Molecular Sieve Adsorbents for Natural Gas Processing
Zeochem Products for the Natural Gas Processing Industry

Natural Gas
Zeochem, a manufacturer of high quality molecular sieves and chromatography gels, was established more than 190 years ago and its headquarters is still based at the original location on Lake Zurich, Switzerland. Zeochem is a subsidiary of the Swiss CPH Chemie+Papier Holding AG.

With manufacturing facilities in Uetikon, Switzerland and Louisville, KY, USA, Zeochem offers a wide range of molecular sieve products for natural gas dehydration and treating to meet final pipeline specifications. Products are also manufactured for Liquid Natural Gas (LNG) quality or downstream processing in petrochemical complexes. Our molecular sieves are effective in removing contaminants from natural gas for equipment protection during processing and for the recovery of Natural Gas Liquids (NGL) or Liquefied Petroleum Gas (LPG) products.
Natural gas dehydration plants have been operating worldwide on a variety of technologies and in a number of process variations for many years. Gases to be dehydrated cover straight natural gas, through heavier associated gases, and sour gases of various types. Many plants use turbo-expander technology to compress, chill down and liquefy the natural gas to enable heavier and more valuable components to be separated out from the feed gas. In order to work at these low temperatures, the natural gas must be dried to very low dew points. For many gas plants this is typically of the order of -100°C. Also LNG plants require very low dew points as do plants where ethane recovery is required. Molecular sieve is the most commonly used technology for this duty, as it is the only one that can give the required very low dew points. It is a duty which is fairly costly in terms of the energy required for pressure loss, for regeneration heating and also in the need to shut the plant down at regular intervals to replace the molecular sieve charge – typically every two to four years. Hence, key-drivers in terms of molecular sieve quality are durability, kinetics and capacity.

**ZEOCHEM® Z4-04**
ZEOCHEM® Z4-04 molecular sieve is a specially developed form of the 4A type crystal structure, which is particularly suitable for use in natural gas dehydration plants and similar processes. The combination of an open crystal structure and a high equilibrium capacity for moisture, together with excellent dynamic characteristics and superb physical properties, marks ZEOCHEM® Z4-04 as the accepted standard for natural gas dehydration. ZEOCHEM® Z4-04 is approved and in use with major natural gas processing companies around the world.

**ZEOCHEM® Z3-06**
ZEOCHEM® Z3-06 molecular sieve is a specially developed form of the 3A type crystal and it is a high value zeolite recommended for dehydration of hydrocarbon gas and liquid streams.
in specific types of units. It has the advantage of excluding other molecules from the internal crystal lattice while still adsorbing water. By limiting the co-adsorption of molecules such as hydrocarbons, carbon dioxide and sulfur compounds, ZEOCHEM® Z3-06 offers a number of economic and technical advantages:

- It reduces hydrocarbon losses from the main gas stream to the regeneration stream when the regeneration stream is not recycled.
- It reduces the formation of carbonyl sulfide (COS).
- It reduces the spiking of hydrocarbons in the outlet gas stream giving a more constant gas composition; this in turn eases the operation of downstream cryogenic units.

In addition ZEOCHEM® Z3-06 can offer extended lifetime by minimizing coking and sulfur and oxygen side reactions.

**ZEOCHEM® Z3-02**

**The Formation of Carbonyl Sulfide (COS) on Molecular Sieve**

The presence of carbon dioxide, hydrogen sulfide and moisture in a gas or liquid can result in the formation of carbonyl sulfide.

\[
\text{CO}_2 + \text{H}_2\text{S} \leftrightarrow \text{COS} + \text{H}_2\text{O}
\]

This reaction is an equilibrium reaction.

While the gas is saturated, the position of equilibrium will favor the presence of only a very small amount of COS. However, in an adsorber, as the amount of moisture is decreased through adsorption, the equilibrium amount of COS formed will increase.

The use of a high exchanged 3A such as ZEOCHEM® Z3-02 will not catalyze the COS formation reaction and will also minimize the co-adsorption of \(\text{CO}_2\) and \(\text{H}_2\text{S}\); hence, the maximum expected COS formation will be around 5% of the equilibrium value.
Zeochem products for natural gas applications have won a reputation for high quality and long life whether used for hydrocarbon dehydration applications only or for dehydration and sweetening purposes. In particular, Zeochem has earned an excellent reputation in hydrocarbon treating applications as a result of its pioneering work in this application. This work involved detailed laboratory trials done to investigate all stages of the adsorptive separation process, including adsorption capacity; adsorption kinetics; order of adsorption and regeneration process conditions. Natural gas treating is an application that can include a wide range of compounds to adsorb, hence it is technically more complicated than straight dehydration. It is an application that sometimes requires the use of a number of different products and technologies to cover the wide variety of circumstances encountered in practice.

**Competition for Adsorbent Sites – Polarity**
When dealing with weakly adsorbed components, one has to consider the order of adsorption, i.e. the polarity of a given impurity against other components in the fluid to be treated. Zeochem is able to predict the order of adsorption for weakly adsorbed components, although in many cases there is inevitably a large amount of co-adsorption.

**ZEOCHEM® Z5-01 and ZEOCHEM® Z5-03HP**
ZEOCHEM® Z5-01 and ZEOCHEM® Z5-03HP are recommended when treating for sulfur removal is required and the sulfur species present are limited to H2S, methyl and ethyl mercaptan. These products have excellent kinetics and minimize the formation of carbonyl sulfide in the presence of hydrogen sulfide and carbon dioxide.

**ZEOCHEM® Z10-03**
ZEOCHEM® Z10-03 is used when higher mercaptans are present, such as propyl and butyl. The larger pore size of the 13X product allows even branched chain mercaptans into the Zeolite pores.

**ZEOCHEM® Z10-07**
ZEOCHEM® Z10-07 is a product which will double up on both the above duties, in that the pore size is large enough for all mercaptans, and COS formation is minimized.
Zeochem Techniques

Over the years, Zeochem has developed a vast know-how on the adsorption processes. Zeochem’s skilled technical team can provide a variety of solutions and technologies to meet the process demands, these techniques include:

- Single layer dehydration/treating
- Multi layers dehydration/treating
- Pressure drop minimization
- COS minimization
- Dehydration with recycle of the regeneration gas
- Retrograde condensation and reflux minimization by optimized regeneration procedure
- Patented regeneration technology for mercaptans desorption (low coke formation)
- Multi columns solutions with energy usage optimization by heat exchanging
- Solutions based on Lead-Guard technology
- Short cycle adsorbers for removal of high CO₂ concentrations

Some weakly adsorbed components are better adsorbed on non-standard sieve types. This has been investigated by Zeochem and recommendations can be made.

Temperature Ramp during Heating
Zeochem recommends that in many cases the regeneration heating temperature is ramped up over a period of time such as 30 minutes. This is done in order to minimize the onset of retrograde condensation in the bed, and the associated attrition of the particles in the bed.

Use of a Layer of Small Beads
Over the large part of the bed, Zeochem recommends the use of large beads to minimize pressure drop. However a layer of small beads of around 1 meter height can help extend the adsorption time by taking advantage of the better kinetics offered by the small beads.

Use of Different Types of Adsorbent in Separate Layers
This practice can help co-adsorption of valuable components, and hence save on money by preventing loss to the regeneration stream.

Short Cycle Adsorbers – The Solution for High CO₂ Concentrations in Natural Gas – A Practical Solution Developed with ZEOCHEM Molecular Sieve
Natural gas streams cover a broad range of compositions and contain a wide number of impurities which have to be removed. New processes using molecular sieves can increase the effectiveness of existing technology.

One such case in point is the removal of carbon dioxide in the range up to >2.5% from natural gas streams in smaller scale plants where a solution based on extraction with amine is not considered suitable.

Advanced Techniques for Advanced Adsorption Solutions
In addition to recommending enhanced adsorbents, ZEOCHEM also employs advanced techniques for the running of such an adsorption unit.
Such techniques include:

- Short cycle times
- Maximizing the effectiveness of heat usage by recycle and heat exchange
- Maximizing the effectiveness of heat usage by internal insulation
Zeochem employs technical service engineers and scientists who have years of experience in adsorber design, operation and maintenance. From the beginning of each project, Zeochem’s technical service engineers can provide conceptual advice and design support. As the project moves forward, Zeochem can review the detailed designs and procedures. In the end phase Zeochem offers consultation on last-minute change orders and start-up assistance when the unit is to be commissioned.

Follow-up service is available for troubleshooting and performance optimization. Of increasing importance is the training Zeochem can provide to customers’ engineers, supervisors and operators. Zeochem’s expertise in the field has been recognized and demonstrated the world over in seminars, conferences, papers and individual presentations.