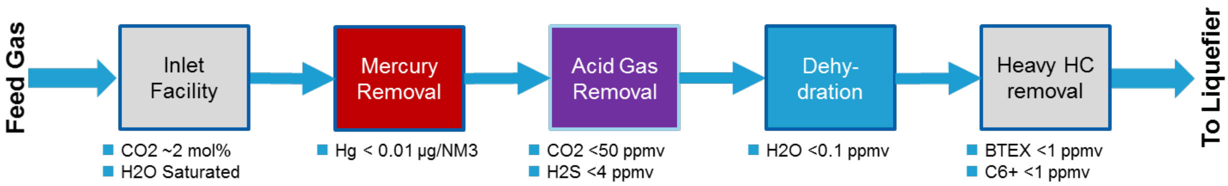

Figure 1

An example of a traditional pretreatment train layout is shown in Figure 1. The sizing of each vessel is determined by the gas flow rate and the amount and type of impurities to be removed. In this paper, the focus is on the dehydrator as a potential source of constraint when considering how to increase the output from the plant. However, unless significant capital can be allocated to increase flow by the simple addition of extra vessels or additional trains, the levers of control are few;

1) Increase gas flow
2) Increase process uptime

As pretreatment trains have been designed to operate at nameplate capacity, either option will significantly affect the performance.

Increasing flow by 10% (for example) can potentially lead to downstream issues such as;

- Plants previously familiar with defrosting heat exchangers only once every six months find that this frequency increases to once per month.
- Bringing in new and unplanned gas sources may bring new contaminants into the mix – e.g., CO_2 increasing in the feed gas will stress the AGRU, and aromatics and/or heavy hydrocarbons not removed upstream can lead to increased risk of freeze-out.

If overall uptime is the approach, the reliability of the train becomes increasingly important.

- Plants familiar with changing out dehydrators or performing compressor maintenance every three years want to increase that interval to four or six years.

Saturated gas from AGRU to dehydrator – faster cycles, shorter ramp

To focus for a moment on the effect of increasing uptime on the dehydration system, clearly the performance of the dehydrator is one of the critical inputs to the downstream liquefaction process. In the typical pretreatment train layout, the dehydrator is directly downstream of the AGRU, so that saturated gas is fed directly into the dehydrator. However, it is well known that the capacity of a molecular sieve is relatively low at saturated conditions when compared to a silica-gel type material (Figure 2).

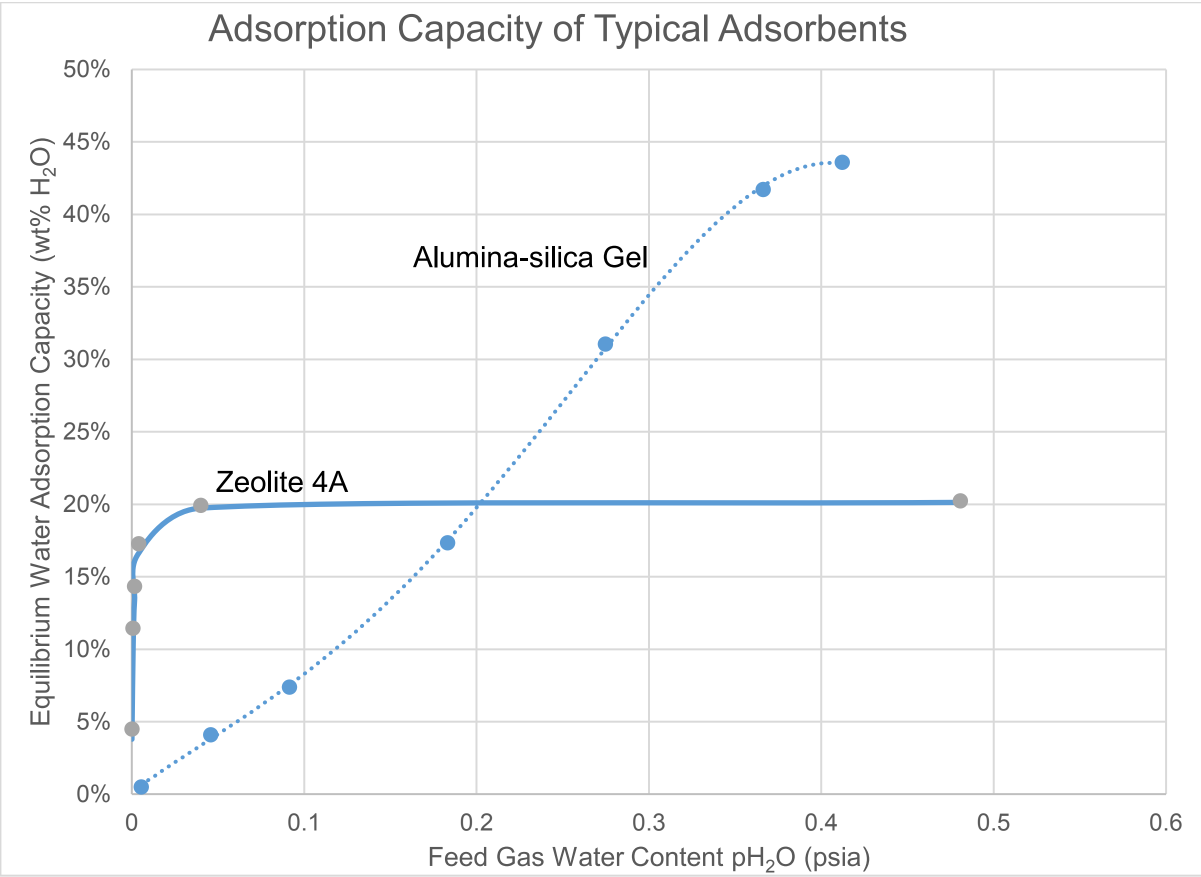

Figure 2 - Variation of Adsorption Capacity with Feed Gas Water Content

BASF has performed time-based multidimensional modeling of a molecular sieve bed under normal regeneration conditions to give a detailed look at the conditions inside the dehydrator during regeneration. An example of the output from such analysis is shown in Figure 3. This plot shows the theoretical capacity of the adsorbent for water under the transient conditions of a regeneration gas thermal wave passing through the bed. A capacity of 1.0 represents saturation of the adsorbent. Capacity >1.0 therefore reflects supersaturation leading to localized condensation. The results show that as the regeneration gas moves through the bed and contacts colder environments (e.g., adsorbent, vessel walls) in the middle to upper part of the bed, the ability of the upper bed to adsorb moisture from the regeneration gas becomes exceeded. At this point, condensation occurs and liquid water

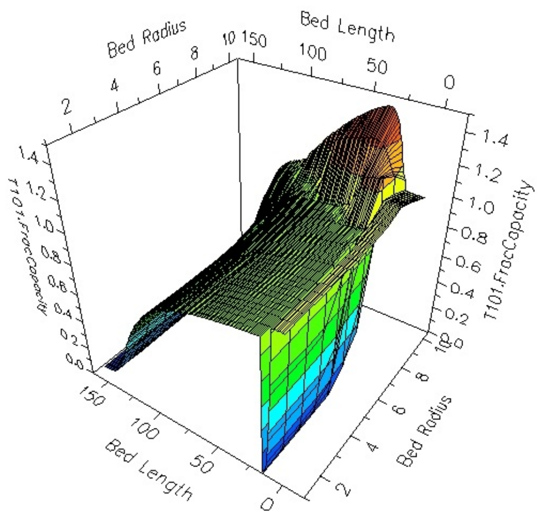

Figure 3

is formed in the bed. The regeneration gas continues to be pushed through the bed, entraining liquid water and leading to a “boiling” effect, commonly known as refluxing.

If the adsorbent would be stable under such conditions, there would be no problem; ultimately the saturated regeneration gas will exit the adsorber and the saturated gas is cooled to condense the water in the regeneration gas separator. However, molecular sieve adsorbents are not completely stable under these conditions; the adsorbent, whether beaded or extruded, is typically formed with a clay binder. It is this clay binder which is attacked by the condensing water, leaching the binder from the adsorbent particle and causing two main effects: 1) deterioration of the adsorbent strength and 2) a “caking” effect as the leached binder is precipitated back onto the exterior of the bead. Such effects can be seen in figures 4 and 5.

Figure 5

Figure 4

Materials Development

Improved molecular sieve binder only goes so far

There are three main areas of focus for reducing the impact of refluxing;

1) Improved thermal management of the regeneration cycle
2) Improved binding mechanism of the adsorbent
3) Modification of the dehydrator design to install a more durable adsorbent

The first is part of good practice in the dehydrator operation. It has been discussed many times (e.g., Ref. 1) and will not be reviewed again here. However, it is important to note that this can only be carried out up to a point; once the gas flow or regeneration time exceeds the design capability of the dehydrator, shortening the operating cycle time by ramping the temperature more quickly may be the only option available.

Improving the binder gives a clear benefit to the overall durability of the process. As part of the development of improved dehydration technology, BASF has introduced a family of adsorbent products under the tradename Durasorb™. This family of products includes molecular sieves with extremely high resistance to the conditions encountered in a refluxing vessel. Details of the development would require a separate paper; a summary of the improved performance as measured in the laboratory is shown here in Figure 6.

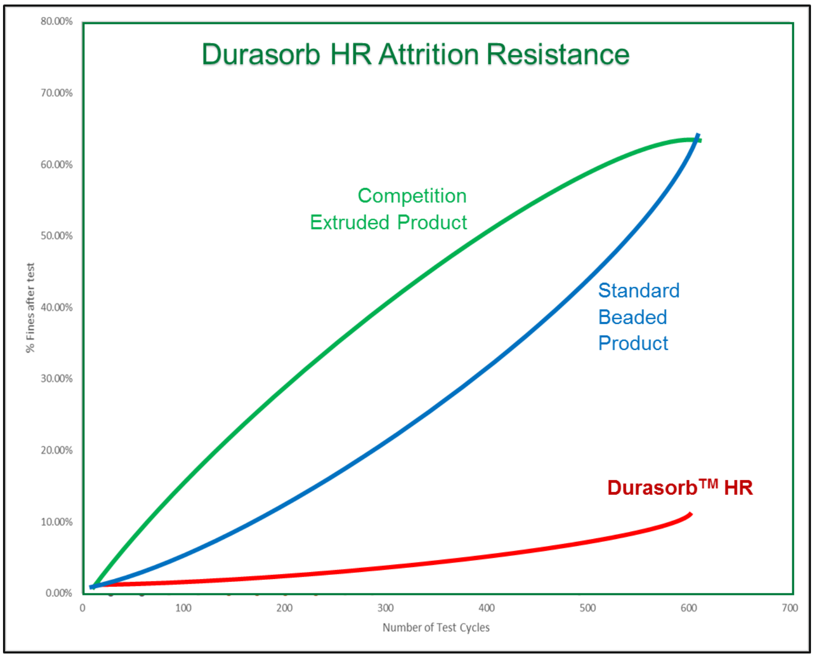

Figure 6

Point 3, modification of the dehydrator design, is the focus of this paper.

High capacity alumina-silica gel offers alternative dehydrator configuration

Referring to Figure 2, it may be noted that molecular sieve has higher adsorption capacity at lower water saturation values than a high-capacity silica-gel such as BASF Sorbead®. However, Sorbead has a higher capacity at higher water saturation than molecular sieve.

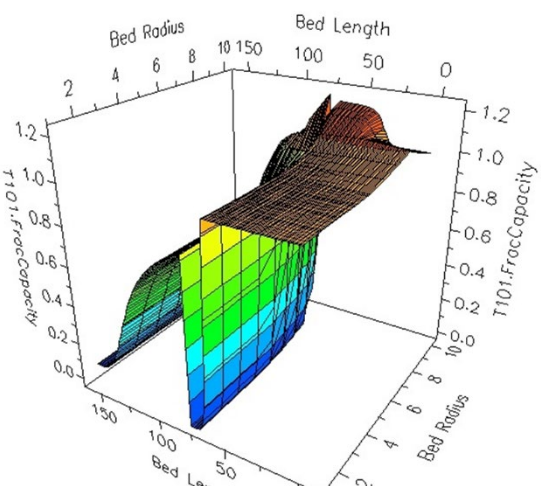

Figure 7

Sorbead by itself is an extremely robust adsorbent. However, it is unable to achieve the very low water dewpoint required by a cryogenic LNG unit. A combination of the two types of products in series is proposed for the optimum combination of dewpoint and durability required.

The advantages of adding a high capacity adsorbent on top of a molecular sieve bed can be seen after a further model run (Figure 7). The calculated super-saturation of the regeneration gas is shown to be significantly reduced. This is not a result of lower moisture content in the regeneration gas, rather it reflects the higher capacity of the alumina-silica gel adsorbent. Of course, a standard silica gel would also show the same benefits of high capacity; it is the superior physical characteristics of BASF Sorbead which allows such a design to be considered.

Sorbead has been used in natural gas treatment applications to protect high pressure gas transmission applications for more than 60 years, initially in relatively small dehydration applications and then combined with dehydration and hydrocarbon dewpoint control.

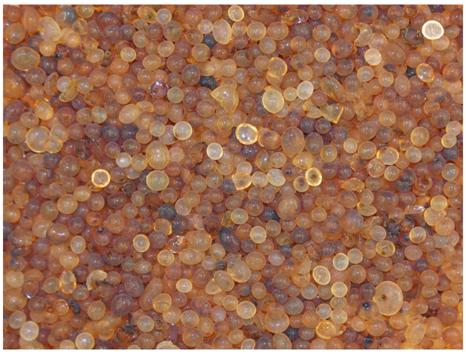

Figure 8 - Sorbead H/R (2-5mm beads)

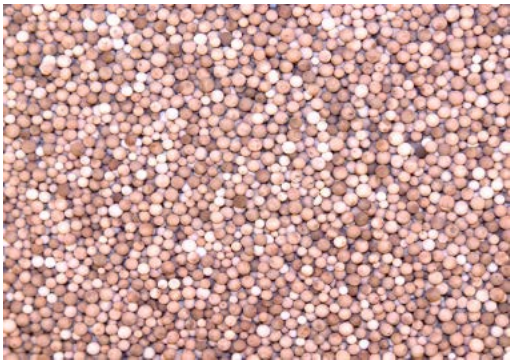

Figure 9 - Sorbead WS (2-5mm beads)

BASF Sorbead adsorbent is a specially formulated partially dehydrated form of polymeric colloidal silicilic acid with the chemical composition $SiO_2*Al_2O_3*H_2O$. Examples of BASF Sorbead products are shown in figures 8 and 9.

Sorbead is manufactured in a unique “oil-drop” process which allows control over the internal structure of the beads. These beads have unique physical properties which allow the optimum combination of adsorption performance, at the same time providing hard, attrition resistant properties.

The bead size distribution can be tailored to meet the required application but are generally supplied in the form of 2 - 5 mm beads which produces the maximum bulk density combined with minimum pressure drop. Because of its properties, Sorbead can be used in very large-scale units with individual beds containing over 100 tons of Sorbead.

Case Study 1: Cryogenic (non-LNG) Application

In the 1980s pioneering developments by British Gas resulted in the confidence to apply the Sorbead technology to very large-scale applications. Between 1985 and 1990 British Gas carried out a study to determine the optimum process for a greenfield onshore gas processing terminal in Barrow, UK, to process gas from the North Morecambe gas field. The original paper (Ref. 2) gives full details of the overall gas processing requirements, including the need for cryogenic nitrogen removal before sending the gas into the National Grid. As part of the overall process, a hydrocarbon dewpoint control system was required upstream of the cryogenic N_2 removal process and a molecular sieve bed was installed between the hydrocarbon dewpoint control unit and the cryogenic section to reduce the water dewpoint of the gas to cryogenic specifications.

The process of selecting the hydrocarbon dewpoint control system is described fully in the reference. The following technologies were considered for the hydrocarbon dewpoint control unit:

a. Refrigeration
b. Joule-Thomson cooling
c. Turboexpander
d. Adsorption

After consideration of Capex, Opex, reliability and environmental considerations, adsorption was chosen using Sorbead.

The North Morecambe field on-shore terminal was commissioned in 1994 with the following gas processing layout (figure 10);

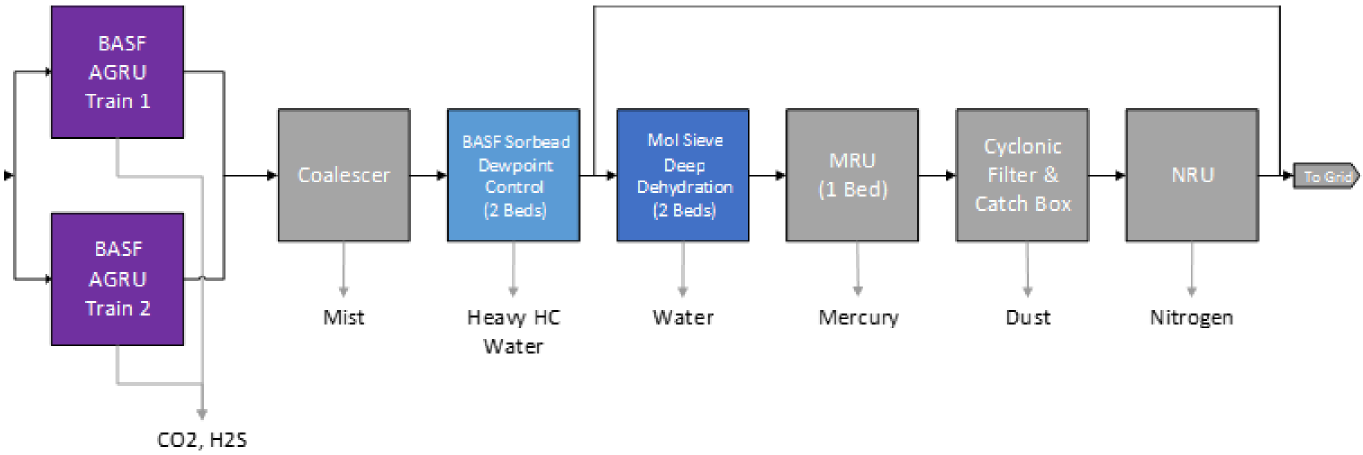

Figure 10

Process studies during conceptual design phase had identified a single train Sorbead unit as the most cost-effective means of controlling both the required water and hydrocarbon dewpoints in addition to other operational and environmental benefits. However, during commissioning trials it became apparent that the water dewpoint that was achieved from the Sorbead unit in HRU mode was lower than expected. A molecular sieve “water polisher” had been installed downstream of the Sorbead unit in the initial design phase to achieve the cryogenic water dewpoint of <0.1 ppm(v); the low dewpoint achieved by the Sorbead unit allowed a very long adsorption cycle time of several days in the polishing unit.

The overall benefit of this layout yielded an extremely long lifetime for the downstream molecular sieve water polisher. Upon changeout of the adsorbent in 2014, after 19 years of operation, it was concluded that the molecular sieve could have lasted much longer. The impact of the upstream Sorbead unit on the reliability of the train cannot be overstated.

The benefits of using both Sorbead and molecular sieve in a dehydration process to achieve the required dehydration for cryogenic processing is thus demonstrated based on experience from the North Morecambe terminal over many years’ operation in terms of extended molecular sieve lifetime.

Development of Durasorb™ Concept

Based on proven benefits of the combination of ultra-stable adsorbents such as Sorbead and highly durable molecular sieve, BASF has recently introduced new products and technology which combines the advantages of both types of adsorbents in a single bed. The Durasorb concept is based on a layer of water stable alumina-silica gel adsorbent above the molecular sieve that is much larger than the typical 10% layer used for protection from liquids carryover. Together with a highly stable molecular sieve to ensure that the cryogenic dewpoint is reached, such a design offers significant improvements in the durability, and thus reliability, of the dehydration process.

Here, as in the North Morecambe example, the upper layer of robust Durasorb HD, which is resistant to exposure to liquids during regeneration, will extend molecular sieve lifetime by protecting the molecular sieve from reflux of liquids during counter flow regeneration heating.

Figures 11-13 show examples of the various configurations possible with the Durasorb technology. Many other combinations are possible and require a close evaluation of the specific conditions within the gas plant to provide an optimized solution.

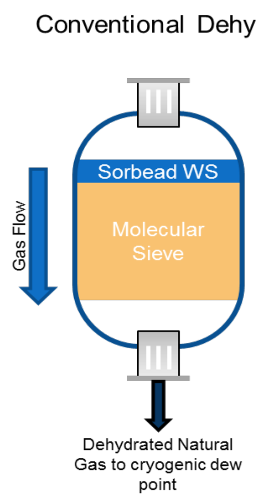

Figure 11 – Conventional Dehydration

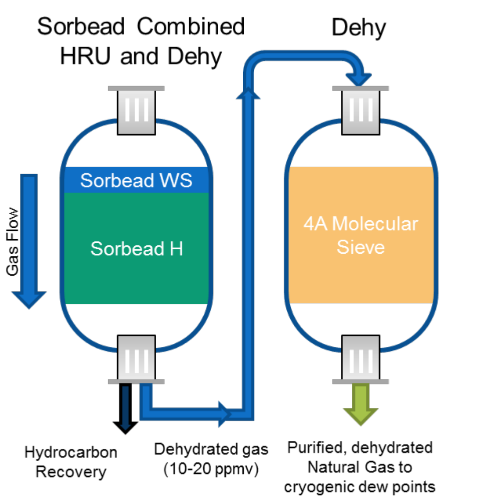

Figure 12 - North Morecambe Cryogenic Dehydration

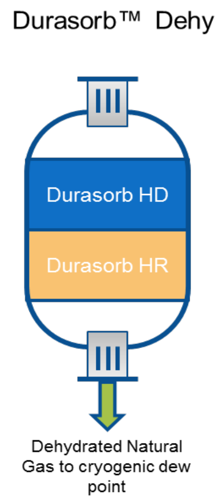

Figure 13 - Durasorb Dehydration Technology

Case Study 2: NGL reliability improvement

Although it is not an LNG application, natural gas liquids (NGL) production, just as the N_2 rejection stage at North Morecambe, requires dehydration of natural gas allowing cooling to cryogenic dewpoint. Such cooling is usually accomplished in a turboexpander, with an upstream molecular sieve dehydration bed to dehydrate the gas to the required dewpoint. Plants tend to be small but are no less dependent upon stable, reliable dehydrator service to permit steady production of valuable NGL.

A US pipeline operator and NGL producer was experiencing significantly reduced dehydrator lifetime, in some cases less than six months before changeout was necessary. In 2014, BASF technologists proposed a Durasorb solution comprising a combination of Durasorb HD liquid stable silica-alumina gel and Durasorb HR3 hydrothermal cyclic stable molecular sieve.

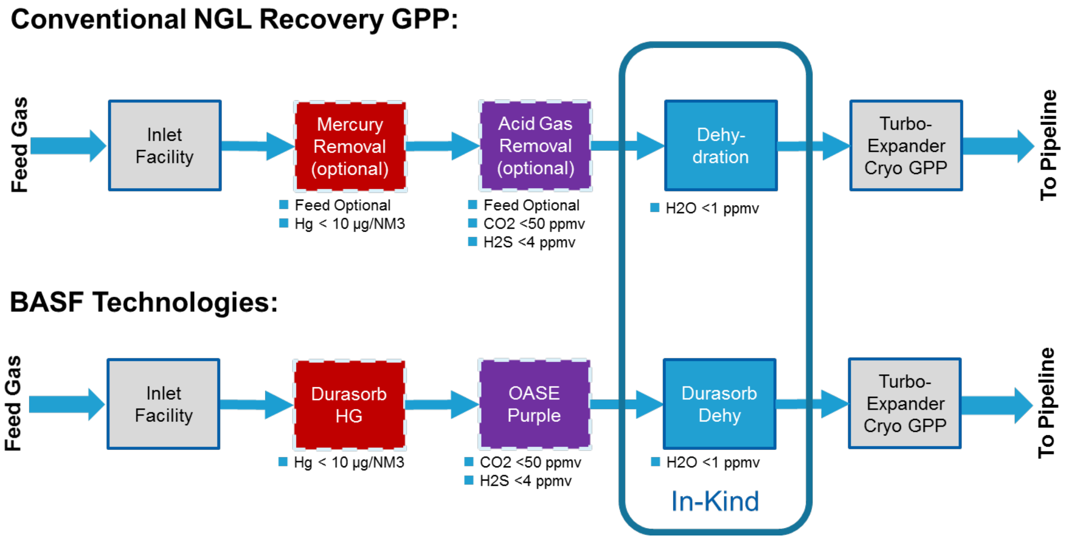

Figure 14 - Durasorb Dehy can be used as a direct replacement in conventional gas processing plants (GPP)

A retrofit installation into an existing NGL plant requires no reworking of any vessels, piping, valves or ancillary equipment. A comparison (figure 14) of a conventional design to a Durasorb design shows the “in-kind” replacement of the adsorbent for dehydration.

After installation, the performance of the dehydrator was closely monitored by the operator and BASF technologists. The lifetime of the train has been extended from six months to greater than two years. BASF continues to work closely with the operator to optimize the design and performance.

Case Study 3: LNG Dehydrator debottlenecking

The first application for the new Durasorb technology in LNG has been installed at a world-scale LNG plant which has been operating over 10 years. The plant has a traditional layout running on a mixture of pipeline gas stripped of NGLs upstream plus wellhead gas. The flow rate is nominally 680 MMSCFD at 71 bar, and the target H_2O content exiting the dehydrator is <0.3 ppmv.

Due to increased flow from a new offshore platform, the dehydrator was performing poorly. Increasing pressure drop and an increasing tendency for exceeding the outlet water concentration at the end of the adsorption cycle was observed within the first 2 years of start-up of a new bed.

Additionally, increasing demand on production was being met with shorter regeneration ramp cycles. These were causing refluxing in the bed, causing binder leaching and ring formation in the vessel.

BASF technologists created a computer model of the existing bed layout. The model output confirmed that refluxing would be expected to occur in the middle-upper portion of the bed during operation. The solution proposed was to install a Durasorb bed consisting of 30% Durasorb HD (water-stable high capacity silica-alumina gel) in the upper layer, and Durasorb HR (new, hydrothermal cyclic resistant molecular sieve) in the lower section of the bed. As COS formation was also considered to be a concern, Durasorb HR3 was chosen as the molecular sieve.

Installation was a simple exchange of adsorbents. No modifications to the internal structure of the vessel were necessary.

Since installation, BASF technologists have worked closely with the client to optimize the regeneration cycle and ramp time to ensure any refluxing takes place in the water-stable Durasorb HD, where no damage to the adsorbent can occur. The dehydrator continues to operate on longer adsorption cycle times compared to previous adsorbent installations, illustrating additional bed capacity and margin. All parameters are within Durasorb design projections and the improved design is expected to give a minimum 2x life over the original configuration.

Path Forward

Retrofit

BASF's new Durasorb solution is proposed as a retrofit for existing LNG dehydrators where longer lifetime and increased durability is required. No physical changes to the dehydration vessel or ancillary equipment are necessary. BASF technologists can identify and propose the optimum combination of products, together with detailed operating parameters, for the specific conditions and goals of each dehydrator.

New designs

A not-insignificant benefit of Durasorb is a positive impact on the design of dehydration vessels for floating LNG (FLNG) installations. The higher capacity of the silica-alumina gel section of the Durasorb configuration makes it possible to design a smaller vessel. Under normal circumstances this would not make a significant impact on project costing as even $1.0 million on the overall cost of a world-scale LNG train is marginal. However, the potential weight savings on a floating platform and the resulting engineering advantages of lower topsides weight offers benefits for owners and operators of such installations. These benefits will be quantified in future publications.

Summary and Conclusions

BASF has built on many years of successful and highly durable adsorbent applications in gas processing to bring an innovative materials development solution to the problems experienced in LNG dehydration. Using BASF's Durasorb family of products, combined with BASF expert designs, can reduce and even eliminate downtime due to dehydrator damage caused by refluxing and retrograde condensation. BASF Durasorb offers the owners and operators of any cryogenic facility significant benefits in reliability and throughput, resulting in increased profitability.

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2. Mayer, M., Crowe, T., THE PRODUCTION AND PROCESSING OF MARGINAL AND/OR DIFFICULT FIELDS: North Morecambe Onshore Terminal, Institute of Chemical Engineers (1996)