NEW TYPE OF MOLECULAR SIEVE WITH LONGER LIFE
FOR NATURAL GAS DRYING

NOUVEAU TAMIS MOLECULAIRE PERMETTANT UNE PLUS LONGUE
DUREE DE VIE POUR LE SECHAGE DE GAZ NATUREL

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ABSTRACT

It has been observed in several NG drying units that the carryover of liquids, particularly amines, had a deleterious effect on mechanical strength of the molecular sieves. Pressure drop increases as well as reduced cycle times were reported.

The molecular sieve degradation by amines has been thoroughly investigated. It occurs at high temperature during the heating step and affects the zeolite cristallinity as well as the binder cohesion. A new type of molecular sieve, which exhibits a greater intercrystal stability, has been developed; besides its amine resistance, it has shown an interesting behaviour in minimising coking.

Consequently, the new absorbent type "SRA", has been installed in a turbo expander plant at Lacq - France, where such problems occurred in the past, and confirmed the expected performances. Successful drying performances and pressure drop levels within design limits allow a longer life for the molecular sieve.

RESUME

Dans plusieurs unités de séchage de gaz naturel, on a pu observer que l’entraînement de liquides, et en particulier d’amines, avait un effet néfaste sur la résistance mécanique du tamis moléculaire. Des augmentations de pertes de charge ainsi que des durées de cycles réduites ont été constatées.

La dégradation du tamis moléculaire par les amines a été étudiée de façon approfondie. Celle-ci intervient pendant la phase de régénération à haute température, et affecte la cristallinité de la zéolithe ainsi que la cohésion du liant. Un nouveau type de tamis moléculaire, présentant...
une plus grande stabilité intercristalline, a été développé ; en plus de sa résistance aux amines, il minimise la formation de coke.

Depuis, ce nouvel absorbant type "SRA", a été installé dans une usine avec turbo expandeur à Lacq - France, où les problèmes cités étaient rencontrés, et a confirmé les performances attendues. Une très bonne efficacité de séchage et des pertes de charges réduites permettent d'assurer une plus longue durée de vie du tamis moléculaire.

INTRODUCTION

Molecular sieves are very often used in natural gas plant to purify the gas whenever severe specifications towards moisture and pollutants contents are needed.

Amine or glycol absorption processes and molecular sieve adsorption processes are complementary used since they are adapted to different level of purification. For example, desulfurization is frequently done by amine absorption to remove the main fraction of impurities and then by molecular sieve adsorption to remove the residual sulfur compounds and moisture.

In such case, some troubles have occurred in the past concerning the global resistance of molecular sieves to physical and chemical constraints (temperature, pressure, attrition, liquids carry over, ...).

This paper deals with this problem, illustrated by the industrial case of Lacq plant - France. We describe how the modification of the molecular sieve has led to successful solution of these troubles.

I - CASE OF LACQ PLANT - FRANCE

In the Lacq plant the different steps of the natural gas treatment are summarized in figure 1. The feed gas is firstly treated with amines and caustic soda scrubbers to remove the H₂S (16 % vol. in the raw gas) and the CO₂ (10 %). After this first step, the water saturated gas is dried in a molecular sieve unit. The dry gas goes to a turbo expander to recover C₂+ hydrocarbons. Because of very low temperature in the turbo expander (until - 90°C/32 bars), the moisture of the gas must be as low as 0.1 ppm.

The drying unit consists of 3 molecular sieve beds, two being in parallel adsorption, and one in thermal regeneration as shown in figure 2.

Since its start up (1987), the drying unit had troubles concerning pressure drop and adsorption capacity. The pressure drop increases so high, or adsorption cycle was so short that molecular sieve had to be replaced before scheduled.
Figure 1. Steps of the natural gas treatment at Lacq plant

Figure 2. Scheme of the drying unit
I-1 On-site investigation

During a planned shut down, it was decided to inspect the internal of the vessel and to take samples of spent adsorbent.

No bed movement was noticed. It was observed a very important presence of fine particles in the molecular sieve pellets and also compact agglomeration of fines and pellets located on the bed walls (mainly in the top of the bed).

The X-ray analysis of these fines and aggregates show important quantity of cancrinite and sodium carbonate whereas zeolite cristalite structure was quite absent. Besides, the water adsorption capacity of these materials was less than 3 %.

Chemical analysis reported on table 1 indicates a large excess of sodium and presence of carbonaceous deposits. Such an excess of sodium can only been explained by caustic soda droplets carry over during adsorption steps.

**Table 1 - Chemical Analysis**

<table>
<thead>
<tr>
<th></th>
<th>Aggregates</th>
<th>Fines</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>18 %</td>
<td>27.8 %</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>12.1 %</td>
<td>17.5 %</td>
</tr>
<tr>
<td>MgO</td>
<td>0.67 %</td>
<td>1 %</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>35.3 %</td>
<td>29.8 %</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.43 %</td>
<td>0.71 %</td>
</tr>
<tr>
<td>CaO</td>
<td>0.14 %</td>
<td>0.28 %</td>
</tr>
<tr>
<td>Carbon</td>
<td>6.7 %</td>
<td>3.6 %</td>
</tr>
</tbody>
</table>

It is well known that the presence of caustic soda, especially at high temperature (heating step) can destroy the zeolite cristalinity. Moreover this hot caustic soda is able to fragilize the binder of the pellets which explains the presence of fines.

Presence of carbonaceous deposits indicates degradations of organic compounds contained in the natural gas or due to liquid carryover (amines foam). The cake formation can be explained by recondensation of water during the initial phase of regeneration. Actually, if heating step is to rapidly performed, it has been shown that the water removed from the bottom of the bed can recondense on the top of the bed walls. So, the mixture of molecular sieve fines, carbonaceous materials and hot liquid water can bind together to give a kind of inert cake.
It is clear that those fines and solid deposits are responsible for the process troubles: reduction of adsorbent material, increase of superficial velocities, bad gas flow distribution causing an increase of the pressure drop and a decrease of the drying step.

I-2 Modifications on the drying unit

In order to reduce the liquids carry over in the adsorbers, separators have been modified to improve their efficiency. The regeneration procedure was also changed so as to have a moderate temperature increase to avoid water recondensation.

By this mean, troubles were minored especially concerning caustic soda carryover (no cancrinite formation) and cake formation. However, rapid ageing of the molecular sieve still remained. So the effect of amine reactivity was clearly pointed out.

Among amines used in absorption processes, Di ethanol (DEA) and Methyl Diethanol amines (MDEA) are frequently used, also with additives. The troubles described here were significantly encountered when additives like Buthyl ethanol amine (BEA) and Di isopropanol amine (DIPA) were employed.

As it can be noticed from table 2, those two additive-amines are more volatile and more basic than DEA or MDEA. So, one can understand that being more reactive and more volatile they can cause much more troubles than the principal amine.

<table>
<thead>
<tr>
<th>Amine</th>
<th>BEA</th>
<th>DI PA</th>
<th>MDEA</th>
<th>DEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>pKa (25°C)</td>
<td>9.5</td>
<td>8.9</td>
<td>8.5</td>
<td>8.88</td>
</tr>
<tr>
<td>Bp (°C)</td>
<td>200</td>
<td>248</td>
<td>247</td>
<td>269</td>
</tr>
<tr>
<td>ρ (g/cm³)</td>
<td>0.89</td>
<td>0.99</td>
<td>1.04</td>
<td>1.09 (at 30°C)</td>
</tr>
<tr>
<td>vap. pressure (20°C)</td>
<td>0.16</td>
<td>0.01</td>
<td>0.016</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>(m bar) (60°C)</td>
<td>3.86</td>
<td>0.22</td>
<td>0.32</td>
<td>0.07</td>
</tr>
</tbody>
</table>

II - NEW MOLECULAR SIEVE DEVELOPMENT

The research of a new more resistant molecular sieve was done in parallel with on-site investigation. Two patents have been taken concerning this new molecular sieve:
- Voirin et al. 1992 deals with coking reaction.
- Plée et al. 1996 deals with resistance to amine reaction.
There, we illustrate this second point by laboratory and then pilot application tests.

In the rest of the paper, we call conventional molecular sieve, for the old one, rapidly damaged by amines, and "SRA" (as "Spécial Résistant aux Amines") or improved molecular sieve, for the new one.

II-1. Laboratory tests

A rapid ageing test at the laboratory scale operated under hard conditions has been carried out.

100 g of molecular sieve in shape of 1.6 mm pellets are placed in a pressurised vessel containing ~ 200 ml of sodium hydroxide or amine solution. The vessel is heated at 180 or 240°C during several hours. The pressure increases to 10-38 bars, corresponding to the vapor pressure of the amine-water mixture.

The consequence is a mechanical degradation of the pellets: formation of fines and broken pellets. The results expressed as the percentage of particles inferior to 0.6 mm are reported on table 3.

As one can see the degradation of the molecular sieve occured mainly for sodium hydroxide and a very reactive amine BEA, whereas DEA caused less damages. It was measured that the 2 adsorbents treated with BEA lost half of their water adsorption capacity.

Table 3 - Comparison of percentage of fines formed by reaction with bases

<table>
<thead>
<tr>
<th>operated conditions</th>
<th>conventional adsorbent</th>
<th>improved &quot;SRA&quot; adsorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 g NaOH 70 h - 180°C</td>
<td>29 %</td>
<td>2 %</td>
</tr>
<tr>
<td>60 g BEA 120 h - 240°C</td>
<td>16 %</td>
<td>9 %</td>
</tr>
<tr>
<td>60 g DEA 120 h - 240°C</td>
<td>2 %</td>
<td>0.5 %</td>
</tr>
</tbody>
</table>

This simple test is a first demonstration that the "SRA" adsorbent is more mechanically resistant than the conventionnal one to hard conditions simulating the thermal regeneration step of a natural gas purification process. To confirm this behaviour pilot tests have been undertaken.
II-2. Pilot tests

A known mass of molecular sieve (~ 600 g), 16 mm pellets, is placed in a tubular adsorber with following dimensions: L = 150 cm; ∅ = 2.7 cm. The pilot is equipped so as to ensure automatically several cycles with adsorption and desorption steps. The operating conditions reproduce the industrial ones.

Adsorption step: T = 30°C
P = 60 bars
Flowrate = 17 Nm³/h
Linear velocity = 0.15 m/s
Gas containing: 650 vpm water
11 vpm amines
Duration: until total saturation with water

Regeneration step: T = 250°C
P = 60 bars
Flowrate = 4 Nm³/h
Linear velocity = 0.04 m/s
Duration: 3 h

During adsorption, a typical curve of water concentration versus time is obtained as presented in Figure 3.

All along the cycles, different parameters have been determined:
• pressure drop: dP (mbar / m of bed)
• dynamic capacity: quantity of water adsorbed at breakthrough time \( t_{0.05} \), per mass of adsorbant (g water / 100 g molecular sieve)
• Height of Mass Transfer Zone: HMTZ, equivalent of column length containing the mass transfer zone

HMTZ is calculated by: \( HMTZ = \frac{L}{t_{0.5}} (t_{0.95} - t_{0.05}) \)

were \( t_{0.05} \) = breakthrough time (C/Co = 0.05)
\( t_{0.5} \) = stoechiometric time (C/Co = 0.5)
\( t_{0.95} \) = saturation time (C/Co = 0.95)
Figure 3. Typical water concentration profile during adsorption pilot test

- Pressure drop evolution

Figures 4 and 5 show the comparison of pressure drop of the two adsorbents during time with two amines, BEA and DIPA.

In both cases, it is clear that the pressure drop increase is much more higher with the conventional adsorbent than with the improved "SRA" adsorbent. It can be noticed that BEA seems slightly more destructive than DIPA.
Adsorption performances

Figures 6 and 7 show the comparison of adsorption efficiencies of the two adsorbents with DIPA. The dynamic capacity of conventional molecular sieve, more important in the first cycles, rapidly decreases because of a fast deterioration of diffusion properties, as shown by the increase of HMTZ. This can be explained by loose of adsorption sites (cristallinity destruction) and cake formation.
The new "SRA" molecular sieve presents a more stable behaviour: slow decrease of dynamic capacity, and slow increase of HMTZ.

Figure 6. Comparison of dynamic capacity of the M.S. (amine = DIPA)

Figure 7. Comparison of HMTZ of the M.S. (amine = DIPA)
During these pilot tests, analysis of amine content in the gas allow some complementary observations: conventional adsorbent presents a higher amine retention during adsorption step and a worse desorption during regeneration step. Moreover, after several cycles, the carbon content of the spent adsorbents was always higher on the conventional one. The improved molecular sieve was less retentive and less reactive towards amines.

III - INDUSTRIAL DEMONSTRATION

Mid-1995, a new "SRA" molecular sieve load has been installed in the Lacq plant drying unit. Since this date, a much better situation prevails. The pressure drop is staying to a reasonable level: less than 500 mbar per adsorber whereas in the past more than 900 mbar could be observed after one year service.

Concerning drying performances, on-site measurements of moisture content until breakthrough limit prove that dynamic capacity is very little affected during time: after 2.5 year service, the molecular sieve has 89% adsorption properties of the virgin product.

CONCLUSION

It has been shown that liquid (particularly amines) carryover onto molecular sieve beds can have troubling effects on process running: increase of pressure drop and reduction of adsorption time.

On-site modifications can minimise those troubles. However, a real solution was find by developing a new "SRA" molecular sieve, more resistant to amine reaction. After lab and pilot evaluation, this improved molecular sieve is being successfully used in Lacq plant, confirming the expected performances as well on its mechanical strength as on its adsorption properties.

References

