# INCREASED DEHYDRATION BED-LIFE REDUCES TURNAROUND COSTS AND ELIMINATES UNPLANNED SHUTDOWN: NGL AND LNG GAS PLANT DURASORB CASE STUDIES

Margaret Greene and Justin Pan
BASF Corporation
New Jersey, U.S.A

Tobias Eckardt
BASF Catalysts Germany GmbH
Nienburg, Germany

ABSTRACT

BASF has developed novel dehydration unit bed configurations to address the problem of premature adsorbent replacement. These bed designs dramatically reduce the effects of regeneration reflux in the molecular sieve section of the bed and reduce coke formation on molecular sieve. Depending on the problem to be solved, BASF experts choose from a broad portfolio of adsorbents, then design the bed with multiple adsorbent layers with the necessary ratio of products to solve the problem.

Durasorb™ Dehydration bed designs rely on the unique properties of Durasorb HD, a high capacity, silica-alumina gel material that is resistant to hydrocarbon liquids and water. Dehydration beds designed by BASF technology experts utilize Durasorb HD at the top of the bed with Durasorb HR, a reflux resistant molecular sieve, at the outlet. Durasorb dehydration beds last, on average, two times longer than the same units filled with competitor materials. Extending the lifetime of the dehydration unit eliminates operational expenses by reducing the number of turnarounds and reduces the costs of lost production from plant downtime.

## Introduction

Effective dehydration of natural gas to cryogenic specification is a critical step in the operation of an LNG production plant or NGL extraction plant.[I] Failure to reach the required water dewpoint can shut down the plant; increase in pressure drop can cause reduced throughput. Both situations result in lost production; as a rule of thumb, 0.5 bar dP increase results in 0.5% loss of LNG production efficiency. Zeolitic molecular sieves are a class of adsorbents capable of meeting the required dewpoint for liquefaction. However, these materials are susceptible to physical degradation.[II,III] A refluxing environment can cause caking and increased pressure drop. Coking of the molecular sieve can occur in the presence of hydrocarbons, causing a decrease in water capacity.

The existence of physical effects such as refluxing 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 coking of the material. The resulting increase in pressure drop and maldistribution of either the regeneration or adsorption flow may ultimately require premature adsorbent replacement. Addressing this challenge has focused previously on improvements to the molecular sieve binder system to increase resistance to refluxing. Other mitigation options include reducing the tendency for refluxing conditions by better management of regeneration and/or new material configurations in the bed.

BASF has developed novel dehydration unit bed configurations to address the problem of premature adsorbent replacement.[IV] These bed designs dramatically reduce the effects of regeneration reflux in the molecular sieve section of the bed and reduce coke formation on molecular sieve. Depending on the problem to be solved, BASF experts choose from a broad portfolio of adsorbents, then design the bed with multiple adsorbent layers with the necessary ratio of products to solve the problem.

To address the issue of molecular sieve degradation due to regeneration reflux conditions, BASF uses proprietary modeling to predict the location of reflux in the bed, then designs a multi-layer adsorbent bed configuration utilizing Durasorb HD on the top and Durasorb HR on the bottom (Figure 1). Durasorb HD is a high capacity, silica-alumina gel material that is resistant to hydrocarbon liquids and water. Durasorb HD protects the Durasorb HR (new, hydrothermal resistant molecular sieve) section of the bed from the refluxing environment, reducing molecular sieve degradation. The ratio of Durasorb HD to Durasorb HR is determined by BASF technologists, aided by the modeling software.

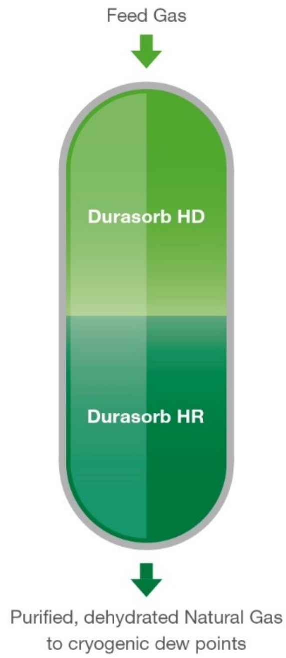


Figure 1. Dehydration bed layered configuration.

The multi-layer bed configuration approach also addresses the issues caused by retrograde condensation. Using simulation tools optimized with decades of experience and high-pressure unit R&D data, BASF technologists can predict the location of each component in space and time. This information aids in designing the bed to prevent retrograde condensation by shifting the phase envelope, removing traces of C10+ hydrocarbons. Adjusting the ratio of Durasorb HD to Durasorb HR and cycle time reduces the concentration of hydrocarbons entering the molecular sieve section of the bed, which reduces the tendency for coke formation.

## Materials for hydrocarbon and water adsorption

The Durasorb technology achieves hydrocarbon and water removal by selective adsorption on fixed beds of adsorbents. The process relies on physical adsorption principles, which can be considered like a condensation process in which the material holds the adsorbed molecules in the internal structure. This process generally follows the rules governing the phase behavior of hydrocarbons and water. The Durasorb HD structure holds a positive charge due to the unbalanced charge on the adsorbent surface. Molecules which exhibit a charge or polarity are attracted to the charged surface, causing water to be readily adsorbed and even displace more weakly attracted molecules. Heavy hydrocarbons condense within the pore structure due to capillary condensation. Thinking about adsorption as a condensation process, the higher the hydrocarbon molecular weight the more readily it will condense. As there is only a fixed pore volume within the material, adsorption continues until the pores have saturated. However, more strongly adsorbed molecules such as water, methanol, aromatics (BTEX), or heavier hydrocarbons can displace previously adsorbed lighter hydrocarbons. Aromatics are more strongly adsorbed on Durasorb HD than the equivalent carbon number alkane.

## Solving the Problem of Short Dehydration Bed Life

### Eliminating the effects of regeneration reflux

Due to the unique physical properties of Durasorb HD, the material is hydrocarbon liquid and water stable. This stability provides the bed with an important performance capability. Not only can the bed now withstand unplanned liquid carryover, the bed can also be designed to protect the molecular sieve section from reflux caused during regeneration. Using proprietary modeling tools, BASF predicts the location in the bed where reflux will occur and uses this prediction to design the bed with the required amount of Durasorb HD on top of Durasorb HR. This approach was used in an Africa LNG plant that was experiencing poor dehydration unit performance.

#### *Case Study 1: Extending the life of the dehydration unit in an Africa LNG Production Plant*

To increase performance and lifetime of the Africa LNG plant dehydration unit, BASF technologists created a computer model of the existing bed layout. The model output confirmed that refluxing would be expected to occur in the upper portion of the bed during operation. One frame of the time-resolved computational analysis is illustrated in Figure 2. The red peak shows significant oversaturation of water in the hot regeneration gas in a defined zone of the bed close to the vessel wall. Condensation of water and subsequent regeneration reflux are known and well described mechanisms for cake formation in molecular sieve beds.

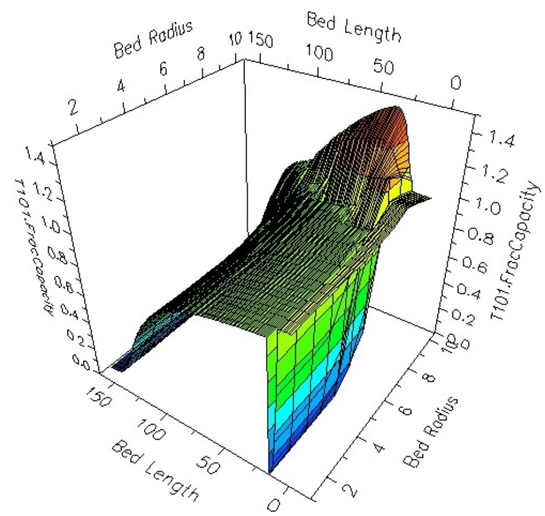


Figure 2. Computational analysis of regeneration reflux.

To solve the problem of short bed life caused by regeneration reflux damage to the molecular sieve, BASF proposed to install a Durasorb bed consisting of 30% Durasorb HD in the upper layer, and Durasorb HR 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. During adsorbent bed unloading, damage to the molecular sieve was confirmed by observation of a significant "donut-ring" crust of molecular sieve powder sticking to the vessel wall (Figure 3).

Figure 3. Donut-ring formation from molecular sieve caking in the dehydration vessel.

Since installation, BASF technologists have worked closely with the client to adjust the regeneration cycle and ramp time to optimize the location of refluxing 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. After two years of operation, all operational parameters are within Durasorb design projections and the improved design is expected to give a minimum two times the life over (4 years) the original configuration.

## Reducing the effects of retrograde condensation

Durasorb HD has the ability to remove heavy hydrocarbons from natural gas. This ability reduces the concentration of hydrocarbons in the gas going to the molecular sieve section of the bed, therefore reducing the tendency for coking. Coking has been shown to be a mode of failure of the dehydration unit in a North America NGL extraction plant. Using the Durasorb multi-layer adsorbent design, the dehydration bed life has been extended three times that of the incumbent.

### *Case Study 2: Extending the life of the dehydration unit in a North America NGL extraction plant with high acid feed gas*

An NGL recovery plant in North America was experiencing very short bed life of the molecular sieve dehydrator.[v] The dehydration unit operates on a variable adsorption cycle with a fixed regeneration cycle time of 20 hours. Feed gas to the unit is associated gas from enhanced oil recovery (EOR) operations and contains a high level of CO2. Feed gas with high CO2 content is acidic, therefore acid-resistant grade molecular sieve, i.e. natural chabazite, is required. Employing specialized acid-resistant molecular sieve in the unit did not solve the problem of premature failure, which occurred within six to nine months of startup. Coking and caking of the molecular sieve material in the dehydrator caused the NGL recovery unit to shut down due to freezing in the distillation column, negatively impacting NGL and oil production.

To extend dehydrator bed life, plant operations conducted an extensive component analysis and found traces of very heavy hydrocarbons (C30+) in the feed gas. It was concluded that, in the presence of heavy hydrocarbons (HHC), the molecular sieve was not fully regenerated under normal regeneration conditions (290°C); the HHC remained on the sieve and caused coking. Based on this finding, operations attempted to mitigate coking by lowering the regeneration temperature to 250°C. Unfortunately, even with lower regeneration temperature, operations continued to observe molecular sieve degradation and loss of about 1 hour of adsorption time per week, resulting in reduced throughput.

As a result of molecular sieve coking, water capacity was reduced and freezing in the distillation column was observed. Over time, the plant was forced to reduce throughput to defrost the column. To reduce freezing, water specification was tightly held at 0.1 lb/MMSCF (2 ppmv) and continuous methanol injection into the top of the column was required. These mitigation measures resulted in additional OpEx costs and only served to modestly extend bed life. Reducing regeneration temperature, closely monitoring water outlet concentration, and methanol injection into the column did not solve the operational challenges and short bed life experienced by the NGL recovery plant. BASF technology experts were consulted and proposed a Durasorb solution.

BASF solved the problems experienced by the NGL recovery plant by first modeling the unit using proprietary design software, then designing a multi-layer Durasorb bed. The Durasorb multi-layer bed solved the coking problem by utilizing Durasorb HD at the inlet of the bed. Durasorb HD adsorbs HHCs, significantly reducing the concentration going to the molecular sieve section of the bed. Durasorb HD material has a lower heat of adsorption temperature, therefore the HHCs are easily regenerated from the material. Durasorb HD also removes water from the feed gas with a high equilibrium capacity. Finally, Durasorb HD is an acid resistant adsorbent, therefore the high acid gas feed conditions do not impact the performance. Employing the Durasorb combination bed design solved the operational issues and extended the bed life from six months to 24 months (Figure 4).

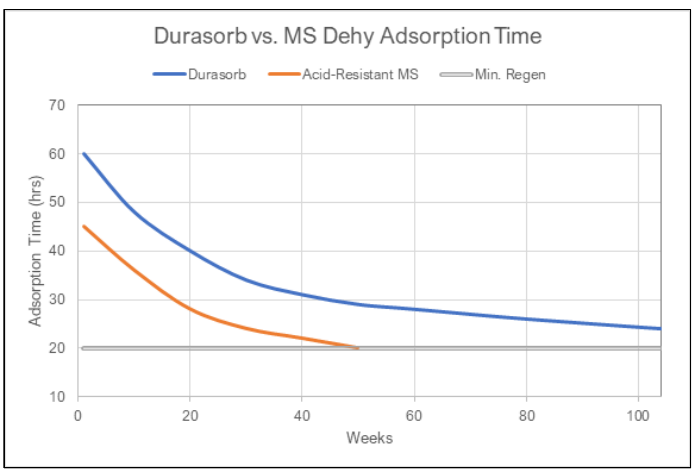


Figure 4. Dehydration bed with a Durasorb design achieves longer cycle times and longer lifetimes than a dehydration bed utilizing acid resistant grade molecular sieve.

## Summary

BASF first introduced Durasorb technology to the market to extend dehydrator unit life by reducing the effects of regeneration reflux on molecular sieve. The approach was to use a water stable adsorbent to protect the molecular sieve and to develop a molecular sieve that was more robust to a refluxing environment. The Africa LNG plant is an example of the successful implementation of this approach. Durasorb multi-layer beds have also been shown to reduce coking of the molecular sieve by reducing the concentration of hydrocarbons in the gas going to the molecular sieve. Furthermore, Durasorb HD material is acid resistant, allowing for use in high acid gas environments where even "acid-resistant" molecular sieves fail. The North America NGL extraction plant is an example of utilizing the Durasorb bed design in a high acid gas stream that also contains HHCs to extend dehydration bed life. The unique properties of Durasorb HD, including water resistance, the ability to adsorb both water and hydrocarbons, and stability in acidic environments, have been instrumental in solving problems in existing units. Durasorb installations have, on average, doubled the lifetime previously achieved in the unit. Operators of Durasorb dehydration units around the world now have reliable operation and performance, leading to a reduction in operating costs and lost production.

## References

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