EXTENDING MOLECULAR SIEVE LIFE IN NATURAL GAS DEHYDRATION UNITS

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ABSTRACT

Today’s natural gas plant designs and operating conditions have led to an increased severity of regeneration conditions for the molecular sieve inlet gas dehydrators. High moisture concentrations, large temperature gradients, high pressure regeneration gas, and dehydrator vessel design practices often trigger the formation and refluxing of free liquid water. During regeneration, hot gas that is saturated with hydrocarbons and water comes into contact with the top vessel head and upper section of the molecular sieve bed causing condensation to occur both in the bed and on the vessel walls. These condensed liquids temporarily accumulate in the top section of the molecular sieve bed, and are subsequently vaporized by the advancing regeneration gas heat front. The intimate contact of molecular sieve with the rapidly vaporizing liquid water and hydrocarbons in this liquid reflux zone results in accelerated particle break-up; leading to (non-uniform) pressure drop build-up through the molecular sieve bed and ultimately channelling and premature water breakthrough. On inspection, such molecular sieve beds have shown broken particles and dust that has compacted in a layer that can vary in depth from several tens of centimeters to, in extreme cases, the majority of the bed. The uses of a protective (guard bed) layer and other process solutions have proven ineffective, or at best, offer only limited relief.

MOLSIV™ UI-94 Adsorbent was developed to overcome the problems of rapid break-up and pressure drop increase caused by such rapidly condensing and vaporizing liquid water and hydrocarbon reflux. This molecular sieve formulation is now installed in many severe service natural gas driers in North and Central Africa, the Far East, the Middle East and North America. Molecular Sieve operational life in these units has doubled compared to standard 4A-type products.
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INTRODUCTION

Molecular sieves have been used in the natural gas processing industry for many years to purify and dehydrate natural gas. Molecular sieves are the product of choice for the deep dehydration required by LNG (Liquefied Natural Gas) or NGL (Natural Gas Liquids) facilities. The active constituent of a molecular sieve adsorbent is a microporous, crystalline, alkali-metal alumino-silicate, referred to as a zeolite. Originally discovered as minerals in nature, zeolite crystals are now grown synthetically under carefully controlled conditions to yield a product of very high purity and precisely uniform properties. The most distinguishing feature of molecular sieves as a class of adsorbents is that they are crystalline rather than amorphous materials. Consequently, they have a definite and highly ordered chemical composition that produces a structure in which all of the unit cells are identical. A unit cell is the smallest repeatable structural unit similar to what a monomer is to a polymer. Essentially the entire adsorption surface is contained inside these unit cells which comprise the zeolite crystal. These unit cells are interconnected by openings (pores) in their adjoining faces. The ability to control the size and uniformity of the pore openings is the key to producing a true “sieving” action on a molecular level.

The size of the pore openings of a molecular sieve controls access to the internal adsorption surface. Molecules that are larger in size than the zeolite pore opening are effectively excluded. Only those molecules with effective diameters smaller than the pore openings are admitted into the internal cavities where they are then strongly adsorbed by the highly charged internal surface. The framework of this internal surface has a net negative electronic charge. Alkaline and alkaline-earth cations are typically present to balance this negative charge but, because of steric hindrance, these cations can only occupy certain sites in the cavities. The internal surface is then composed of islands of positive and negative charge. This environment is perfect for molecules that exhibit polarity themselves. Therefore, polar molecules are strongly preferred in zeolites. This feature makes zeolites a perfect choice for natural gas dehydration and purification since the natural gas components (methane, ethane, propane, etc.) are non-polar and the usual contaminants are polar compounds (water, carbon dioxide, hydrogen sulphide, etc.). This is the main reason that, for example, the equilibrium capacity for water at low partial pressures is much higher for molecular sieve than activated alumina or silica gel. This higher capacity for water is why molecular sieve zeolites are chosen for gas processing applications where there is a requirement for extremely low dew points.

The choice of the alkaline or alkaline-earth cation can change the size of the pore openings and thus the selectivity of the adsorbent for different size molecules. This is the basis for the UOP Molex™ process where based on size alone, normal paraffins can be easily separated from isoparaffins of the same carbon number. The choice of cation is also important depending on the particular contaminants which one wishes to remove. For dehydration, the sodium cation is an excellent choice because of its high selectivity and affinity for water. The sodium form of UOP Type A zeolite is the adsorbent of choice for natural gas dehydration.

Another key variable in the selection of a molecular sieve product, and the principal focus of this paper, is the binder used to hold the zeolite crystals together. Most commercial molecular sieve products used in process applications are in the form of shaped particles (e.g., extrudates or beads). In these forms, the zeolite crystals are usually embedded in a binder. While only a minor component in the product, the binder plays an absolutely vital role in the performance of the product. The binder is
necessary to give the zeolite crystals their aggregate shape but it cannot interfere with access of the process fluid to the zeolite crystals. The zeolite crystals themselves are microporous solids (pore size in the range of 3 to 10 Å in diameter, depending on the zeolite and cation type). The binder particles are smaller than the zeolite crystals and serve as a bridge between the crystals “gluing” them together. Since the binder is amorphous in nature, it will introduce mesopores (10-300 Å) and macropores (>300 Å) into the overall structure. These larger pores are necessary to bring the impurities to the zeolite crystals where they can be adsorbed. However, too many large pores will lead to excessive co-adsorption of the heavier hydrocarbon components in the feed, catalytic effects upon regeneration, and liquid entrainment. Any of these effects could have a significant impact on the life of the product ranging from coking, to pore blockage and particle break-up. By developing a product with the appropriate binder, UOP can tailor a molecular sieve to a specific application, whether it be low catalytic activity or break-up resistance. Binder selection must also allow for mechanical strength of the adsorbent particle, it must have an open structure to allow easy transition of adsorbate molecules from the bulk fluid phase to the zeolite crystals and it must remain stable when subjected to numerous regenerations.

**DISCUSSION**

**Molecular Sieves in Gas Plants**

Although molecular sieves are crucial to the well-being of a modern gas plant, they aren’t always given appropriate attention due to their relatively minor cost compared to the overall cost of the plant. Unless careful consideration is given to the design conditions for the dehydration unit, it is easy to underestimate the severity under which the molecular sieves are expected to perform. Proper understanding of sieve capabilities, operating requirements and above all their limitations can greatly simplify plant operations and will have a significant impact on future plant operating and maintenance costs.

Modern natural gas plant designs and operating conditions have tended to exacerbate the aggressive regeneration environments that cause problems to a molecular sieve such as free water, high temperatures and high pressures. Reflux tends to occur during the preliminary heating stage in natural gas driers operating with a high pressure regeneration gas. During the early stage of the heating step of the regeneration cycle, hot regeneration gas that is saturated with hydrocarbons and water comes into contact with the top header at ambient temperature and upper section of the molecular sieve bed (especially at the side walls) before they have had time to heat up. This results in significant condensation both in the bed, at the sides and on the top section of the vessel. The condensed liquids accumulate in the top and side sections of the molecular sieve bed and form a liquid zone that the rising, hot regeneration gas must pass through. The liquid hydrocarbons will boil off as the temperature rises through the bed. The vaporization of the hydrocarbons leaves free water in physical contact with the adsorbent. Certain components of the binders used in standard 4A products are somewhat soluble in liquid water. The degree of solubility that occurs in each regeneration cycle will depend on the pH (a measure of the acid/base content), temperature, and length of time that this free water is in intimate contact with the adsorbent. Some of the soluble components can ion exchange with the zeolite and/or combine with anions in the liquid water to form solid salts (i.e. Na<sub>2</sub>CO<sub>3</sub>, CaCO<sub>3</sub>, MgCO<sub>3</sub>, NaNO<sub>3</sub>, etc.) when the water evaporates. The solid salts then cement the remaining pellets or beads together to form a solid mass. This solid mass will not allow gas to pass through and consequently reduces the effective diameter of the bed. Occasionally the solid salts form as a crust on the top of the bed or build-up along the vessel walls. In either case, this condition leads to reduced performance such as accelerated
molecular sieve particle break up, increased pressure drop, channelling and premature water breakthrough. After a certain number of cycles, molecular sieve beds operating in this manner may exhibit broken particles, dust, and a caked layer that can vary in depth from several tens of centimeters to, in extreme cases, the majority of the bed.

Figure 1 is an actual observation recorded at a plant site by UOP Field Technical Service (FTS) personnel. UOP FTS was present to investigate dehydrator performance anomalies and to assist the operator in reloading the bed with a compound mix of adsorbents including UOP’s UI-94™ Adsorbent. In addition, UOP FTS confirmed pressure drop and moisture measurements of the customer’s instruments. Prior to dumping, UOP FTS observed that the top of the sieve bed appeared normal and the ceramic balls and wire-mesh screening were removed without incident. The bottom manhole was removed to unload the spent adsorbent. After the free-flowing material was removed by gravity dumping, a crust of agglomerated material remained in the vessel as depicted in Figure 1. This solid and caked material was removed with some difficulty. Analysis in UOP’s laboratory indicated that approximately 50% of the agglomerated mass was sodium carbonate and sodium bi-carbonate.

Figure 1 – Photo and detailed description of an actual customer bed at recharge that exhibits severe refluxing during regeneration.

There are a few options available to reduce the impact of the reflux problem. Process solutions such as reducing the regeneration gas pressure, or ramping up the heating gas temperature more slowly have been proposed as a means of eliminating the reflux phenomena. It is usually not economically feasible to reduce the regeneration gas pressure because of recompression costs if the regeneration gas is to be re-injected into the well to maintain pressure. Also, most of the natural gas driers with a reflux problem do not have sufficient drying capacity to allow them to add an additional 2 – 3 hours to the regeneration cycle so that the temperature can be ramped up slowly. In any case, these engineering solutions offer only a limited reduction in the condensation-reflux problem.
Another cause of breakup/crust formation in natural gas driers is carryover from upstream liquid treating processes such as glycol dehydrators and acid gas treating units (i.e. amine treaters). Normally these processes are well controlled and usually a liquid separator is installed before the gas reaches the molecular sieve drier. However, upsets in these upstream systems do occur and can overload the gas-liquid separator or the separator itself can be under-designed for the gas flow. Pigging operations can also create a problem by pushing excess liquid trapped in low spots along the pipeline.

Alternate product solutions, such as layers of activated alumina and silica gel have been offered to protect the molecular sieve zones in an attempt to remediate the break-up problem. The concept of a protective layer of these alternate products as a way of protecting the molecular sieve has proved ineffective in the past for the following reasons:

- The sacrificial layer approach is ineffective in a two phase flow situation, since entrained liquids pass through the 30 – 60 cm layer of the sacrificial bed and reach the molecular sieve bed below almost immediately.
- Activated alumina and silica gel have significantly lower water capacity than molecular sieve at the operating conditions in most of these natural gas driers. Therefore, all this “solution” really does is to sacrifice critical water capacity in the drier bed.

UOP recognized that the optimal solution to this problem was a product modification and that a more robust molecular sieve needed to be developed that was resistant to the aggressive conditions found in these units. Molsiv™ UI-94 Adsorbent was formulated to overcome the problems of rapid break-up and premature pressure drop increase caused by the reflux effect. It is now installed in many natural gas driers that are subject to severe service, in areas like North and Central Africa, the Far East, the Middle East and North America. Performance life in these units using a standard 4A type product was often reduced to less than 12 months as a consequence of the build up in pressure drop. With the installation of Molsiv™ UI-94 Adsorbent the pressure drop increase has lessened to approximately one third and resulted in a doubling of the operational lifetime of the unit.

**Case Histories**

**Case 1:**
A North African operator has a five train natural gas/ NGL recovery plant where each train has the capability to process ~420,000 Nm³/hr. The feed pressure is 1120 psia. The design feed composition is:

<table>
<thead>
<tr>
<th>Feed Gas Composition</th>
<th>Mole %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>85.9</td>
</tr>
<tr>
<td>Ethane</td>
<td>7.88</td>
</tr>
<tr>
<td>Propane</td>
<td>2.77</td>
</tr>
<tr>
<td>i-Butane</td>
<td>0.63</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.68</td>
</tr>
<tr>
<td>i-Pentane</td>
<td>0.25</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>0.17</td>
</tr>
<tr>
<td>C6+</td>
<td>balance</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.61</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>0.78</td>
</tr>
</tbody>
</table>
A portion of the product gas after hydrocarbon extraction is used to regenerate the beds. Since the regeneration gas is to be re-injected to maintain pressure in the underground reservoir, the regeneration is carried out at high pressure (~1062 psia) with a semi-closed loop configuration. This results in a stripping limited regeneration condition and puts additional stress on the adsorbent. In addition, the beds were susceptible to liquid carryover from time to time. Also, the carbon dioxide would build up in the regeneration loop adding acidity.

Prior to installation of the new Molsiv™ UI-94 Adsorbent, this operator was changing out the feed gas dehydrators every 14-16 months. With the current adsorbents, change-outs now occur from 36 to 66 months depending on the frequency of liquid carryover events. The adsorbent life has been increased to at least twice and in one case to 4 times as long.

Case 2:
A Central Africa processor has a natural gas liquid extraction plant designed to process 600 MMSCFD of associated gas. The feed gas is dehydrated with a three-bed molecular sieve adsorption system. Two beds are on parallel adsorption while one bed is being regenerated. Initially, a 3A type adsorbent was installed but this failed after 1 year in service. After consulting with UOP, it was recommended that the unit should be recharged with a compound bed of UOP adsorbents. (See Figure 2, below) With the UOP adsorbents, the unit life doubled to two years. Following this success, the customer wanted to improve the operation further and instituted a ramped heating to the regeneration cycle which also resulted in a 3 hour cycle increase. Fortunately, there was room in the design to accommodate this increase. The combination of these two solutions resulted in increasing the life of the adsorbent to just over three years. The third charge of Molsiv™ UI-94 Adsorbent was loaded in November 2004. This charge is currently still in operation and based on the increase in pressure drop, it is expected to last at least 4 to 5 years.

Figure 2 – UOP Molecular Sieve Adsorbers at Central African Customer
July 1999 – April 2006. Pressure Drop Evaluation
Case 3:
In the late 1990s, a North American producer revamped their three-train cryogenic liquids recovery plant to meet increasing demand and duty[1]. After start-up, their molecular sieve adsorbent experienced very short life, on average 6 months.

Regeneration is carried out in an open loop with residue gas at 1050 psig. The beds are operated with an 8-hour cycle processing a total of 30 MMSCFD, greater than the 25 MMSCFD which the system was designed to handle. It was felt that the extra flow rate coupled with liquid carry-over from an upset excessively challenged the molecular sieve adsorbent and performance declined. At this point, UOP recommended UI-94 Adsorbent due to its stability in severe duty and ability to recover from upset conditions. While earlier charges of molecular sieve adsorbents had lasted less than 12 months, UI-94 Adsorbent loaded in April 2002 exceeded 24 months performance life, over triple the lifetime of the previous charge.

SUMMARY

Tight designs, changing process conditions, and upsets can all lead to severe duty and extra challenges to a molecular sieve dehydrator system. Evaluation of these conditions and their impact on molecular sieve life has led UOP to develop MOLSIV UI-94 Adsorbent. It is an inherently robust product that retains its integrity under a variety of challenging operational conditions. UOP’s UI-94 Adsorbent is now a proven product that offers natural gas processors the opportunity to increase the life of molecular sieves in natural gas dehydration units by minimizing pressure drop increase over the life of the adsorbent.

REFERENCES CITED