MOLECULAR SIEVE Z4-01 FOR AMMONIA SYN-GAS PURIFICATION

Introduction
Molecular sieves are currently used in many ammonia plants for the purification of the make-up synthesis gas. Other ammonia plants are considering or are in the process of installing molecular sieve units as part of their energy conservation strategy. Opportunities exist for the replacement of current charges and in addition there are future prospects for the design of new units and sale of initial charges for this.

ZEOCHEM® Z4-01 is a high capacity 4A molecular sieve particularly suitable for use in such plants where in addition to an optimum capacity for the adsorption of moisture a capacity for small amounts of carbon dioxide is also required.

The combination of an open crystal structure giving outstanding adsorptive properties, together with excellent physical characteristics ZEOCHEM® Z4-01 as an ideal molecular sieve for these applications.

Zeochem AG – The Company
Zeochem AG is an established Swiss chemical company, having been in business since 1818. We have produced adsorbents for over 50 years, while in molecular sieves, the ZEOCHEM® business group of Chemie Uetikon has a wealth of experience stretching back over 25 years.

ZEOCHEM® molecular sieves are supplied world-wide from two plants situated in Uetikon Switzerland, and Louisville, Kentucky, USA.

Application
The primary application of molecular sieve in ammonia plants is in the removal of water, carbon dioxide and trace ammonia from the fresh make-up gas prior to its addition to the synthesis loop. Secondary applications may also exist in units for the purification of the loop purge stream prior to hydrogen recovery, the purification of the recycle hydrogen stream, the purification of by-product argon and helium streams (which may include ammonia adsorption).

A typical syn-gas feed stream will contain the following components

nitrogen	24.7% mole
hydrogen	74.1% mole
methane	0.7% mole
argon	0.5% mole
water	saturated
CO / CO_2	< 10 ppm

Components to be removed

water	< 0.1 ppm
CO_2	< 1 ppm
trace ammonia	< 0.1 ppm

The economic justification for the purification unit is:

a) it decreases synthesis loop pressure drop and compression costs
b) it lowers refrigeration energy requirements
c) it increases production capability and operating flexibility
d) it increases the efficiency of the heat exchanger network.

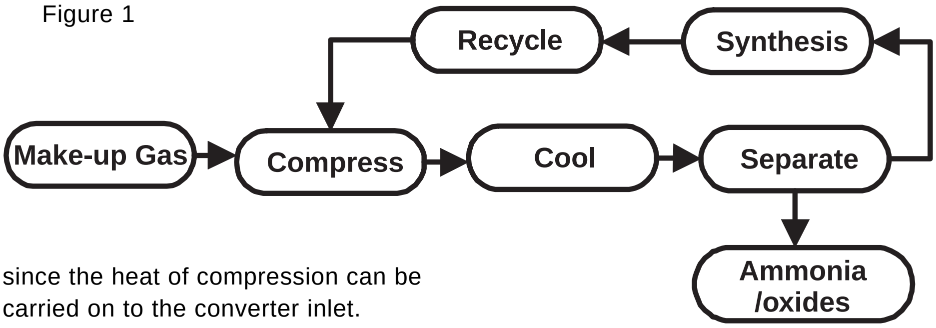
Molecular Sieve Recommendations
The standard molecular sieve for the syn-gas purification application is a Z4-01 molecular sieve. Some older plants also use Z10, but the small extra capacity (10-15%) is more than offset by the lower density (10%) and price considerations.

In both cases a large bead is recommended to minimise pressure drop for the large volume flows encountered. The argon / helium purification can be done with either 3A or 4A molecular sieve.

Process and Energy Considerations
The use of molecular sieves to purify the make-up gas allows a relatively simple alteration to the process flow scheme which results in significant energy savings. Previously the fresh make-up gas was added to the converter effluent, which was then compressed and cooled. Water and CO_2 contained in the make-up were removed in solution with liquefied ammonia. The recycle gas was then reheated and supplied to the converter inlet. (see figure 1).

In the newer process, oxides of carbon are removed from the make-up gas prior to its addition to the synthesis loop. The make-up gas is then fed directly to the converter. After reaction, the increased inlet ammonia concentration in the product recovery section allows condensation at higher temperatures, reducing the refrigeration load. Cooling water may be used for further condensation and this reduces the refrigeration costs still further. The fresh make-up is then combined with recycle and fed to the circulating compressor, after which it can be fed directly to the converter heat exchangers for heat up (see figure 2). There is no need for a circulating compressor after-cooler since the heat of compression can be carried on to the converter inlet.

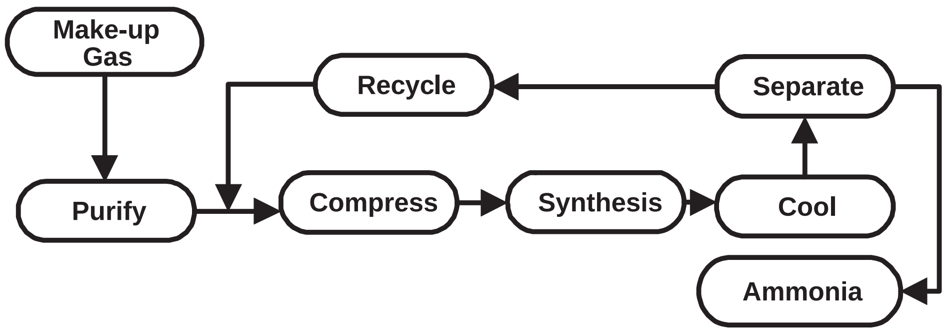
Figure 1



Compression energy requirements are significantly reduced in the modified process. The product ammonia is no longer compressed prior to condensation. In addition the lower overall flow rate and decreased pressure drop in the synthesis loop allow lower compressor discharge pressures for the same synthesis pressure.

Ammonia synthesis efficiency may also be increased if there is sufficient catalyst volume available. Since the recycle gas is mixed with the make-up gas after the product condensation step, the ammonia concentration in the converter feed is reduced, allowing a higher conversion per pass. Ammonia production may be increased due to the lower loop pressure drop and available compression power. Alternatively, lower purge rates and higher inert levels can be accepted with little penalty.

Figure 2



Typical Molecular Sieve Design Conditions

The make-up synthesis gas is normally purified with molecular sieve prior to the first stage compression at 300-500 psi, or between the first and second stages at 800-1000 psi.

Normal inlet temperatures are between 5 and 35°C, and molecular sieve performance is excellent over the whole of this range. The beds are typically sized to remove the saturated water plus up to 10 ppm wt CO_2 for 12-24 hours. Actual inlet CO_2 should be less than 2 ppm wt if the upstream methanator is functioning properly.

In keeping with the goal of reducing energy costs the beds are designed with a low length to diameter ratio to minimise pressure drop.

Regeneration

The molecular sieve must undergo regeneration on a regular basis to remove the adsorbed components. A dry CO_2 free gas is used to heat the beds to 280°C counter-current to the direction of adsorption. Typical regeneration gas may be recycled purified synthesis gas, a purge stream after hydrogen recovery, or a pure natural gas feedstock. The regeneration gas is normally disposed of to fuel, although synthesis gas may be recycled to the CO_2 adsorbers or to the methanator inlet.

In most cases the sieve vessels will be internally insulated. This reduces regeneration gas requirement by up to 50% because the heavy high pressure steel vessels do not need heating.

Advantages of ZEOCHEM® Molecular Sieve

1. High Density Beads
   The high density beads produced by Zeochem AG give a higher adsorption loading per unit length and hence a better usage of space inside the columns.

2. Good Dynamic Performance
   A second important measure of performance in addition to the equilibrium capacity is the rate of adsorption as measured in terms of MTZ or mass transfer zone length. This maximises the use of the bed by minimising this lost bed length or MTZ length.

3. High Strength Beads
   ZEOCHEM® molecular sieve beads have a high crush strength, a very smooth surface and very round beads allowing us to out-perform competitive products on physical properties.

4. Good Attrition Resistance.
   Allied to the absolute strength of the particles is the ability to resist the high abrasion forces present in the beds. The regular temperature and pressure changes tend to produce attrition between the individual beads.

5. Good Flow Distribution
   The carefully controlled bead size ranges are narrow and are designed to suit this particular application. Perfectly formed spherical particles within this narrow size range ensure an evenly packed bed, and hence an even flow distribution.

Technical Service

In addition to offering the optimum product for the application Zeochem AG also offers considerable technical service back-up:

a) Zeochem AG is happy to work with the customer to optimise the unit design to their individual requirements.

b) Back-up technical service and trouble shooting services are also available.

Typical Plant Design Conditions

1250 ton per day Ammonia Plant

Inlet Flow	12,700 lb per hour
Temperature	48°F
Pressure	905 psia
Water at inlet	saturated (8 lb / MMSCF)
CO_2 at inlet	10 ppm wt
Number of beds	2
Insulation	Internal
Bed Diameter	6 ft
Bed Height	10.5 ft
Molecular Sieve Type	Z4-01
Quantity	13,300 lb per bed
Total	26,600 lb

Cycle Times

Adsorption	12 hour design downflow
Regeneration heating	4.5 hours upflow
Regeneration cooling	2.5 hours upflow
Regeneration gas	Purge waste gas
Flow rate	300 lbmol per hour
Heating inlet temperature	500°F
Pressure	500 psi

certified
Quality System
SQS
SN EN ISO 9001 : 2000

Zeochem AG
CH-8707 Uetikon/Switzerland
Telephone +411/922 93 93
Fax +411/920 20 93
www.zeochem.ch

Associate of
CPH Chemie + Papier Holding AG