Molecular Sieves Contaminants:

Effects, Consequences and Mitigation

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ABSTRACT

Molecular sieves have been widely used to dry and purify natural gas in the past 50 years. Sometimes it is the only solution to achieve the water dewpoints required for LNG production and NGL recovery. The adsorption principles on molecular sieves are easy to understand, but practice sometimes reveals traps to avoid. In some plants, contaminants present in the feed gas can cause less than expected service life (premature breakthrough), and unsatisfactory performance (high pressure drop, COS formation,..).

This paper describes several of the most common contaminants, and how to minimize sub-optimal performance and reduced service life.

1. Introduction

In the natural gas processing chain, pre-treatment typically includes acid gas and sulfur removal, mercury removal, and dehydration. The moisture specification of the gas depends on the downstream equipment. In some cases, several solutions are available (for instance for pipeline specification of 2 to 7 lb/mmscf, one can choose from glycol, activated alumina, silica gel,…) But when cryogenic processes are involved like in NGL recovery or LNG production, avoiding hydrates requires water dew points that only zeolite-based molecular sieves can satisfactorily achieve. Mercaptans and limited quantities of hydrogen sulfide, carbon dioxide or methanol can also be removed on these adsorbents.

The principles of adsorption on molecular sieves are easy to understand, but practice sometimes reveals traps to avoid. The porous crystalline structure and the large surface area exhibiting a high electronic activity give molecular sieves their outstanding adsorption properties.

However, one must be aware of the possible side effects. "Contaminants" (used here in a wide and general meaning) can disturb the adsorption process in several ways: adsorption competition, degradation of the structure, partial blocking of the adsorbent bed, side reactions. The compounds involved and the causes are varied, but the consequences are always the same: poor performance of the beds ultimately leading to premature breakthrough, unacceptable pressure drop or adsorbent unloading difficulties.

After a brief reminder regarding zeolite industrial adsorption basics, this paper describes the causes and consequences related to the presence of the most common contaminants. It shows that even though it is usually possible to mitigate contaminants effects, being aware of the potential problem at design stage is key to implementing the best answer.

2. Industrial adsorption on zeolite molecular sieves

2.1. Zeolite structure and adsorption principles[1],[2]

Zeolites are crystalline alumino-silicates. There are close to 200 different crystal networks: about 40 are from natural origin, and the others are industrially synthesized for different purposes such as catalysis (catalytic cracking), ion exchange and separation (drying and purification).

2 types of zeolites are widely used for separation: zeolite A and zeolite X (also known as Faujasite and 13X). They are made of a three-dimensional succession of SiO_4 and AlO_4 tetrahedra that define a basic structure known as sodalite cages "SOD" (Fig.1).
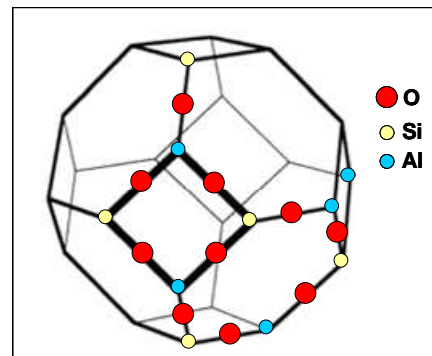

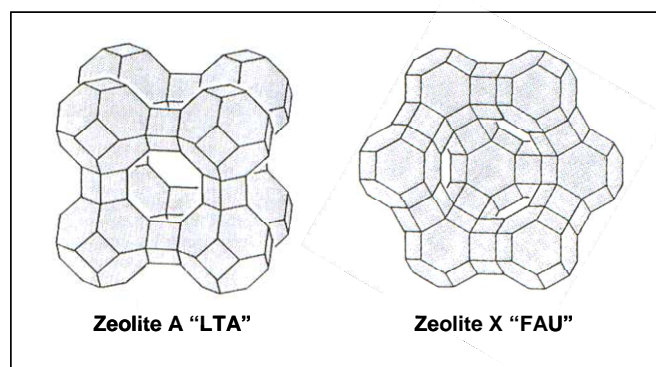**Figure 1 : Sodalite (SOD) structure**

Figure 2 : Structure or the basic Zeolite A and X crystals

The way sodalite cages arrange together to form zeolite A ("LTA" crystal structure) or zeolite X ("FAU" crystal structure) depends on the synthesis operating conditions and on the Si/Al ratio (Fig. 2). Aluminum being trivalent, the resulting edifice is negatively charged and needs to be balanced by a metal cation. The final network of repeated crystals form channels with cavities (known as porosity), that exhibit a very large and electronically active surface area (up to 800 m^2/g), and that attracts polar molecules.

In the separation applications, the aim is to selectively retain molecules that form low energy bonds with the structure (2 to 45 kJ/mol: Van der Waals forces and other low-energy interactions). This exothermic phenomenon is called physisorption and follows adsorption isotherms (Fig. 3). To be efficiently adsorbed, the polar molecules must be small enough to enter the cavities via their aperture (pores). The diameter of the pores and cavities depend on the type of zeolite and on the nature and size of the charge compensating cations which are situated around the pores. For instance 4A zeolite (A type with sodium cations) shows 4 angstrom pores and thus allows smaller molecules to enter its 11.5 angstrom cavities. If Na^+ is partially replaced by bigger K^+, the result is a smaller pore opening of 3 angstrom ("3A" zeolite). When Ca^{2+} replace $2Na^+$, "5A" zeolite is produced. Zeolite X pores, in the sodium form, are 7.4 angstrom large.

It also has to be noted that the structure vibrations can sometimes allow slightly bigger molecules to enter the cavities.
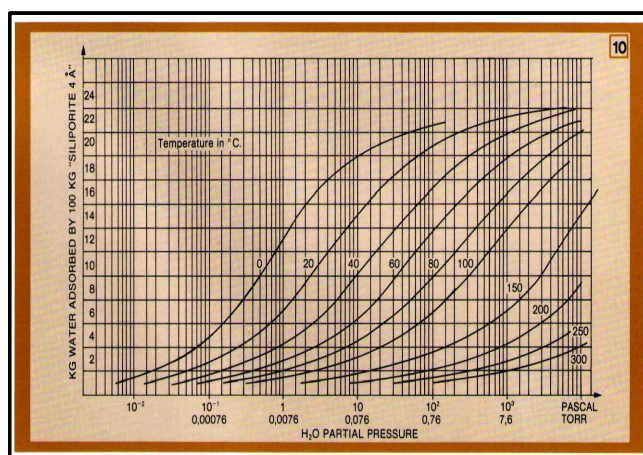

Figure 3 : Water adsorption isotherm on 4A molecular sieve

Depending on the application and molecules to be separated, one will choose the appropriate type of zeolite.

Additionally, to be used as fixed beds in vessels, the powder of synthetized crystals is compounded with a binding clay in order to form 0.5 to 5.0 mm beads or extrudates. The resulting material exhibits a complex network of micropores (the crystal windows of the active sites mentioned previously), mesopores (20 to 50 angstrom) and macropores (larger than 50 angstrom).

By changing the adsorption equilibrium conditions (pressure, temperature or both), the adsorbed molecules can be desorbed from the active sites, and the zeolite can recover most of its original adsorption capacity: it is "regenerated". Regeneration is a key principle that is described further in the next chapter.

The foregoing gives a short description of the zeolite molecular sieves structure and operating principles. From that, one can understand that the complexity and the activity of the structure may lead to side reactions. Some molecules can form a real chemical bond with the zeolite material (chemisorption) and cannot be desorbed. Others can react together, sometimes helped by the zeolite and / or the binder catalytic properties. In presence of certain aggressive species and operating conditions, the binder, and sometimes the crystals themselves can be destroyed, leading to powdering or to the formation of aggregates.

2.2. Basics of industrial adsorption

Molecular sieves for natural gas treatment are loaded in vertical adsorbers, most of the time on a support system. The impurities in the treated stream saturate the molecular sieve bed generally within a few hours or days (typically 12 to 36 hours in the case of natural gas dehydration). Therefore, at least 2 beds have to be used: one in the adsorption phase, while the other is being "regenerated". In order to accommodate high flow-rates and acceptable diameters, several adsorbers are often used in parallel with a time lag during which they are alternatively regenerated (Fig. 4).
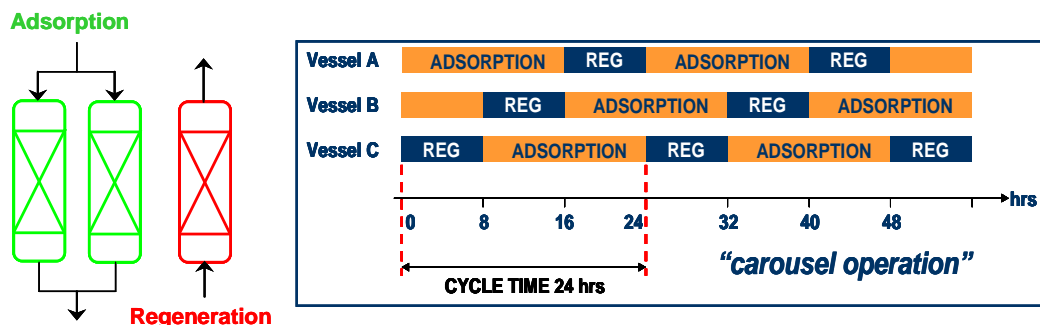

Figure 4 : Example of a "2+1" system with 16 hours adsorption and 8 hours regeneration

During adsorption, a molecular sieves bed can be modelized by a 3 zones system (Fig. 5). Close to the inlet is the Equilibrium Zone (EZ) where the adsorbent is in equilibrium with the process fluid, that is to say saturated at the partial pressure and temperature conditions. The next area, known as Mass Transfer Zone (MTZ), is where the dynamics of adsorption take place. The MTZ shows the impurities concentration decreasing gradient and can be defined as the length it takes the adsorbent to bring the impurities from their initial concentration to the final specification. The MTZ depends mainly on the diffusion kinetics and flow velocity. The larger the accessible surface, the shorter the MTZ. Nowadays, to optimize the surface area and therefore the global bed length, most designs involve smaller particles in the MTZ compared to the EZ. The third area is made of fresh adsorbent that, for a given adsorption time, has not been in contact with the impurities.

During the adsorption phase, the EZ extends and the MTZ moves forward and slowly reduces the fresh adsorbent area. All along its life and repeated cycles, the adsorbent slowly looses its properties (fouling and destruction). Therefore for the same service (same overall adsorption capacity), the EZ and the MTZ get longer.

Some units are operated on a "fixed" cycle time: the cycles always have the same duration. At the beginning of the lifetime, when the adsorbent is new, there is still fresh unused molecular sieve in the vessel. For these units, the design is optimized when, at the end of the last adsorption phase of the foreseen product lifetime, the third zone is close to zero, and the MTZ almost reaches the limit of the bed.
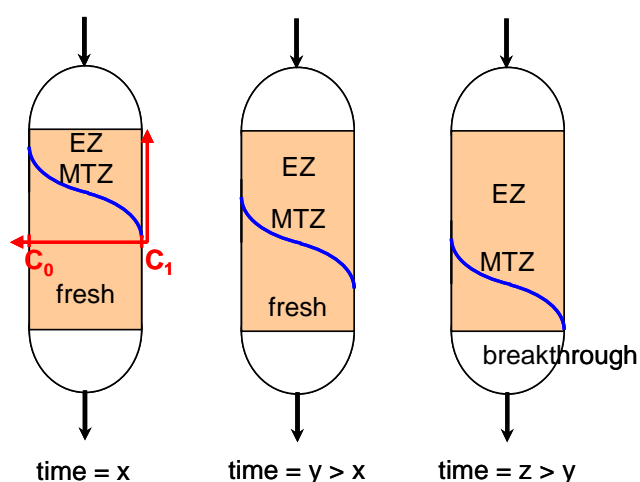
Figure 5 : Equilibrium Zone and Mass Transfer Zone

Other units are operated under "breakthrough" conditions: the end of the adsorption time is defined by impurities detection at the outlet of the bed. In that case, the adsorption time decreases slowly all along the product lifetime.

Generally, in order to optimize the vessel diameter and the flow pattern, gas treatment is processed downwards and liquid treatment is processed upwards. The regeneration step is generally performed counter current in order to avoid pushing the desorbed impurities through the MTZ and the fresh adsorbent zone.

There are basically 2 main ways to regenerate a molecular sieves bed. They are referred to as PSA (Pressure Swing Adsorption) and TSA (Temperature Swing Adsorption). In the first case, the change in the adsorption equilibrium is obtained by decreasing the pressure. PSA based units are mainly used for industrial gases treatment (PSA H_2, PSA N_2), medical applications (PSA O_2), or ethanol dehydration (PSA EtOH). In the second case, which is more efficient for thorough impurities desorption, a hot gas (typically 180-300°C) is passed through the adsorbers. This regeneration heating step is critical for several reasons: the gas has to be clean enough not to lead to side effects (which are most of the time exacerbated at high temperature); and it has to carefully address the required regeneration energy duty (temperature, flow-rate, duration). After heating, a cooling phase is needed before switching back to adsorption in order to avoid a temperature peak that would most of the time significantly disturb the downstream process (especially heat exchangers)[3].

3. Common symptoms due to the presence of contaminants

For a given lifetime, a good unit design guarantees a specified purity during a given adsorption time, and a maximum pressure drop.

The main consequence of poor operation or contaminant effect is premature breakthrough of the impurities. It is sometimes possible to correct the problem by modifying the operating conditions (adsorption time, regeneration procedure), but usually, it requires a change out of the adsorbents. Another reason for premature replacement of the adsorbent is when the pressure drop rises to unacceptable levels.

This paper does not detail the consequences of poor operation strictly related to process parameters or too short designs. One can understand that wrong choices in the adsorbents type, size and quantity; or unsuitable operating parameters (temperature, pressure, flow-rate, heating temperature and duration, etc.) sooner or later lead to discrepancies between the expected unit behavior and reality.

The enclosed information focuses on the effects - expected or not - of the feed components - expected or not. In the following we assume that the operating parameters are correct and match the design specifications, at least from a theoretical stand point. However, to solve the impurities-related problems often involves some modifications of these parameters.

3.1. Premature breakthrough

Premature breakthrough happens when the adsorbent becomes unable to meet the impurities specifications. Before the expected end of the adsorption time, impurities content at adsorbers' outlet increases higher than tolerated.

Reasons for premature breakthrough can be:

- Competition with other adsorbed species which quantity and / or impact were underestimated at design stage. When the attraction force of these molecules is similar or stronger than the targeted compounds, they can be difficult to displace (which lengthens the MTZ), or can even stay adsorbed and decrease the remaining capacity allocated to the specific job.

- Porosity fouling. As explained previously, molecular sieve capacity slowly decreases with time. One of the main reason is that the porosity gets partially fouled with heavy carbonaceous components. These compounds, often referred to as "coke" (Fig. 6) are caused by heavy hydrocarbons (HC) present in the feed and which sometimes remain in the bed along the cycles. The MTZ is lengthened and the overall porosity is decreased. Normal fouling is taken into account in the unit design, among many other factors that define the product "ageing" rate. However in some cases, fouling is much more important than anticipated, leading to premature breakthrough. The real issue is that a part of the deposit is not removed during regeneration and is subject to cracking and "polymerization". It ultimately forms heavy growing carbonaceous deposits that build up in the porosity[4], especially at zeolite acidic sites. In normal operation coke shouldn't be a problem in natural gas treatment. However, under certain circumstances (like HC condensation, see 4.4.), coking can be severe, and molecules such like aromatic rings (from cyclo-pentadiene to dimethyl-naphthalene) or heavy aliphatic compounds (C8 – C10 and more) have been identified[5].

Figure 6 : Coked pellets

- Destruction of the adsorbent. This can come as a result of chemical attacks by aggressive species. In severe cases, not only the binder is destroyed, but the crystal structure itself can suffer and be slowly altered and turned to powder, thus reducing the quantity of active material. In other cases liquid reflux at high temperature (detailed below) can destroy and agglomerate large parts of the beds, especially around the vessels walls.

- Channeling (preferential path). Channeling occurs when the flow is not well distributed on the cross section of the bed. If this happens during adsorption, the adsorbent is not evenly used: some areas in the bed have to treat more flow than they are supposed to, while some others, in the worst cases, can almost be considered as "dead volumes". If it happens during the regeneration phase (which is more often the case, as regeneration flow-rates are lower than adsorption ones), the product is not well regenerated, and some areas in the bed still shows high impurities residuals when switching back to adsorption. In both cases premature breakthrough is around the corner. There are several "mechanical" or "process" reasons that can lead to uneven flow distribution (poor loading, support grid failure, low flow-rate, etc.). Here we focus on the causes related to feed composition, which are often the same as the ones responsible for product destruction (leading to dust and agglomerates that block large parts of the bed).

3.2. Unacceptable pressure drop

Pressure drop in natural gas treaters typically ranges from 0.1 to 0.5 bar SOR (Start Of Run: beginning of lifetime). Along the cycles, pressure drop slowly increases ("normal" fouling due to HC deposit, light dusting due to thermal stress and attrition). A rule of thumb says that in normal conditions, pressure drop more or less doubles within 4-5 years. In favorable conditions (lean gas, optimized products and process) it can be less; while in difficult conditions it may happen much faster.

In most serious cases, HC condensation, liquid reflux and heavy dusting can lead to a dramatic increase of the bed resistance. All these phenomena are describes later. Actually channeling and high pressure drop levels very often go together as different symptoms for the same causes.

Sometimes pressure drop rises so high that it is no longer possible to process the normal flow-rate, and the product has to be replaced (if premature breakthrough does not happen first).

3.3. Mitigation

In most cases, solutions exist to minimize or eliminate the foregoing described consequences of contamination. But of course the real issue is to anticipate the troubles before having to cure them. And this is why it is so important to be aware of all the potential problems as soon as possible in the design process of a unit.

Basically, when the cause is due to a real contaminant which was not theoretically expected, the solution typically involves, or to cut the contamination source, or to find process / product based solutions to live with it. This can be for instance a lower regeneration temperature that limits the reactivity, a guard layer that is able to cope with the species and protect the molecular sieves, or the use of specific resistant grades.

When it comes to normal components of the feed which cannot be avoided (especially HC, water and sometimes sulfur species), the answer cannot be to cut the problem source! However here again solutions sometimes involve product, process or equipment solutions, such as the implementation of efficient upstream gas / liquid separator - typically based on coalescence -, modifications of the regeneration procedure, guard layers, etc.

In the following we describe the specific effects of typical contaminants, and the available solutions to eliminate or mitigate the potential associated problems.

4. Typical contaminants, effects and solutions

Below is a list of the most common contaminants (and natural gas components) that often play a role in the problems described above, or that can be the result of unwanted side reactions (typically COS).

4.1. Presence of oxygen

Oxygen is not supposed to be part of a typical fossil natural gas composition. However the presence of oxygen is sometimes reported (generally at low levels - in the range of 10 to 50 ppmV -, but sometimes more). Reasons for the presence of oxygen is not always obvious, and several possible explanations related to process or equipment (compressors, pipe maintenance), are found here and there. Oxygen can be present in the feed and / or in the regeneration gas (which often have the same origin).

Oxygen has 2 potential bad effects

- Oxidation reactions (partial or complete combustion) of HC. In natural gas drying, the regeneration gas often mainly consists of methane (most of the time a slip stream of the dried gas is used). When passing through the heater, iron oxides (covering the steel surfaces, and itself favored by the presence of oxygen) can catalyze the oxidation of the HC at typical regeneration temperatures (250-300°C). Once initiated and if oxygen is present, the combustion reactions continue and propagate in the vessel. Methane and oxygen form water and carbon dioxide, which of course plays against the desired final specifications by increasing the residuals in the reactivated bed. Reactions involving heavier HC are more complex and can lead to intermediates such as oxygenates and olefins that ultimately form heavy coke deposits. As a result, the MTZ length and the overall adsorption capacity of the molecular sieves

are rapidly affected. In serious cases, pressure drop can rapidly and significantly increase. It has been shown that up to 50% of the oxygen can be converted, and that significant problems start with oxygen concentrations in the feed as low as 15-20 ppmV.

-   In the presence of sulfur compounds like hydrogen sulfide, and even at ambient temperature, oxygen forms sulfur dioxide and water, and ultimately elemental sulfur. This elemental sulfur is deposed in the porous structure, and clusters can even form and partially block the flow-rate, leading to channeling, high pressure drop, and eventually to premature breakthrough.

While the second problem is difficult to address, except by minimizing as much as possible sulfurs and oxygen levels, efficient answers exist for the first one. To start with, taking into account the higher water post-regeneration residual loading can be done at design stage, at least by considering a margin, provided one is aware of the potential problem. In any case the most efficient solution is to dramatically decrease the heating temperature down to 160-180°C. At these temperatures, the combustion reactions will almost be eliminated. Of course, there are several drawbacks like, again, the higher water residual due to the low temperature level, and the fact much more regeneration gas is required.

4.2. Liquid water

4.2.1. Liquid water carry over

In natural gas treatment, droplets of liquid water are generally carried over onto the molecular sieve bed when the upstream gas / liquid separator experiences upset operating conditions, is undersized or not efficient enough. However, liquid water can also come from low points or dead volumes in the piping where vapor can condense to liquid during some phase of the process, waiting for the next switch to be entrained on the bed. (This not only concerns water, but HC as well.)

Of course the most obvious consequence is that more water has to be handled by the molecular sieves, which has an impact on the adsorption time, possibly leading to premature breakthrough. In fact this is not the main issue.

Water droplets strongly react with molecular sieves, both physically (adsorption heat release) and mechanically (hammering the structure). This results is local "hot spots" where the clay binder is damaged and powdered. In severe cases, dusting becomes significant, leading to pressure drop increase, channeling, and premature breakthrough.

Several solutions are available to reduce the effects of liquid water. Stopping the upstream carry over is indeed the most efficient, and can be done by implementing a suitable gas / liquid separator, typically a vertical coalescer with a liquid specification of less than 0.1 ppmwt. By the way, it is important to express the specification as a liquid content instead of as droplet size limit (which gives no clue regarding liquid quantity, unless one has the size distribution curve of the droplets…) The case of low points and dead volumes is not always easy to diagnose, and requires a careful review of the piping configuration. But once the problem has been identified, some modification or drain pot installation can easily solve it.

Last but not least, and even though some authors do not agree, CECA internal experience shows that a 300 to 500 mm layer of silica gel on top of the molecular sieves generally offers a good protection. It is part of most CECA designs for natural gas treatment.

4.2.2. Hydrothermal damaging[6]
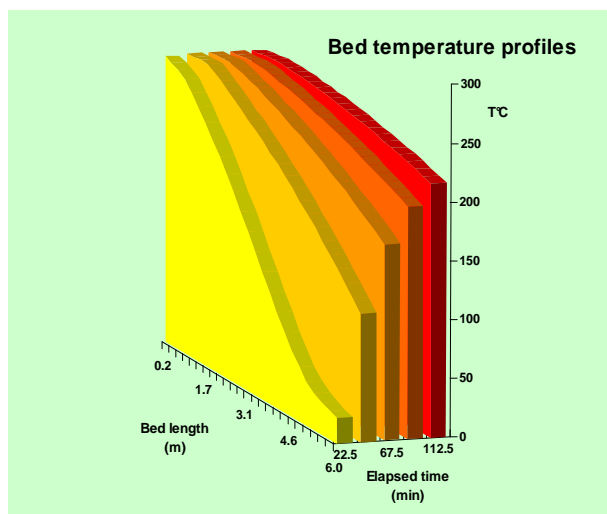
Figure 7 : Evolution of bed temperature profile with time

Another destructive effect of liquid water is likely to occur when the heating step is done too fast, and is often referred to as "hydrothermal damaging".

By heating too fast at a high temperature, water rapidly desorbs from the lower layers, while the bed experiences an important temperature gradient (Fig. 7): its bottom is already hot, but its upper section is still at adsorption temperature.

When arriving onto these colder parts of the bed, the regeneration gas gets oversaturated, and water "retro-condenses" on the top layers, especially near the vessel wall. This phenomenon can be seen on the outlet temperature curve of the regeneration gas that shows a plateau (typical of a change of physical state). As the temperature increases, it soon results in boiling the water in the molecular sieve bed. This phenomenon is enhanced by high pressures and low regeneration flow-rates.

The consequence of water condensation (also known as "water reflux") is obviously the weakening of the binder and of the zeolite structure. The binding clay is leached from the molecular sieve structure and disaggregates to dust and powder. Eventually it also rearranges to form agglomerates all around the vessel wall (Fig. 8) under the action of water soluble salts that can ion exchange with the zeolite and cement the structure[7]. In some cases, the agglomerates can take very significant volumes of the bed, causing preferential paths and high pressure drop. A hammer is sometimes required to remove those clusters during unloading.

Figure 8 : agglomerated product

All these gas / liquid interactions at high temperature are mechanically damaging. They create attrition and can result in bed movements, also leading to uneven distribution of the flow and pressure drop increase.

Zeolite crystal structure itself is affected by an overall loss of capacity. Zeolite X crystals can be destroyed, while zeolite A crystals see a decrease in their kinetics of adsorption; This is due to a "pore closure" effect that concerns mainly the external surface of the crystals (especially in the case of the 3A type).

Hydrothermal damaging can be significantly reduced, and sometimes stopped, by the use of a suitable heating procedure. Typically a heating ramp of a few degrees per minutes, together with a preliminary heating step around 80 to 130°C are usual and efficient implementation. To increase the regeneration gas flow-rate (to convey more water out of the bed and heat faster the upper sections), or to lower the regeneration pressure can also be recommended when this is possible.

4.3. Salts (NaCl)

Salts such as sodium chloride can sometimes, depending on the origin of the gas, be present in the entrained water (see 4.2.1.). Once they are in the pores, they are not easily removed as they stay in the product when water is vaporized. They accumulate and build up along the cycles, hindering the access to the pores and damaging the structure (binder and crystals), both physically and chemically. The phenomenon takes place essentially on the top of the bed, causing powdering of the material, participating to agglomerates formation (pressure drop

increase) and leading to a drastic decrease of the adsorbents performance. Even at very low salts content (< 0.5 ppm), the destruction of more than half the adsorption capacity within 2 years has been reported.

Again the best solution (if not the only one), is to avoid liquid water carry over onto the sieves (see 4.2.)

4.4. Liquid hydrocarbons

Like liquid water (See 4.2. above) and amines / caustic (See 4.5. below), the entrainment or the formation of liquid HC can be in some case highly damageable to the sieves.

Same as for water, liquid HC can be entrained with the feed gas. Another origin, known as "retrograde condensation" is difficult to diagnose, but is scientifically founded and admitted by a majority of authors[8],[9],[10],[11] . Figure 9 shows for 2 cases (a lean gas and a heavier one), the corresponding phase diagrams (also known as "phase envelope")[12]. It shows that a heavy gas at HC dew point, when operated at high pressure can be subject to HC condensation when the pressure is decreased. Therefore for such gas, one can expect liquids to form due to pressure drop across the bed (dashed arrow). Even though it can be computer-simulated, it is difficult to accurately estimate how much liquids form and stay in the molecular sieves porosity.
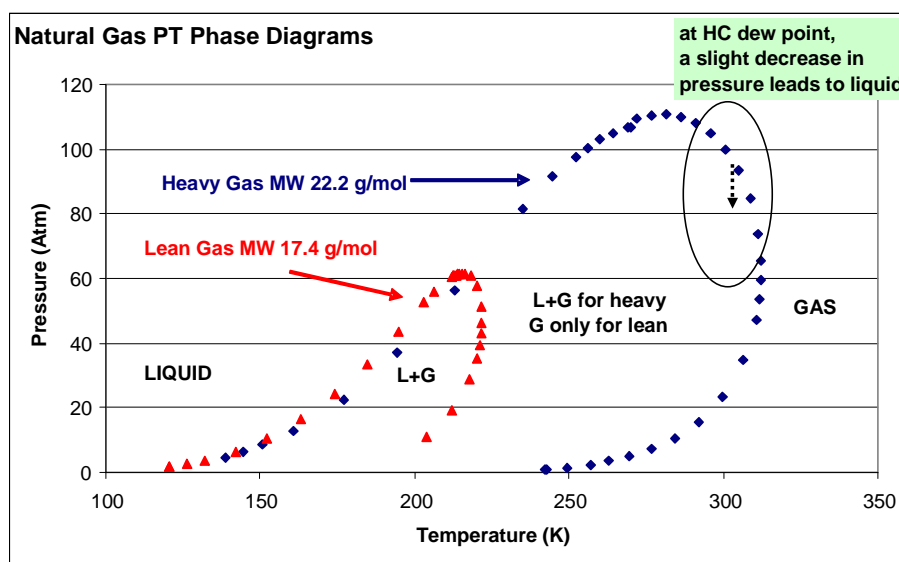

Figure 9 : PT diagram of natural gas; retro-condensation

As already depicted at chapter 3.1, the HC deposit blocks access to micro-pores, and therefore extend the MTZ, which results in an overall decrease of the adsorption capacity. In addition to that, the heavier HC can crack and polymerize during regeneration; build up and worsen the problem. Pressure drop increases and channelling may appear.

For such gas at HC dew point, the most efficient solution is to preheat the inlet stream by 3-5°C.

4.5. Liquid amines and caustic carry over

Amine and caustic based processes are widely used to remove "acid gases" (hydrogen sulfide and carbon dioxide) and some mercaptans, upstream molecular sieves units. It may happen that, under upset circumstances, amine foams or caustic droplets are carried over onto the molecular sieves.
Commonly used amines (such like DEA, MDEA, BEA or DIPA), due to their chemical structure and polarity, can adsorb in the material porosity, with two main consequences:

- When heated, they easily decompose and participate to coking, to an extent that can be very significant if the carry over is important and frequent.

- Also when heated, ammonia can form and further react with water, leading to ammonium $NH4^+$ that is able to replace the cation in the structure. On the one hand, the resulting weak structure fast collapses to powder (X-ray analysis of the sieves show that the adsorption capacity is destroyed). On the other hand, the released cations are not necessarily eliminated: some find their way in the bed porosity and are able to hinder normal adsorption kinetics.

Caustic chemically attacks the binder and the zeolite structure itself, which can be turned to power.

Of course amine and caustic carry over can be minimized by acting on the upstream processes. Also, like in the case of water carry over, an efficient gas / liquid separator has to be implemented, and a protective layer of silica gel can help significantly. However, resistant molecular sieve products are also part of the solution, as shown below.

In the late 90's, CECA R&D studied amine and caustic resistance[13]. A special resistant grade was developed (Siliporite® SRA), and successfully tested on the Total plant of Lacq in the south west of France. The product formulation, that has been continuously improved since then, exhibits a higher inter-crystal stability and shows some coke minimizing ability.

Two patents were granted and today, Siliporite® SRA and his cousin Siliporite® Optisieve 4 are used in many LNG trains around the world.

Based on laboratory tests, Table 1 shows the percentage of fines produced by the amine resistant product in comparison with a typical formulation.

Conditions (100 g product in 200 mL solution)	Conventional Product	Improved (SRA) formulation
250 g/L NaOH 70 hrs / 180°C	29%	2%
300 g/L BEA 120 hrs / 240°C	16%	9%
300 g/L DEA 120 hrs / 240°C	2%	0.5%

Table 1: Percentage of fines produced by reactions with bases, comparison between 2 formulations

In the case of the industrial facility, the pressure drop level was kept less than 500 mbar EOR (End Of Run, that is to say end of the lifetime) whereas beforehand it increased to more than 900 mbar after only 1 year service (Fig. 10 shows the pressure drop evolution for a given amine, here BEA, at pilot scale). After 2.5 years service, the new product's dynamic capacity remains 89% of the initial one, which is a very good value, generally expected for "easy" conditions.
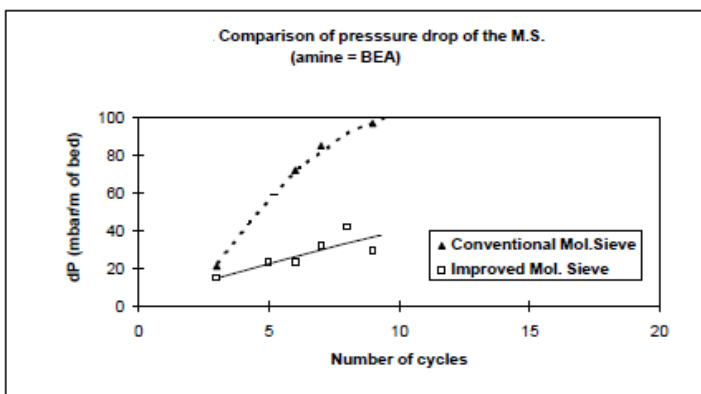
Figure 10 : example of pressure drop evolution (pilot scale)

4.6. Competition between species

It is of course not possible to give an exhaustive list of the species than can compete with each other during the adsorption step. And it is most of the time difficult to accurately quantify such competition. In fact, one could consider that all the feed compounds (polar and non polar), with a size smaller or comparable to the pore size of the zeolite can enter the structure.

Therefore, even though small and polar molecules have no problem to displace them, it takes time and has an effect on the MTZ length. If competition is really hard between 2 molecules, and if one of them was not taken into account at design stage, there is a good chance that the MTZ exceeds prevision and that breakthrough happens earlier than expected.

At least two very common examples deserve to be cited:

- Water and methanol. Methanol is often injected to avoid hydrates formation[14]. It is well adsorbed on 4A (and larger) molecular sieves, and require some effort from water molecules to displace it. Therefore presence of methanol very significantly increases the MTZ length, and has to be taken into account at design stage. (Problem being that, most of the time, methanol flow is not constant and a realistic scenario has to be assumed).

- Heavy mercaptans (C_3SH, C_4SH) and BTX (Benzene, Toluene, Xylene). Heavy mercaptans are efficiently removed on 13X molecular sieves. But again, beware competition of BTX that are also a little adsorbed on 13X molecular sieves.

See also 4.9.

4.7. Acids

All acids are able to alter and destroy the zeolite framework by a de-alumination process[15] (Fig. 11). No need to explain how detrimental this can be for the molecular sieve structure, again causing dust and leading to premature pressure drop increase and breakthrough. However acid attack and de-alumination process is only very active at high temperature; and this is why the problem mostly occurs during regeneration.
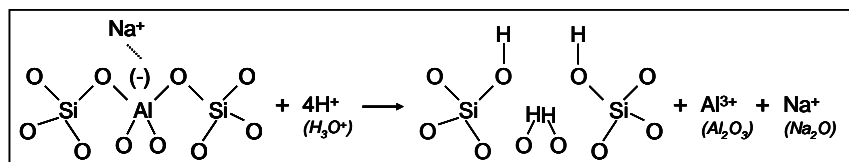

Figure 11 : De-alumination process by acid attack

To avoid related problems, one should use a specific acid-resistant molecular sieve such as CECA's Siliporite® RA, which is the result of an extensive R&D work (patent granted[16]).

4.8. COS formation

COS can form according to the following balanced reaction: $H_2S + CO_2 \Leftrightarrow COS + H_2O$

The thermodynamic constant of the reaction is as follows: $K = [COS][H_2O] / [CO_2][H_2S]$
(K value ranges from $1.77 \cdot 10^{-6}$ at 25°C to $2.38 \cdot 10^{-3}$ at 330°C)

When "sour" natural gas enters the adsorbent bed, it is usually water-saturated. Therefore, it is composed of hydrogen sulfide, carbon dioxide and water. Usually COS is absent (or assumed at very low levels).

Then, during the adsorption process (and regeneration), molecular sieves tend to favor the formation of COS for several reasons:

- water adsorption shifts the thermodynamic equilibrium to the right,
- zeolite and binding clay can catalyze the reaction by co-adsorbing CO_2 and H_2S,
- during regeneration, temperature increases the reaction kinetics (to a limited extend, as the increase of temperature also limits the adsorption of the formed water).

Usually COS has to be avoided or minimized as much as possible, the main concern being if it converts back to H_2S in presence of water in some downstream processes, causing important corrosion problems.

Not all molecular sieves act the same. 3A molecular sieves, as they are unable to significantly adsorb CO_2 and H_2S, only form very low levels of COS. 5A molecular sieves co-adsorb CO_2, H_2S, and COS as well, which delays the COS breakthrough. CO_2 and H_2S conversion to COS is more significant on 5A compared to 3A, but it stays limited. 4A type molecular sieve is very active, and leads to high conversion levels. Studies have shown that this is mostly due to its basicity and to the fact it has the right pore opening[5]. Faujasite (13X type molecular sieve) is very active as well. The binding clay has also a meaningful influence, especially via the presence of basic sites in the structure.

Molecular sieve vendors have developed specific products for minimizing COS formation. Usually these products are 3A-based. CECA's Siliporite® NK30COS is a combination of 3A type molecular sieve with an adapted pore size, and a low activity binder. Same for Siliporite® RA (See 4.7), which produces a very limited conversion to COS.

4.9. Other chemicals

The foregoing list is of course not exhaustive, but is representative of what typically can happen. We could have added others species that can be entrained in the feed, such as Oils (typically from compressors lube systems) or amine-based corrosion inhibitors. These species can stay in the bed and build up as coke, or act like an obstructive film that hinders diffusivity.

Some other compounds already cited can decompose at medium temperature (methanol) and involve a soft regeneration procedure. Others (heavy sulfurs) are not efficiently removed during regeneration and tend to stay in the bed…

5. Conclusions

Don't try to memorize the above information. Use it as a troubleshooting reference to narrow down to the problem and solution. But it is only a pretext to deliver the following messages, especially for new projects and revamps:

- be aware, as soon as possible, of the potential composition-related issues,
- don't underestimate the impact of the upstream processes (glycols, amines, caustic, etc.),
- address the related concerns by involving, from the earliest stage of the project, experienced molecular sieve manufacturers whom not only sell products, but also bring reliable solutions and added value technical advice.

To conclude, molecular sieves are very efficient and reliable materials. At the end of the day, the vast majority of the operating units worldwide are doing very well, especially those related to natural gas treatment. Even though molecular sieves cannot handle everything, almost all the potential problems mentioned in this paper can be solved with the help and follow-up of your experienced vendor.

6. Acknowledgements

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