



Molecular Sieve Applications

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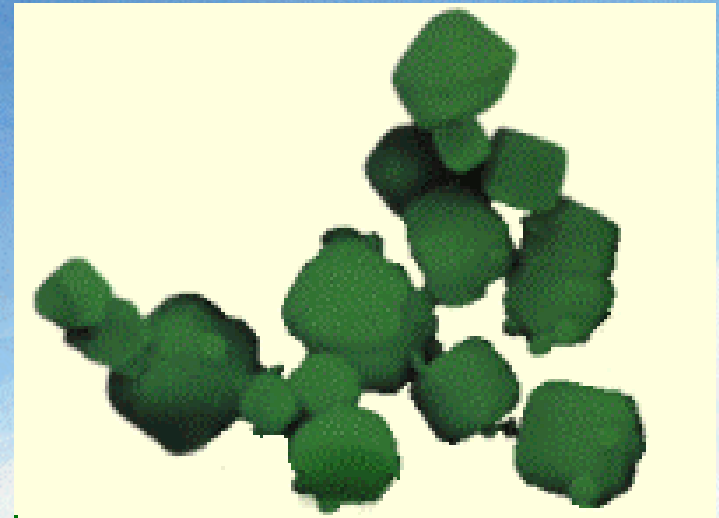
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Outlines

- ◆ Introduction - Molecular Sieve Adsorbents
- ◆ Adsorption Principles
- ◆ “Dynamic” Adsorption
- ◆ Regeneration Methods
- ◆ Applications in Titan
- ◆ Molecular Sieve Life and Contaminants
- ◆ Thermal Effects (Safety Aspects)
- ◆ Services Provided
- ◆ Conclusion

Introduction - Molecular Sieve Adsorbents

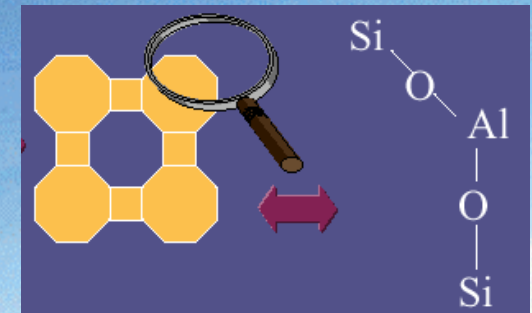
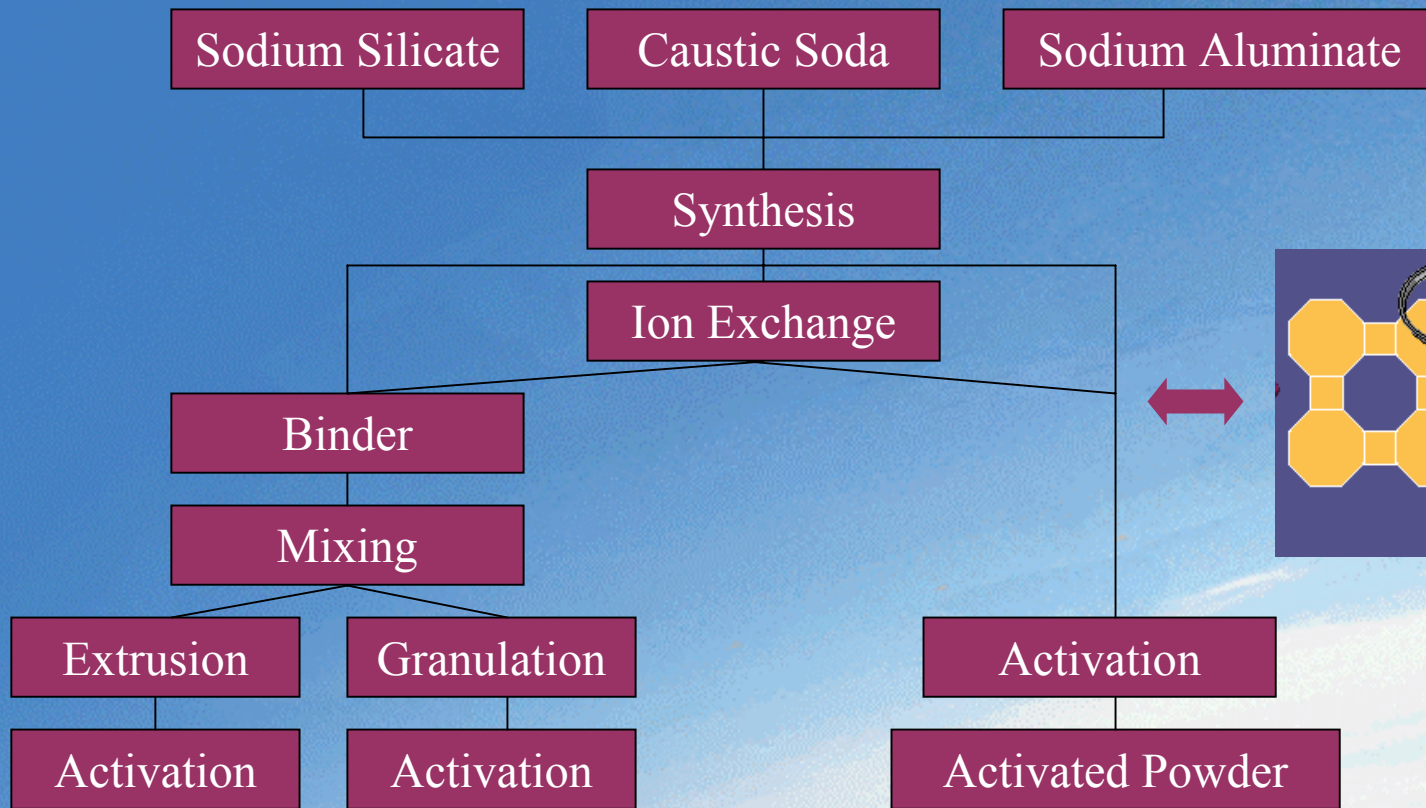
- Crystalline aluminosilicate or synthetic zeolites
- Unique structure with regular pore size



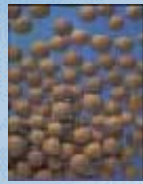
Introduction - Molecular Sieve Adsorbents

- Strong adsorptive force to remove many gas or liquid impurities to very low levels (ppm or less)
- Differ from other adsorbents in the form of their isotherms which have a high adsorption capacity for relatively low concentrations of the adsorbate

Synthesis and Preparation of Molecular Sieves



1.6 - 3.2 mm



0.7 - 1 - 1.5 - 2 - 5 mm



Adsorption Principles

- A phenomenon of a surface on which a molecule contained in a fluid is fixed on a surface of a solid
- Adsorption of the impurities having lower and/or same size as the pores of the molecular sieve.

Adsorption Principles

- When several impurities having the same size have to be removed, the more polar of them is first adsorbed.
- Physisorption of the impurities (Van der Waals interaction) on the molecular sieve following an extended Langmuir equation.

“Dynamic” Adsorption

- ◆ The most common mode of adsorptive separation process employs a fixed bed, cyclic operation.
- ◆ Mass Transfer Zone (MTZ) is defined as the bed length (h) through which the concentration of the adsorbate is reduced from initial C_0 to desired C_s

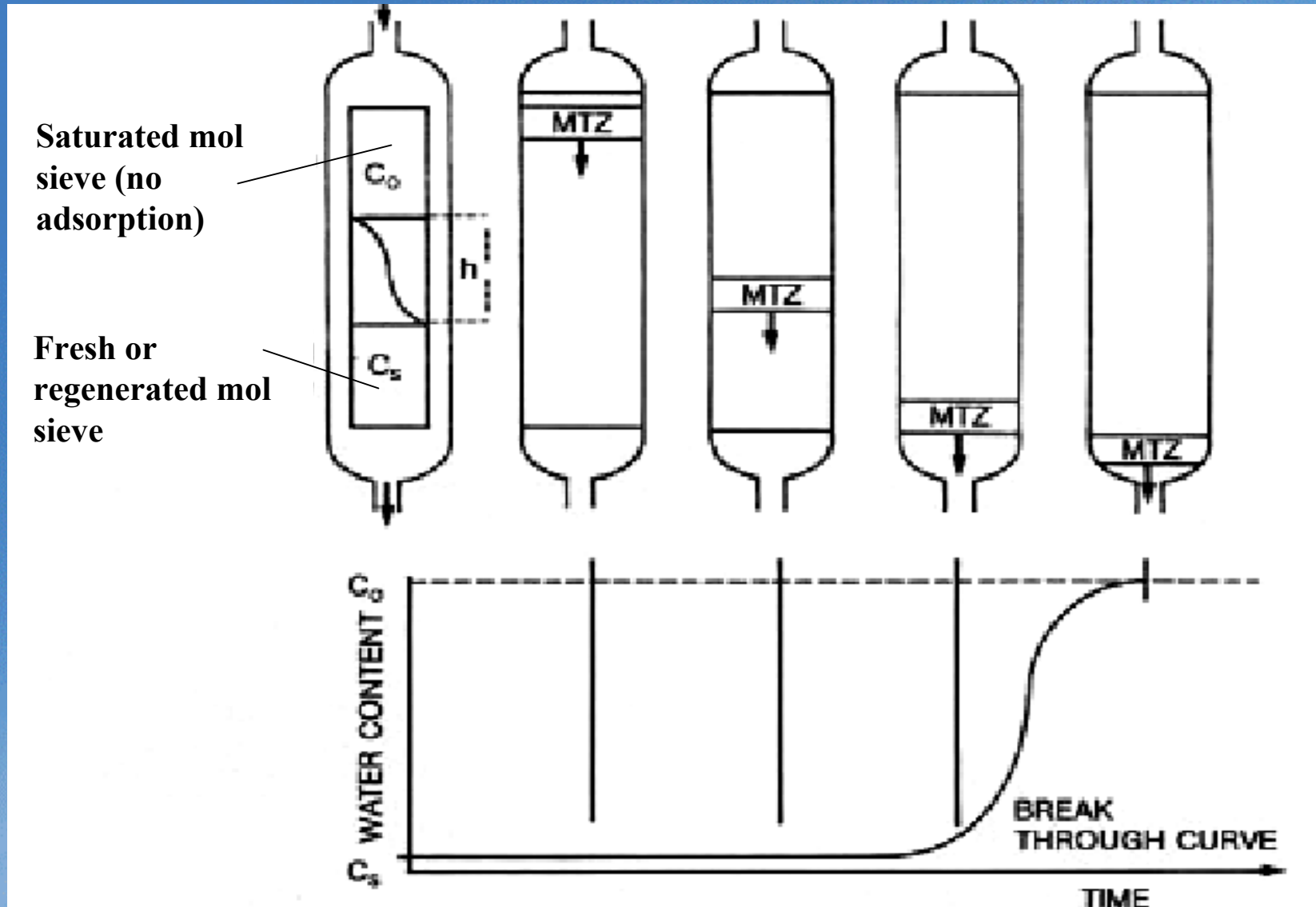
“Dynamic” Adsorption

- ◆ Water vapor is adsorbed in a finite length of bed (MTZ) as wet process stream enters fresh molecular sieve bed
- ◆ As wet gas continues to flow, the bed may be divided into 3 zones, saturated (equilibrium) zone, MTZ and active (fresh or regenerated) zone

“Dynamic” Adsorption

- ◆ When the MTZ reaches the outlet end of the bed, the bed is exhausted and regeneration is required
- ◆ The water content is shown to increase in the breakthrough curve as the MTZ moves towards the outlet

“Dynamic” Adsorption



Regeneration Methods

- The saturated mol sieve recovers its adsorption capacity after desorption - this is regeneration
- Four methods available commercially:
 - * Thermal swing - heating the bed to a temperature at which the adsorptive capacity is reduced to a low level
 - * Pressure swing - reducing adsorptive capacity by lowering pressure at constant temperature

Regeneration Methods

- * Inert purge stripping - passing a fluid containing no adsorbable molecules and in which the adsorbate is soluble without changing temperature or pressure
- * Displacement desorption - passing a fluid containing a high concentration of an adsorbable molecule without changing temperature or pressure

Applications in Titan

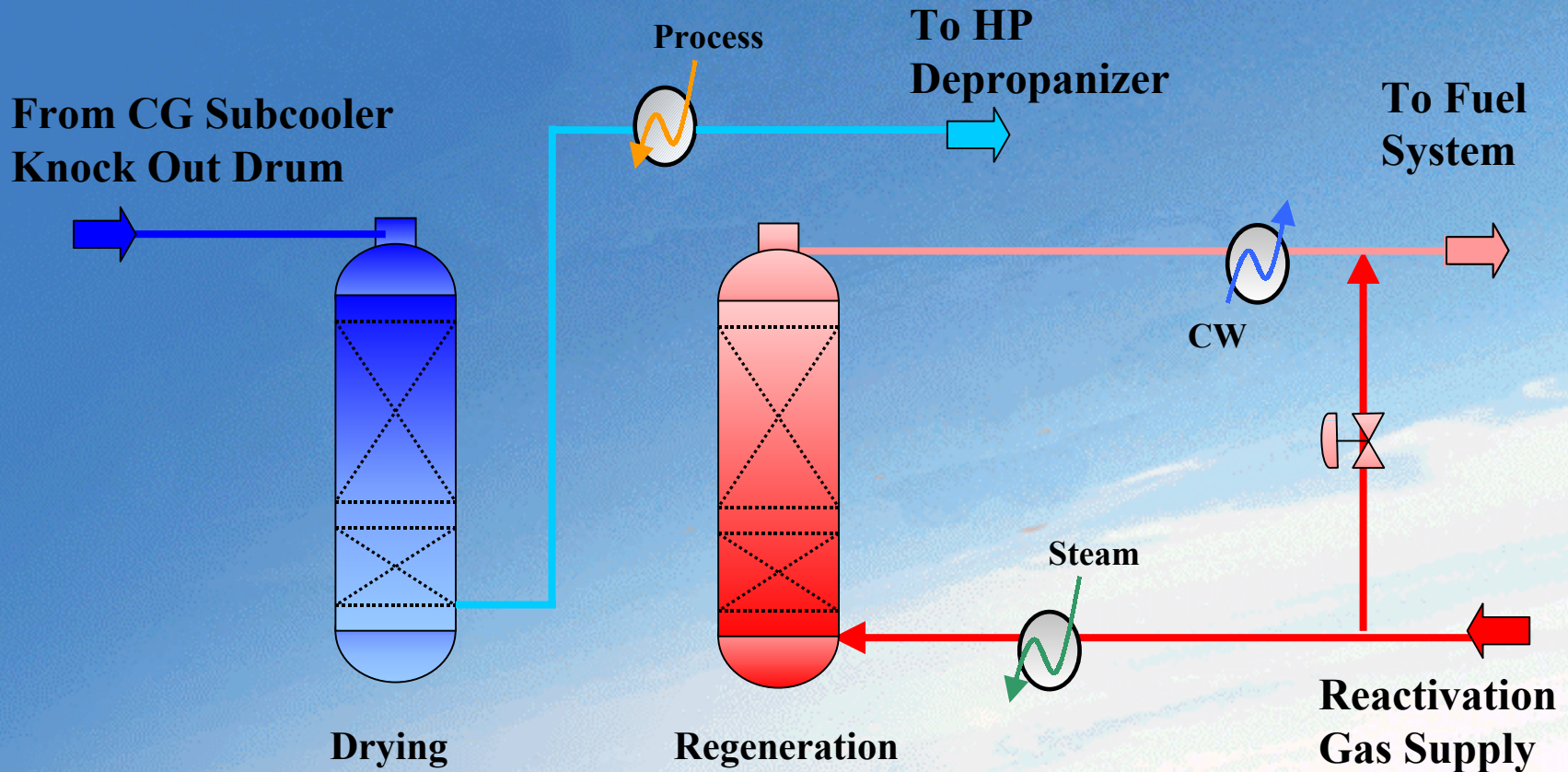
- The necessity of water removal is to prevent any hydrates in subsequent low temperature equipment.

Discussion of molecular sieves application in Titan will be limited to the following:-

- Cracked Gas Dryers
- Liquid Dryers
- Hydrogen Dryers

Cracked Gas Dryers

◆ Process Flow Diagram



Cracked Gas Dryers

◆ Operating Conditions (Adsorption Step)

Cracker 1

- One vessel on drying mode and one vessel on regeneration or standby mode
- Presently, the dryer vessels are loaded with mol sieves from two different vendors
- Fixed adsorption cycles of 60 to 70 hours

Cracked Gas Dryers

◆ Operating Conditions (Adsorption Step)

- Design operating conditions are:
 - * Temperature $\sim 10.5^{\circ}\text{C}$
 - * Pressure $\sim 15 \text{ kg/cm}^2\text{g}$
 - * Flow rate $\sim 76 \text{ ton/h}$
 - * Water content $\sim 886 \text{ ppmv}$

Cracked Gas Dryers

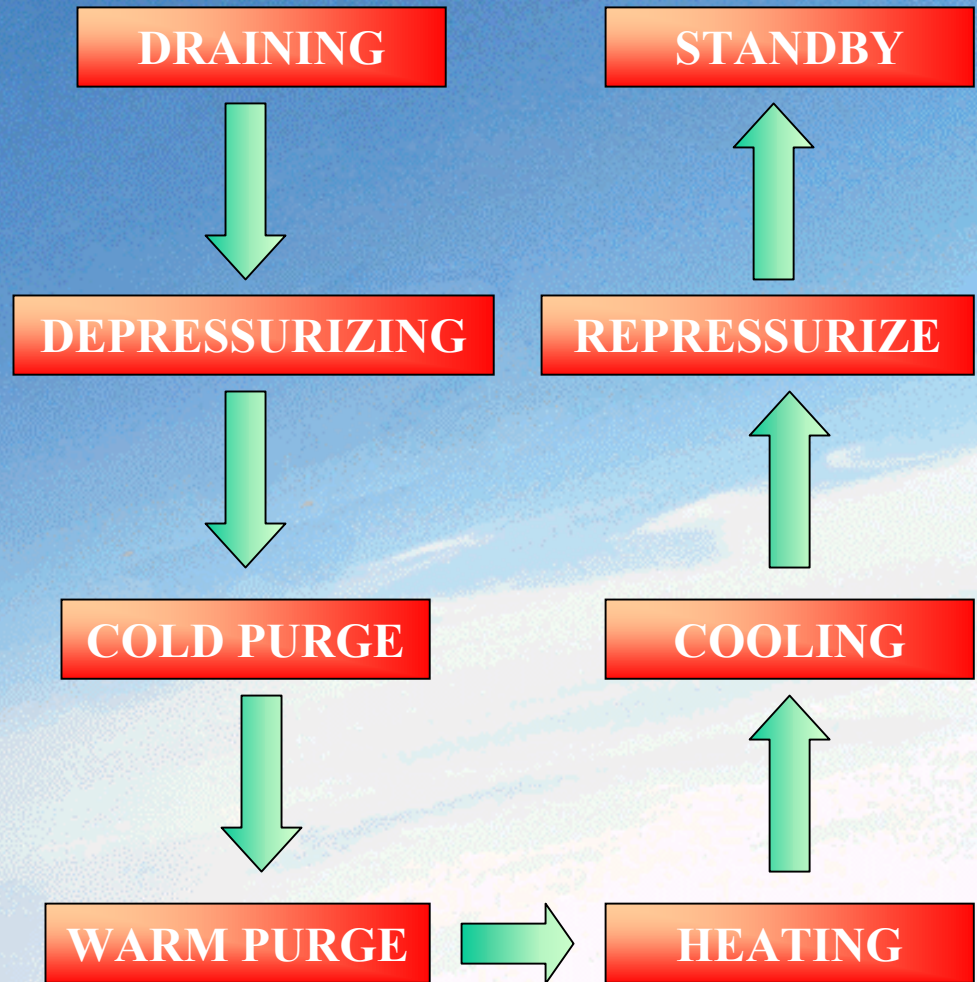
◆ Comparison of Breakthrough Test

<i>Parameter</i>	<i>Vessel A Mol Sieve X</i>	<i>Vessel S Mol Sieve Y</i>
Mol sieve type	1/8" and 1/16" 3 Å	1/8" and 1/16" 3 Å
Date of b'thru test	Mol sieve life of 4 months	Mol sieve life of 7 months
Feed rate	59.6 ton/h	58 ton/h
Water content	787 ppmv	900 ppmv
Adsorption time	83.5 hours	76 hours
Adsorption capacity	13.78 gH₂O/100g mol sieve	13.92 gH₂O/100g mol sieve
Mol sieve life	42 months to date	18 months to date

Cracked Gas Dryers

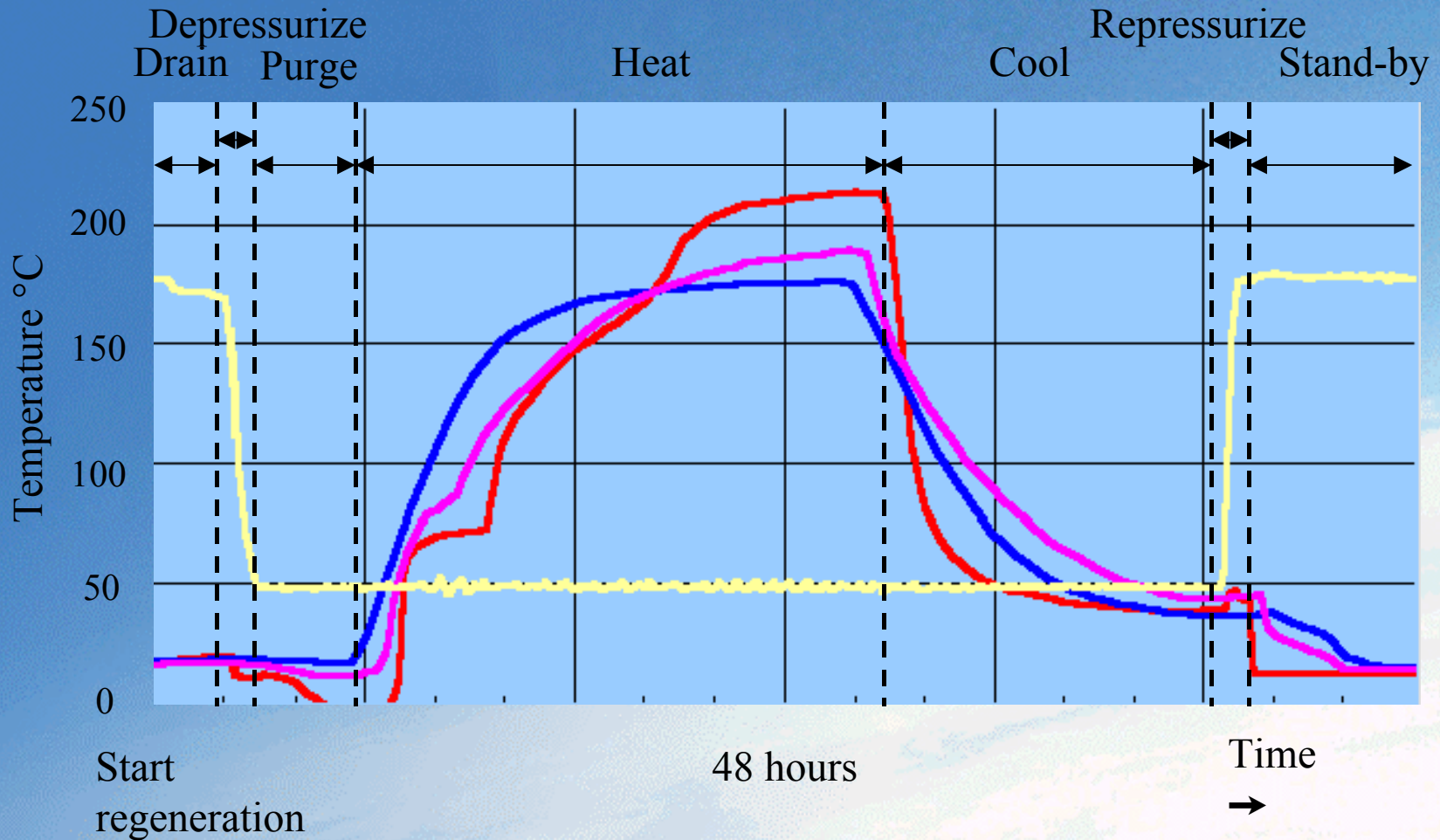
◆ Operating Conditions (Regeneration Step)

- Regeneration period of 48 hours
- Design regeneration conditions are:
 - * Depressurised to 4 kg/cm²g
 - * Heat to bed temperature of 200°C
 - * Regen gas flow rate is 6 tons/h



Cracked Gas Dryers

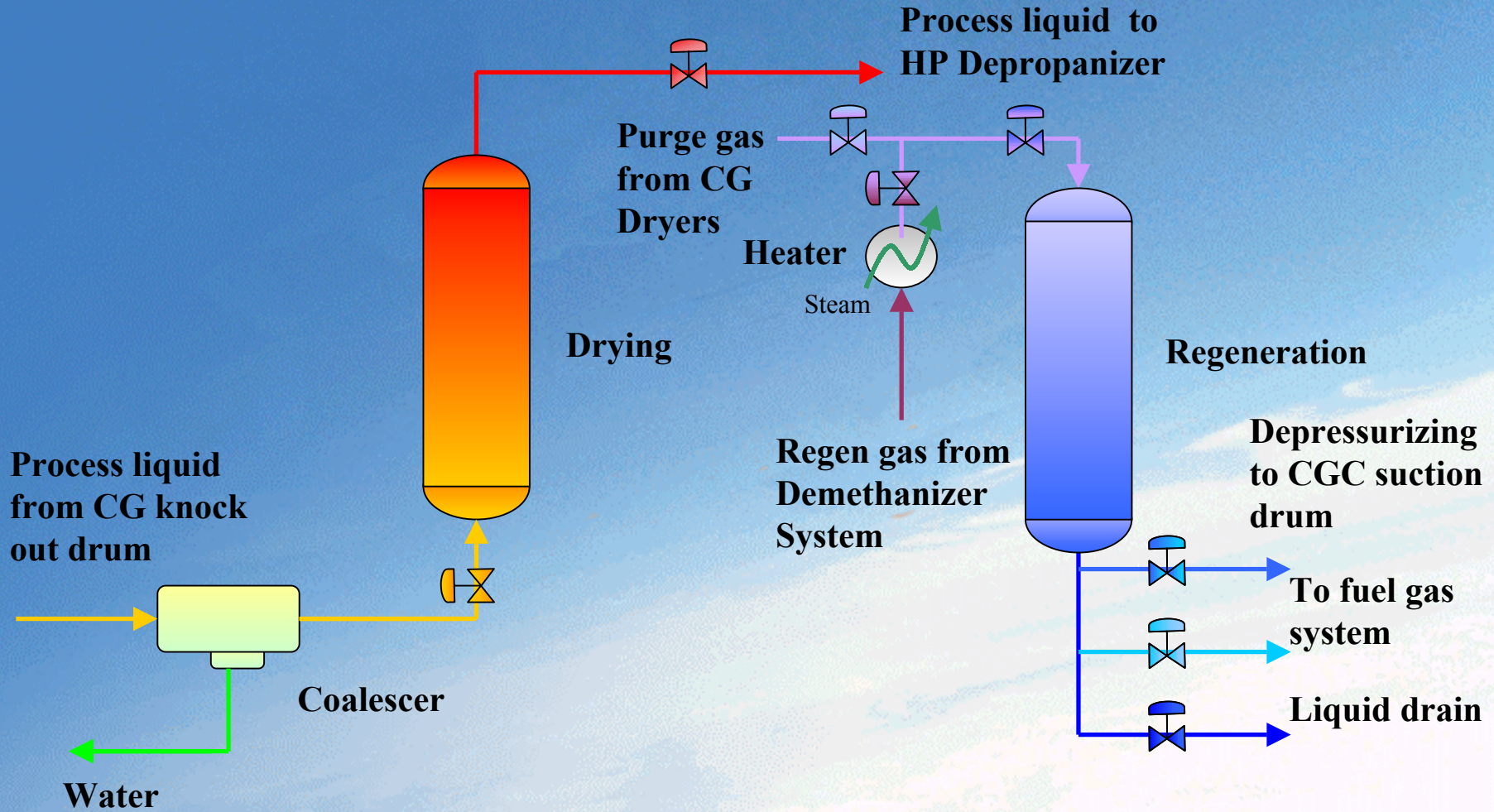
◆ Typical Regeneration Curve (Mol Sieve Y)



- Mol Sieve X has similar regeneration curve

Liquid Dryers

◆ Process Flow Diagram



Liquid Dryers

◆ Operating Conditions (Adsorption Step)

Cracker 1

- One vessel on drying mode and one vessel on regeneration mode
- Fully automatic operations by PLC
- Fixed adsorption cycles of 24 hour
- Have used mol sieves from two different vendors

Liquid Dryers

◆ Operating Conditions (Adsorption Step)

- Design operating conditions are:
 - * Temperature $\sim 10.5^{\circ}\text{C}$
 - * Pressure $\sim 18.6 \text{ kg/cm}^2\text{g}$
 - * Flow rate $\sim 7736 \text{ kg/h}$
 - * Water content $\sim 420 \text{ ppmw}$

Liquid Dryers

◆ Comparison of Breakthrough Test

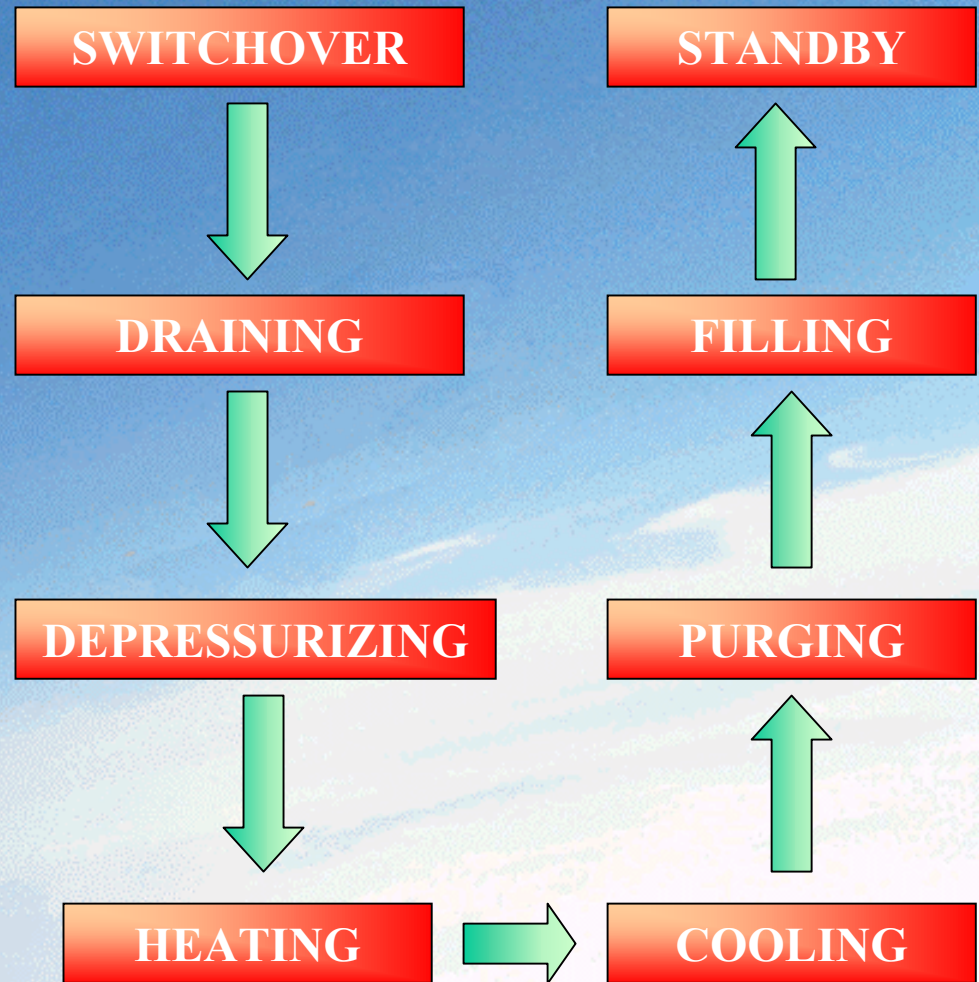
<i>Parameter</i>	<i>Mol Sieve X</i>	<i>Mol Sieve Y</i>
Mol sieve type	1/16" 3 Å	1/16" 3 Å
Date of b'thru test	Mol sieve life of 7 months	Mol sieve life of 15 months
Flow rate	9300 kg/h	12500 kg/h
Water content	420 ppmw	420 ppmw
Adsorption time	36 hours	25 hours
Adsorption capacity	15.62 gH₂O/100g mol sieve	14.58 gH₂O/100g mol sieve
Mol sieve life	35 months	24 months *

* Short run life due to different regeneration conditions

Liquid Dryers

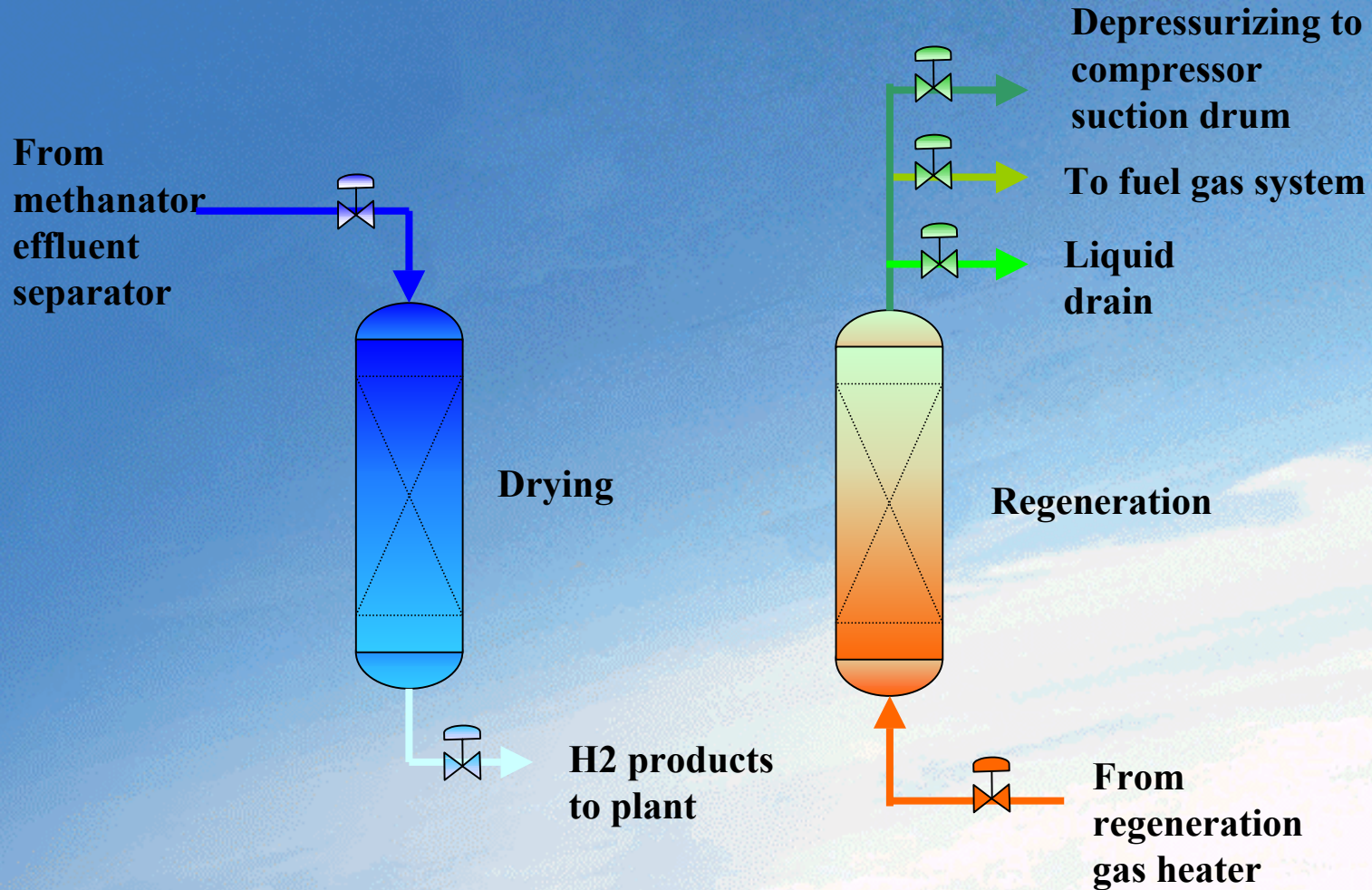
◆ Operating Conditions (Regeneration Step)

- Regeneration period is 24 hours
- The typical operating conditions are:
 - * Depressurised to 4 kg/cm²g
 - * Heat to bed temperature of 200°C
 - * Regen gas flow rate is 135 kg/h



Hydrogen Dryers

◆ Process Flow Diagram



Hydrogen Dryers

◆ Operating Conditions (Adsorption Step)

Cracker 2

- One vessel on drying mode and one vessel on regeneration or standby mode
- Only used mol sieves from one vendor
- Fixed adsorption cycles of 48 hours

Hydrogen Dryers

◆ Operating Conditions (Adsorption Step)

- Design operating conditions are:
 - * Temperature $\sim 12^{\circ}\text{C}$
 - * Pressure $\sim 30 \text{ kg/cm}^2\text{g}$
 - * Flow rate $\sim 1226 \text{ kg/h}$
 - * Water content $\sim 475 \text{ ppmv}$

Hydrogen Dryers

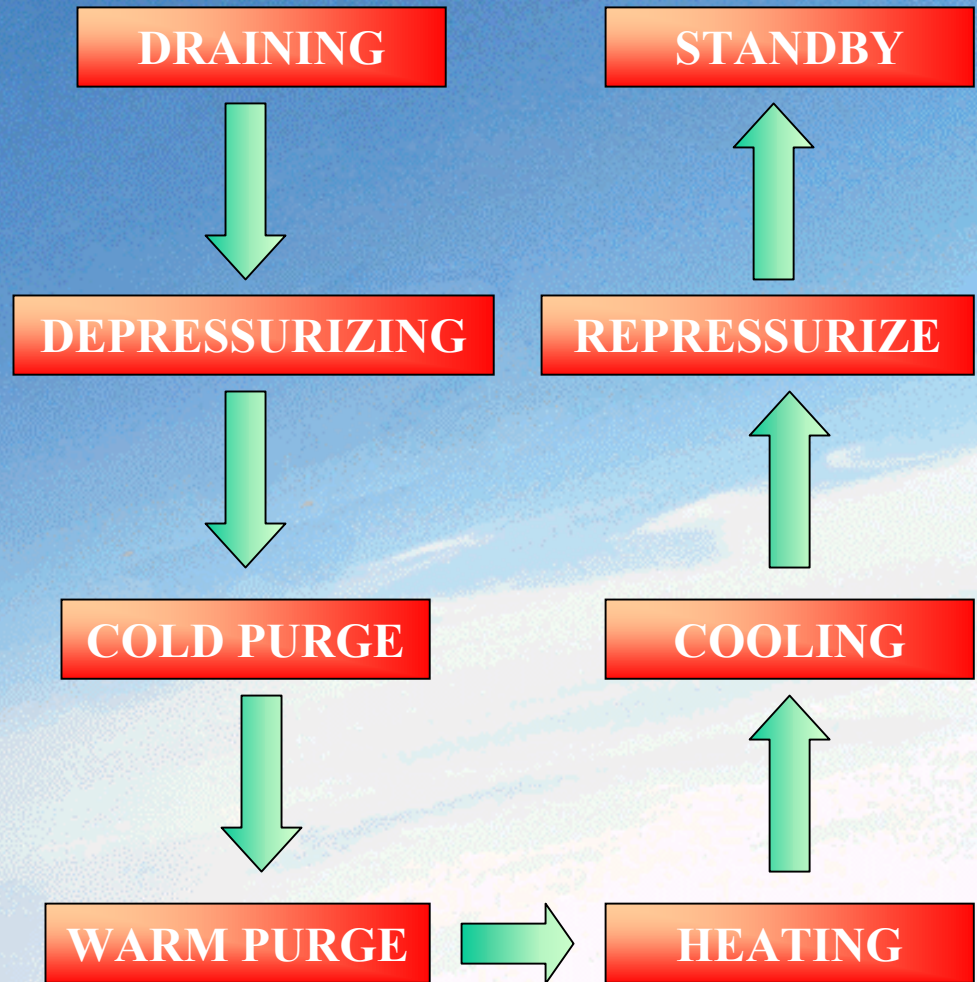
◆ Performance

<i>Parameter</i>	<i>Vessel A/S</i>
Mol sieve type	1/8" 3 Å
Flow rate	1300 kg/h
Water content	475 ppmv
Adsorption time	48 hours
Adsorption capacity	7.59 gH₂O/100g mol sieve
Mol sieve life	31 months to date

Hydrogen Dryers

◆ Operating Conditions (Regeneration Step)

- Regeneration period of 48 hours
- Design regeneration conditions are:
 - * Depressurised to 4 kg/cm²g
 - * Heat to bed temperature of 200°C
 - * Regen gas flow rate is 600 kg/h



Services Provided

Comparison is made on the two vendors for the services rendered to Titan

- Both vendors are technically well versed
- Both vendors are experienced and well known
- Both vendors are willing to conduct breakthrough test but requires planning in advance

Services Provided

- One vendor has regional technical support that can conduct the testing while the other technical support team is based in Europe
- One vendor is able to predict the mol sieve end of run using a model

Molecular Sieve Life

Degradation of mol sieve is shown by:-

- shortfall in capacity
- pressure drop increase across the bed
- The aging of mol sieve leads to more frequent regeneration than forecast
- The rate of aging depends on type of service, design and feed characteristics

Contamination of Molecular Sieve

Premature bed aging can be caused by contaminants such as:-

- Oil
- Olefins, diolefins
- Free water or “excess” water

Contamination of Molecular Sieve

- During normal regeneration in the presence of heat, some of the hydrocarbon contaminants decompose and polymerize forming a deposit of coke on the sieve surface
- This blocks the actual adsorption sites and impedes diffusion within the macro pores

Contamination of Molecular Sieve

- Free water attacks the interface between the active zeolite material and clay binders leading to a separation of the two constituents
- This will lead to formation of powders and eventual caking of mol sieve beds

Thermal Effects (Safety Aspects)

Temperature rise from heat of adsorption can be caused by:-

- addition of moisture (water) without flooding the bed e.g. during bed loading when vessels are not completely dry
- sudden contact with high concentrations of hydrocarbons having high heats of adsorption such as olefins e.g during start ups

Conclusion

- Molecular sieves used in each application has been satisfactory
- Mol sieves life for cracked gas dryer and hydrogen dryer are expected to last up to 4 years
- Mol sieves life for liquid dryer was shown to last 2 to 3 years

Conclusion

- Have used molecular sieves from two different vendors
- Vendors are technically competent and services are satisfactory

Thank You

Q & A