10. Natural Gas Dehydration

- Natural gas stream from production wells is saturated with water vapor, which will condense and form gas hydrates if the gas temperature is cooled below its hydrate formation temperature.
- Also, water vapor may condense in pipelines, resulting in erosion and corrosion. When accumulated in the pipelines, it might form liquid plug, reducing the pipeline flow capacity.
- To avoid these potential problems, the gas stream needs to be dried to lower its **water dew point**.
- Pipeline specifications typically call for water content to be no more than 7 lb/MMscf for US pipeline systems, 4 lb/MMscf for Canadian pipeline systems, and even lower 1-2 lb/MMscf for Alaskan environment.
- There are several methods for dehydrating natural gas, including **absorption**, **adsorption**, and **direct cooling of the wet gas**.
- The absorption using liquid (glycol) and adsorption using solid desiccants are the most common, when a low water dew point gas is required for pipeline gas or for NGL recovery.
- The direct cooling method by expansion or refrigeration, with injection of hydrate inhibitors, is common for less dew point depression in the production of pipeline gas in mild weather regions.
- Several other advanced dehydration technologies (i.e., membranes and supersonic processes) offer some potential advantages, particularly for offshore applications due to their compact design. However, they have limited commercial experience.

10.1. Glycol Dehydration

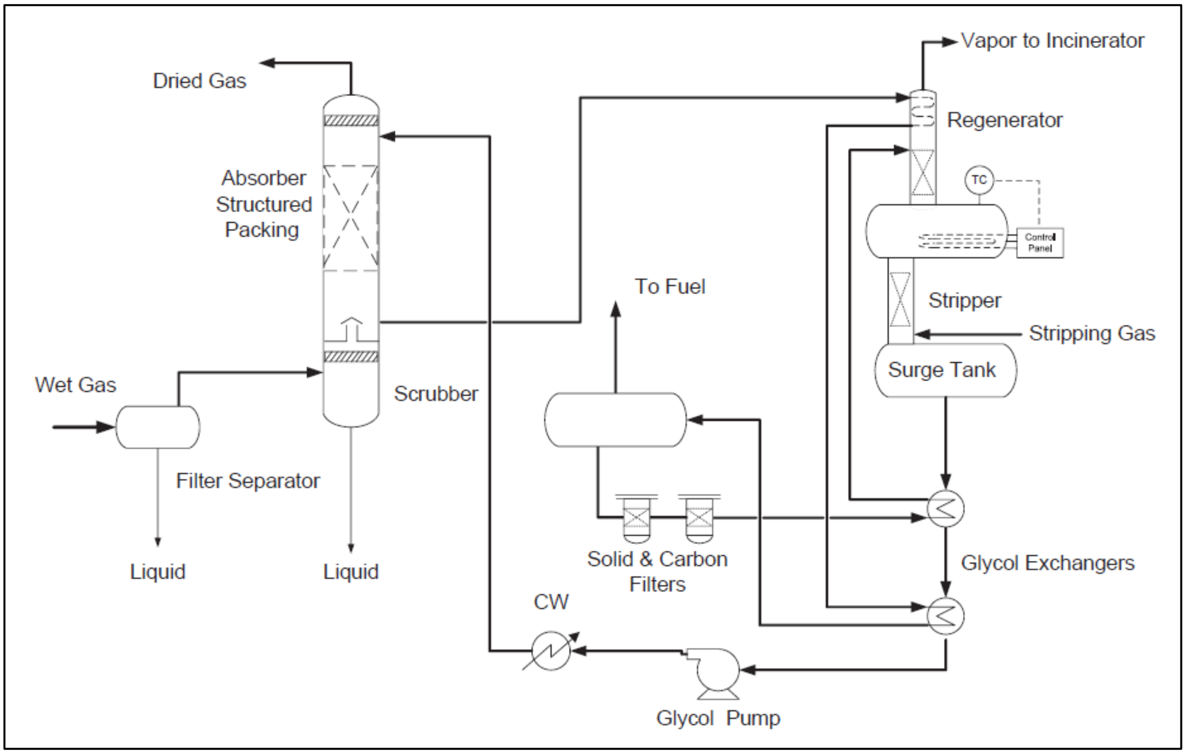
- Among the different natural gas dehydration processes, **absorption** is the most common technique, where the water vapor in the gas stream becomes absorbed in a liquid solvent stream.
- Glycols are the most widely used absorption liquids as they approximate the properties that meet the commercial application criteria.
- Glycol, any of a class of organic compounds belonging to the alcohol family; in the molecule of a glycol, two hydroxyls (—OH) groups are attached to different carbon atoms. The term is often applied to the simplest member of the class, ethylene glycol.
- Several glycols have been found suitable for commercial application.

1. Monoethylene glycol (MEG) ($C_2H_6O_2$)
2. Diethylene glycol (DEG) ($C_4H_8O_2$)
3. Triethylene glycol (TEG) ($C_6H_{14}O_4$)
4. Tetraethylene glycol (TREG) ($C_8H_{18}O_5$)

10.1.1. Conventional TEG Dehydration Process

- Fig. below shows the scheme of a typical TEG dehydration unit. As can be seen, wet natural gas is processed in an inlet filter separator to remove liquid hydrocarbons and free water.
- The separator gas is then fed to the bottom chamber of an absorber where residual liquid is further removed. It should be cautioned that hydrocarbon liquids must be removed as any entrainments will result in fouling of the processing equipment and produce carbon emissions.
- The separator gas is then contacted counter currently with TEG, typically in a packed column. Typically, the liquid loading on the tray (GPM per square foot) is very low,

due to the low liquid to gas ratio. To avoid liquid maldistribution, structured packing or bubble cap trays should be used.



Typical flow diagram for conventional dehydration system

- TEG will absorb the water content, and the extent depends on the lean glycol concentration and flow rate.
- TEG will not absorb heavy hydrocarbons to any degrees; however, it will remove a significant portion (up to 20%) of the BTEX (benzene, toluene, ethylbenzene, and xylenes) components.
- Dry natural gas exiting the absorber passes through a demister, and sometimes through a filter coalescer to minimize TEG losses.
- The rich glycol is used to cool the TEG regenerator overhead, minimizing glycol entrainment and losses from the overhead gas. Rich glycol is further heated by the glycol heat exchanger and then flashed to a flash tank.
- The flash gas can be recovered as fuel gas to the facility. The rich TEG is filtered with solid and carbon filters, heated, and fed to the regenerator.

- The filtration system would prevent pipe scales from plugging the column and hydrocarbons from coking and fouling the reboiler.
- The water content in the glycol is removed with a reboiler. The water vapor and desorbed natural gas are vented from the top of the regenerator.
- The dried glycol is then cooled via cross exchange with rich glycol; it is pumped and cooled in the gas/glycol heat exchanger and returned to the top of the absorber.

10.2. Solid bed dehydration

- Solid bed dehydration is the process where a solid desiccant (adsorbent) is used for the removal of water vapor from a gas to meet water dew points less than -40°F.
- The desiccant material becomes saturated as moisture is adsorbed onto its surface.
- A good desiccant should therefore have the greatest surface area available for adsorption.
- The mechanisms of adsorption are of two types: **physical and chemical**.
- In physical adsorption (or physisorption), the bonding between the adsorbed species and the solid-phase hold liquids (condensed water vapors) and solids together give them their structure.
- In chemical adsorption, involving a chemical reaction that is termed “chemisorption,” a much stronger chemical bonding occurs between the surface and the adsorbed molecules.
- Physical adsorption is an equilibrium process, where for a given vapor-phase concentration (partial pressure) and temperature, an equilibrium concentration exists on the adsorbent surface that is the maximum concentration of the adsorbate on the surface.
- The measurement of the amount of gaseous compound adsorbed over a range of partial pressures at a single (fixed) temperature results in a graph known as an **adsorption isotherm**, which can have very different shapes depending on the type

of adsorbent, the type of adsorbate, and intermolecular interactions between the adsorbate and the adsorbent surface.

10.2.1. Adsorption capacity

Adsorption capacity (or loading) is the amount of adsorbate taken up by the adsorbent per unit mass (or volume) of the adsorbent. The adsorption capacity of a solid desiccant for water is expressed as the mass of water adsorbed per mass of desiccant. There are three water-adsorption capacity terms used as follows:

- ***Static equilibrium capacity*: ** the water capacity of a new (fresh) solid desiccant (usually expressed in weight percent) as determined in an equilibrium cell at a fixed temperature and 100% relative humidity.
- ***Dynamic equilibrium capacity*: ** the water capacity of solid desiccant as the fluid is flowing through the desiccant at the design flow rate, temperature, and pressure.
- ***Useful capacity:*** the design capacity that accounts for the loss of solid desiccant capacity with time due to the fact that the total desiccant bed cannot be fully utilized.
- The static adsorption capacity is greater than the dynamic adsorption capacity. The dynamic equilibrium loading is generally 50%-70% of the static equilibrium capacity.
- The static adsorption capacity is the maximum theoretical capacity of the desiccant and can be used for comparison of different desiccants while the dynamic adsorption capacity is used to calculate the required filling amount of adsorbents.

10.2.2. Adsorbent Selection

- A variety of solid desiccants is available in the market for specific applications. The selection of proper desiccant depends on the given application and sometimes is a complex problem. For solid desiccants used in gas dehydration, the following properties are desirable:

1. High adsorption capacity: this reduces the adsorbent volume, requiring smaller vessels, resulting in lower capital and operating costs.

2. High selectivity: this permits removal of only the undesirable components and reduces operating expenses.

3. Easy regeneration: low regeneration temperature reduces the heating requirement for solid desiccant regeneration.

4. Low pressure drop design: this makes more pressure available for the turboexpander operation in an NGL recovery process.

5. Good mechanical integrity: high crush strength, low attrition, low dust formation, and high stability against aging reduce the frequency of adsorbent change-out and downtime-related losses in production.

6. Environmental friendly properties: the materials should be noncorrosive, nontoxic, and chemically inert to permit safe handling.

7. Reasonable adsorbent price.

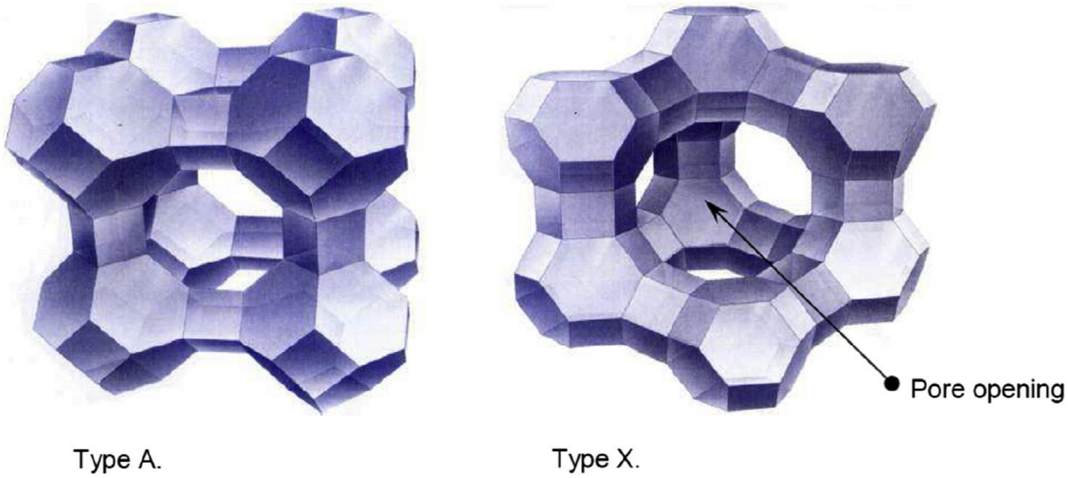
10.2.3. adsorbents

The common commercial adsorbents used in solid-bed dehydrators are **molecular sieves**, **silica gels**, and **activated alumina**,

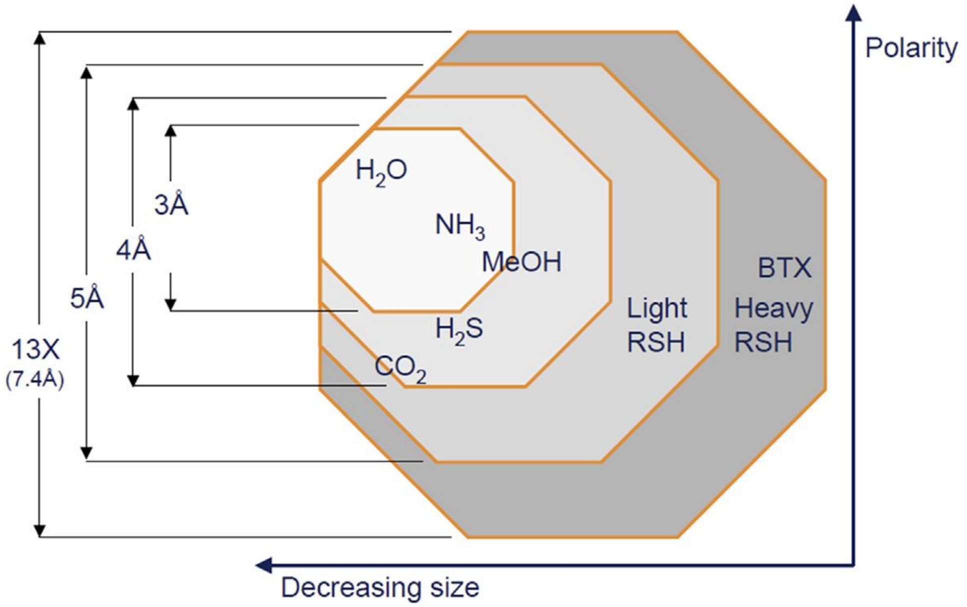
1. Molecular Sieves

- Molecular sieves or zeolites are crystalline alkali metal alumino-silicates with a typical structure of the form $M_{x/n}[(AlO_2)_x(SiO_2)_y]zH_2O$, where n is the valence of the cation and M is the metal ion inside each aluminosilicate cage.
- The zeolite is a three dimensional tetrahedral structure of silica and alumina. The alumina tetrahedra carry a net negative charge, and need to be balanced by a cation such as Na^+.
- In the zeolite structure, the cations determine the pore opening size, and depending on the type of cation, molecular sieves with a specific pore opening can be created.

- The benefit of having an adsorbent with a specific pore opening can be seen when observing nominal diameters of typical molecules within a hydrocarbon feed stream.
- To be efficiently adsorbed, the polar molecules must be small enough to enter the cavities via their pores. Hence, water molecule (with the nominal size of 2.6 A°) can be adsorbed on 3A, 4A, 5A, and 13X molecular sieves.
- Molecular sieve is the most versatile adsorbent because it can be manufactured for a specific pore size, depending on the application.
- Molecular sieves are the only choice for natural gas dehydration to cryogenic processing standards (less than 0.1 ppmv water or -150°F dew point).
- Molecular sieves can also provide a solution for removal of carbon dioxide and sulfur compounds such as hydrogen sulfide, mercaptans, carbonyl sulfide, and other sulfides (with the exception of carbon disulfide) from natural gas and NGLs to very low outlet specifications, either as a stand-alone unit or as a polishing unit within a combination of gas treating processes.
- The choice of molecular sieve type depends on the type and concentration of contaminants in the feed gas.



Molecular sieve types A and X structures



Molecular sieves selection chart.

2. Silica Gels

- Silica gel is a generic name for a gel manufactured by adding aqueous sodium silicate to sulfuric acid. It is an amorphous product similar to alumina.
- There are different grades of silica gel commercially available for natural gas drying. Silica gels can be used for heavy hydrocarbon and water removal to meet a water dew point of or lower with specialty grades silica gel.
- Silica gel can be used to process sour gases, but not alkaline materials such as caustic or ammonia. Although there is no reaction with H_2S, sulfur can deposit and block their surface pores. The H_2S content in the feed gas should stay below 5%.
- Silica gel is typically used in feed gas pretreatment units for removal of trace components of heavy hydrocarbons and water, such as feed gas to a membrane separation unit, or conditioning flash gas to the fuel gas system.
- It is not used in drying feed gas to NGL and LNG production plants because of its lower adsorption capacity, and inability to meet low water dew point. The adsorption capacity of silica gel is typically exhausted in a short time, in the range

of dozen of minutes up to 2-3 h, which increases the number of adsorption cycles and reduces the life time of the silica gel.

3. Activated Alumina

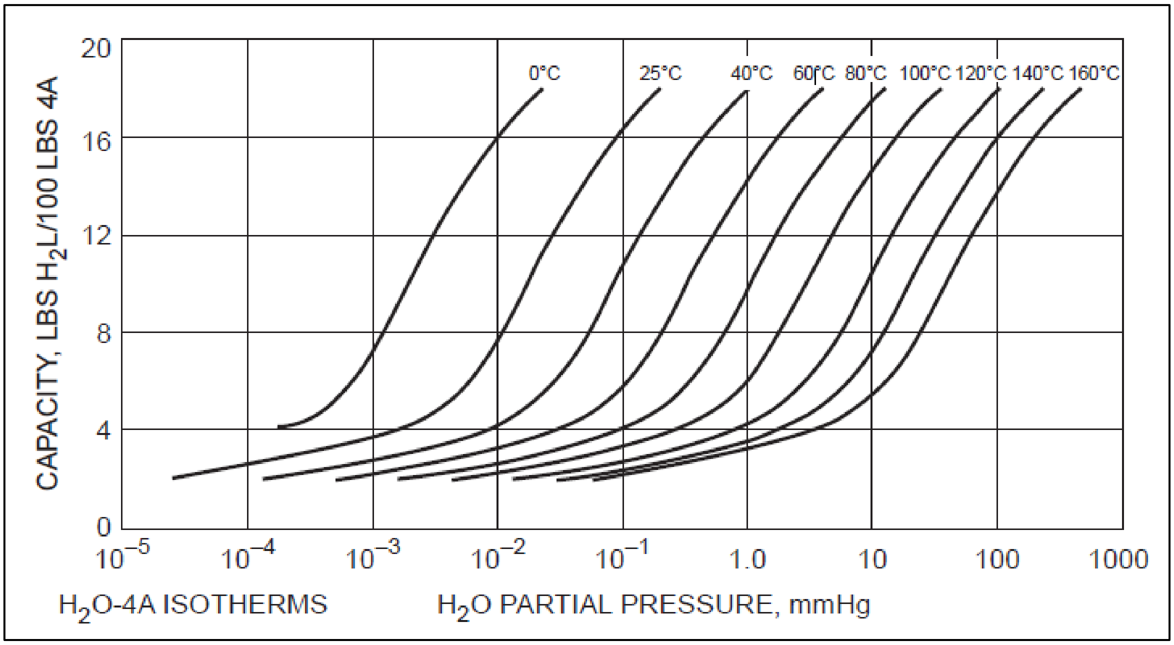
- A hydrated form of aluminum oxide ($Al_2O_3.3H_2O$), alumina, is the least expensive adsorbent for gas dehydration. Alumina is alkaline which should not be used for drying gas with high concentrations of acid gases (CO_2 and H_2S).
- Alumina does not have a precise pore opening the way molecular sieves do. Consequently, it is not selective since more molecules have access to the active sites.
- Activated alumina is a manufactured or naturally occurring form of aluminum oxide that is activated by heating.
- Activated alumina holds onto water less strongly than molecular sieves and therefore requires lower regeneration temperature and less regeneration heat duty.
- Similar to molecular sieves, feed temperature should be kept at below 120°F to avoid overloading the adsorbents.
- Activated alumina is typically used to dry a wet lean natural gas to a dew point of -60°F.
- Activated alumina has a higher equilibrium water capacity than molecular sieves. It can adsorb water of 35%-40% of its own weight.
- Activated alumina is usually applied as a top layer on the molecular sieves to reduce cost, and to protect the molecular sieves.

10.3. Adsorption Technology

1. Adsorption Principle

- There is an equilibrium relationship between the fluid and the solid adsorbents in the mass transfer applications, which can be expressed in the form of isotherms as shown in Fig. below.

- As the isotherm shows, the concentration of the adsorbate, which in this case would be water, is a function of the concentration of water in the fluid phase and the adsorbing temperature.
- The level to which gas is dried is a function of the regeneration conditions.

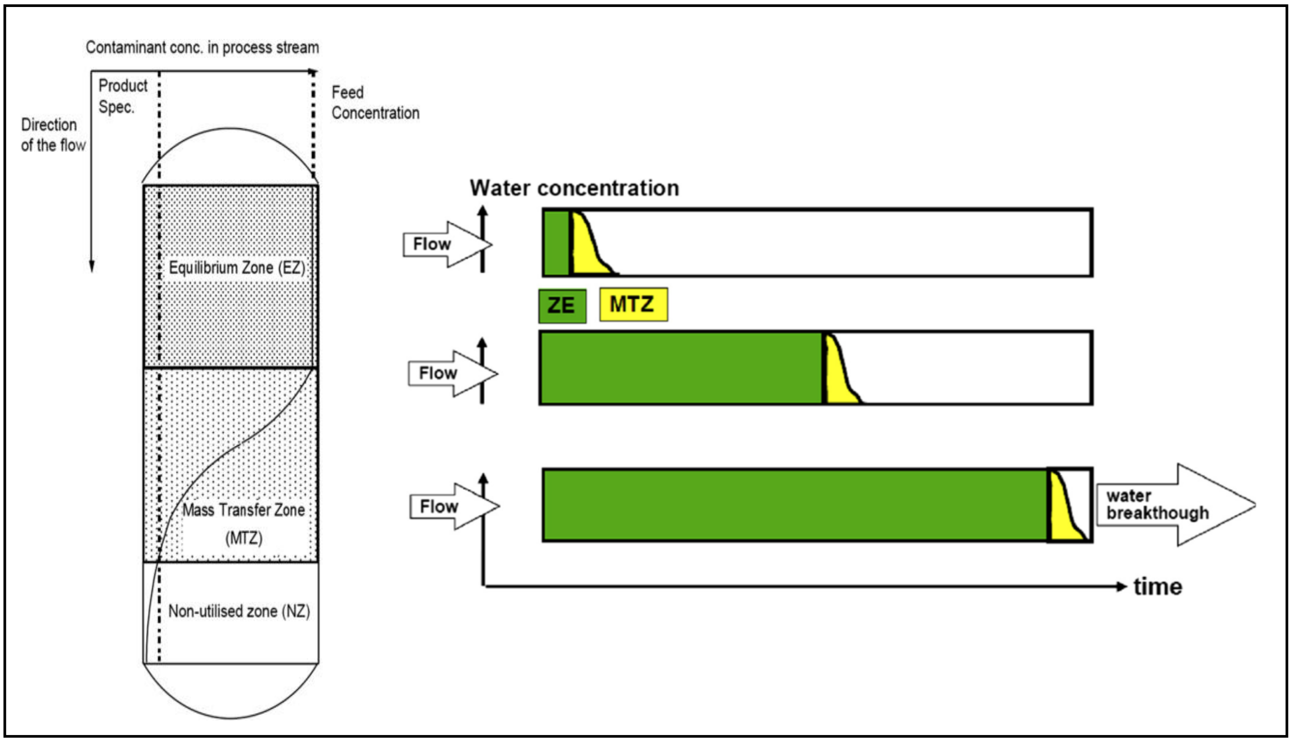


Typical water adsorption isotherms of a 4A molecular sieve.

- A thoroughly regenerated bed will be in equilibrium with the gas used for regeneration. The concentration of water left on the bed at the end of the regeneration cycle determines the performance of the bed because the outlet gas will be in equilibrium with the last particle of adsorbent.
- The adsorption process is dynamic as the adsorbent removes the water content from a continuously flowing stream.
- In commercial practice, adsorption is carried out in a vertical, fixed bed of adsorbent, with the feed gas flowing down through the bed.
- The feed gas entering the bed from the top and the upper zone becomes saturated first, where equilibrium between the water partial pressure in the gas and the water

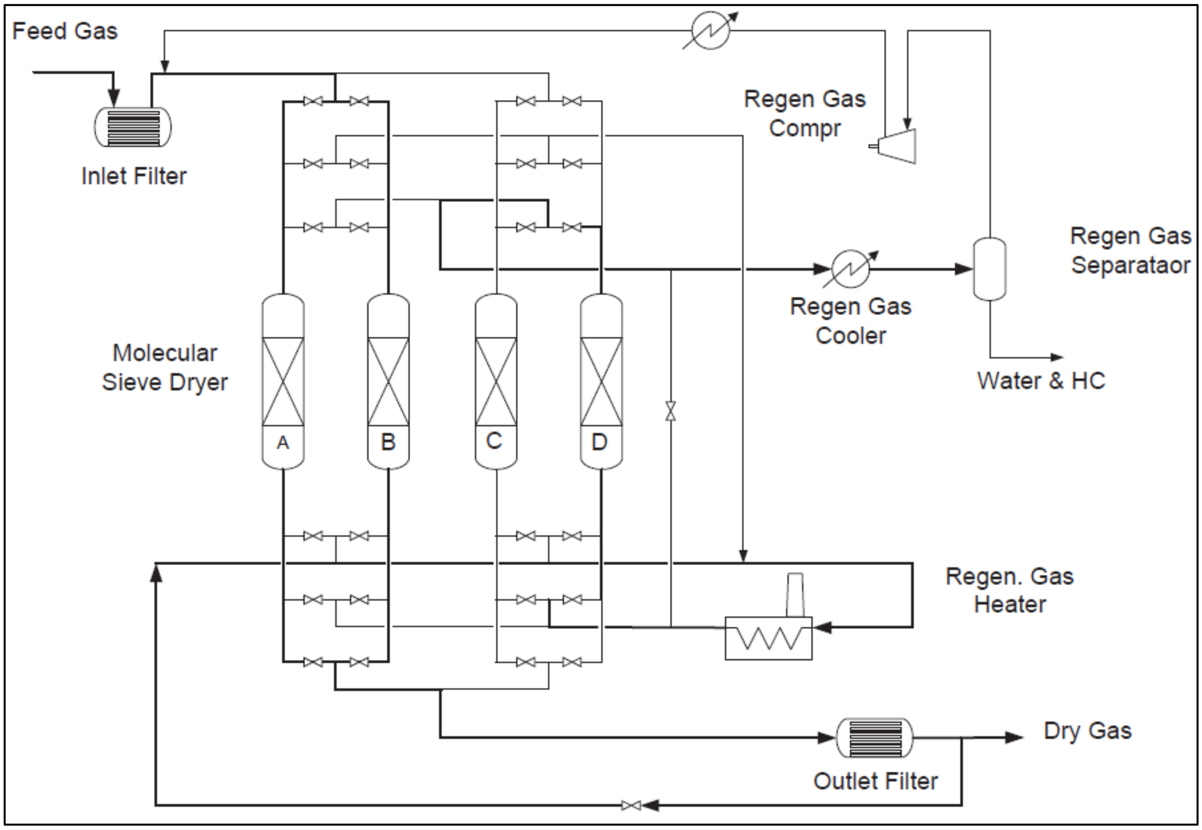
adsorbed on the desiccant is established and no additional adsorption occurs. This zone is called **equilibrium zone (EZ)**.

- With the adsorption going on, the EZ will grow and more and more water will be adsorbed.
- The length of the adsorber bed across which the concentration of the adsorbate is reduced from inlet to outlet conditions is known as **the mass transfer zone (MTZ)**. This is simply a zone or section of the bed where a component is transferring its mass from the gas stream to the surface of the solid desiccant.
- **The nonutilized zone (NZ)** is the part of the bed that has not encountered water yet because all water molecules were adsorbed in the EZ and MTZ. This zone will only serve for drying when the EZ and MTZ have lost their adsorption capacity.
- As the flow of gas continues, the mass transfer zone moves downward through the bed and water displaces the previously adsorbed gases until finally the entire bed is saturated with water vapor.
- When the leading edge of the MTZ reaches the end of the bed, breakthrough occurs. At this time, the adsorber vessel should be switched to the regeneration mode.



10.4 Operation of Solid-Bed Dehydrator

The process flow schematic of a typical molecular sieve dehydration unit is shown in Fig. below. The illustrated dehydration system is for a large gas processing plant, which typically consists of four solid-desiccant beds, packed with molecular sieve and activated alumina. The number of drying beds varies depending on the feed gas flow rate and the mode of operation.



Process flow schematic of a typical molecular sieve dehydration unit.

a) 3 + 1 Mode of Operation

- The dehydrators can operate in a 3 + 1 mode, i.e., three parallel beds drying and one bed on regeneration. In fact, three vessels will be on-line removing water vapor from the feed gas while one bed is being regenerated with a slipstream of the dry (product) gas.

- The advantages of three-bed parallel operation are lower pressure drop and an extended molecular sieve lifetime, due to less frequent regeneration.
- The direction of flow for the solid bed gas dehydration system is designed in such a way that the adsorption, depressurizing, and repressurizing steps are downward flow through the bed, and the heating and cooling steps are upward flow.

1. Adsorption Step

For three-bed parallel operation, the approximate cycle time for adsorption is 18 h followed by a 6 h regeneration cycle. The regeneration is comprised of a 30 min depressurizing step, a 3 h heating step, a 2 h cooling step, and a 30 min repressurizing step. The dry gas leaves the drying beds and enters the outlet filters. The function of these filters is to remove molecular sieve or any other solid particles.

2. Depressurization Step

At the completion of the 18 h adsorption cycle, the dehydrator must be depressurized to prepare the environment for the regeneration heating step, which uses dry residue gas at low pressure. The normal depressurization lines for the four dehydrators should have flow restriction orifices to effectively limit the rate of depressurization. The depressurization rate should not exceed 75 psi/min to prevent bed movement and fluidization. The gas will flow downward via the restriction orifices in order for the vessel to depressure within the allotted time of 20 min.

3. Heating Step

Once the dehydrator has been depressurized, the heating step begins. The residue gas is continuously compressed by the regeneration gas compressors and flows through the bypass valve to the regeneration gas heater. The gas outlet temperature is controlled to 570-600°F. The hot gas flows upwards through the dehydrator being regenerated and heats up the bed to a temperature at which the water content of the molecular sieve is reduced to the required low level. As a result, the water leaves the surface of the molecular sieve and is removed by the regeneration gas flowing upward through the bed.

4. Cooling Step

Following the heating step, the dehydrator is cooled with cold compressed regeneration gas to cool the molecular sieve to the normal adsorption temperature prior to repressurizing and returning it to normal service. The cool gas flows upward through the dehydrator and then to the regeneration gas heater, so that the fired heater can be operated continuously.

5. Repressurization Step

After the cooling step, the dehydrator must be pressurized to prepare the vessel to be brought back on-line. The normal repressurization lines for the four dehydrators have flow restriction orifices to effectively limit the rate of repressurization to no more than 75 psi/min downwards.

b) 2 + 2 Mode of Operation

- The dehydration process can also be arranged in the 2 + 2 mode of operation. In this operating mode, two dehydrators are in the adsorption cycle and two dehydrators are in the regeneration cycle at any given time.
- In the regeneration cycle, one dehydrator is in the heating cycle and one dehydrator is in the cooling cycle, simultaneously. This allows circulation of the regeneration gas in series, which flows first to the vessel that is being cooled, then to the heater, and finally to the other vessel that is being heated.
- The regeneration in series reduces the regeneration gas consumption and uses the energy of the dehydrator that is being cooled down.

- The only drawback is the higher capital cost compared to the 3+ 1 mode, but it provides a more robust operation.

c) Other Modes of Operation

- There are other modes of operation, depending on the number of beds and the dehydration unit operating conditions. It can be operated on 2 +1 mode where two dehydrators are on the adsorption cycle and one dehydrator is on the regeneration and heating cycle.
- For smaller gas dehydration units, it can be arranged on 1 + 1 mode, with one dehydrator on adsorption cycle and one on regeneration and heating cycle.

10.5. Operational Problems

Problems associated with molecular sieve operation generally relate to mis operation of the upstream units and improper installation and operation of the molecular sieve beds. The following sections summarize these problems and provide guidelines to mitigate these problems.

1. Inlet Conditions

Often a small change in the inlet temperature can significantly increase the water content in the feed gas, which can impact the solid-bed dehydration system performance. Also the adsorbents capacity drops as the temperature increases. A drop in inlet gas pressure will evaporate more water, increasing its water content. The lower feed pressure will also increase the gas velocity through the bed and will extend mass transfer zone which may result in an earlier breakthrough. If the inlet gas source is changed from lean gas fields to rich gas fields, more liquids can enter the dehydration unit.

2. Contamination

The most frequent cause of solid desiccant bed failure is the incomplete removal of contaminants from the inlet gas.

3. Liquid Carryover

Liquid carryover can be due to design deficiency of the feed separator or malfunctioning of the upstream amine treating unit. The cause can also be due to upset of the regeneration gas separator. In the worst scenario, the liquid (hydrocarbon liquids and water) can flood the dehydrators and pulverize the adsorbents.

4. Salt Entrainment

Salt contamination comes from the treating units from salt water bearing formations, or from salt dome storage caverns. Salt will accumulate and block the opening and pores in the sieves. In extreme cases, all the voids between the molecular sieve beads will plug up, resulting in an increase in pressure drop. Eventually, the adsorbent must be replaced.

5. Corrosion Products

Corrosion materials can come from upstream equipment and piping. H_2S in the feed gas can react with carbon steel equipment during regeneration to produce pyrite flakes. These can deposit on the molecular sieves surface and can block the bottom outlet screen, which can result in maldistribution among the dehydrators.

6. Oxygen

If there is any oxygen in the feed gas stream, it may react with H_2S and other sulfur compounds on the molecular sieves surface to form elemental sulfur. In extreme cases, this will not only block macro and micropores but also the spaces between the sieves, resulting in one large “lump” blockage, which is difficult to remove. Oxygen can also react with heavy hydrocarbons in the feed gas to form coke during the regeneration cycle, causing fouling of the molecular sieves and the regeneration heater.

7. Incomplete Regeneration

Insufficient or incomplete regeneration of the adsorbent beds will lead to a sudden loss in adsorption capacity and premature breakthrough. Insufficient adsorbent bed regeneration is a result of one or all of the following factors:

- low regeneration gas flow rate/temperature,
- insufficient regeneration time, and
- change of regeneration gas composition.

8. Bed Refluxing

Heating up the adsorber without using a heating ramp or an intermediate heating step may result in a large temperature difference across the bed. During regeneration, as the regeneration gas flows from the bottom to the top, water is desorbed, and re-adsorbed many times. Often it is carried off at such a rapid rate that it condenses on the cool top head of the vessel and dripped back down onto the bed. This phenomenon is called **water refluxing** which increases with high pressures and low regeneration flow rates. At some point, the ascending heat zone mixes with the descending water resulting in boiling, which may cause hydrothermal damaging of the molecular sieves. Hydrothermal damaging may alter the binder material and destroy the crystal structure of the zeolite. In order to prevent hydrothermal damaging of molecular sieves, it is not only important to choose the right formulation of the molecular sieve (binder and zeolite) but the proper regeneration conditions.

9. Improper Bed Loading

The same quantity of each adsorbent grade in each vessel must be used to prevent unequal flow distribution among the different beds to avoid premature breakthrough.

For optimum bed loading, the bed may require a mixed bed of large and small particles, typically with the small particles being at the bottom of the bed. If the adsorbents are loaded differently among the beds, the mass transfer zone may be different among beds which may prolong the adsorption time to meet dew point specifications.

10. Unequal Flow Distribution

Sometimes premature breakthrough occurs on only one vessel and this is the case when working with several vessels in adsorption in parallel. If there is a problem with one vessel only it is in general an issue of bed configuration and not of the molecular sieves. Unequal flow distribution due to bed configuration or internal misalignment can be detected by a high pressure drop difference in the vessels during adsorption.

11. Bottom Support

Experience shows that more and more problems of solid bed failure are caused by failure of the support grid. The mechanical design of the support bed must be strong, and the quantity and size of ceramic balls must be according to manufacturer guidelines.

12. Bed Bumping

A rapid depressurization possibly from a sticking valve can lift the bed and even fluidize it. Bed pumping will crush the molecular sieves making them inoperable. Severe damage may require dumping and replacing the sieves.

13. Switching Valve Leakage

The switching valves on the molecular sieve beds ensure extreme temperature and pressure fluctuation on a daily basis, varying from ambient temperature during the adsorption cycle to 500 °F during the regeneration cycle. These cyclic operations impose undue stress on these valves, which may affect the valve performance. If leakage occurs, this may result in off-spec product. The switching valves must be monitored and maintained routinely.

14. Moisture Analyzer

To optimize the life of the molecular sieves, reduce energy, and prevent wet gas from contaminating downstream equipment, a highly reliable and rapid-response moisture analyzer is crucial. Some of the recent advances in noncontact laser type detector are now available. The moisture analyzer must be selective so that interferences from other compounds (such as methanol) are eliminated. The response rate of the analyzer must be fast, detecting rapid breakthrough in the molecular sieve beds.

15. Internal Insulation Failure

The internal insulation in the molecular sieve beds also goes through severe thermal stress during the adsorption and regeneration cycles. If the insulation is damaged, moisture may be retained within the insulation, which may be the cause of off-spec products. The insulation should be repaired and replaced as necessary.

16. Molecular Sieve Handling Safety

Many vintage gas processing plants have been operating for many years without any incidents. Typically, the H_2S content of the inlet feed gas has increased over the years. Contractors and staff in these plants must be constantly reminded of the danger and hazards associated with operating a molecular sieve unit. Typically, during shutdown, molecular sieve units are purged with nitrogen to remove H_2S content from the vessel before entering. However, there are still H_2S that are tightly adsorbed by the molecular sieve. When molecular sieves are changed out, they are usually dumped into water to avoid the pyrophoric reaction. When molecular sieves are in the water, H_2S will be displaced from them, as sieves have higher affinity towards water than H_2S. There were accidents in the past relating to fatality from H_2S poisoning during the change-out operation. The molecule sieve operation program must insist personnel to carry H_2S monitors and escape masks even when the unit feed gas contains low levels of H_2S.

10.6. Other Gas Dehydration Processes

Other less frequently used dehydration methods can be applicable to some operations listed in the following.

1. Calcium chloride

Calcium chloride can be used as a consumable desiccant to dry natural gas. Anhydrous calcium chloride combines with water to form various calcium chloride hydrates. As water absorption continues, calcium chloride is converted to successively higher states of hydration, eventually forming a calcium chloride brine solution. Calcium chloride dehydrators may offer a viable alternative to glycol units on small feed rate remote dry gas wells. Calcium chloride must be changed out periodically. Brine disposal is an environmental issue.

2. Methanol Refrigeration

Dehydration of natural gas to -150°F using methanol as the hydrate inhibitor has been used for ethane recovery in the Empress plant. The condensed water and methanol streams can be decanted in the cryogenic unit and can be separated by distillation. The difficulty in the methanol refrigeration process is the high methanol losses associated with the high vapor pressure. The process must work with cryogenic temperature refrigeration to minimize losses. The methanol process is more complex in terms of operation than the molecular sieves process.

3. Membranes and Twister

The Membranes and Twister technology can be used to remove water and hydrocarbons from the natural gas to meet water and hydrocarbon dew point specifications of pipeline gas.