Molecular Sieve Applications

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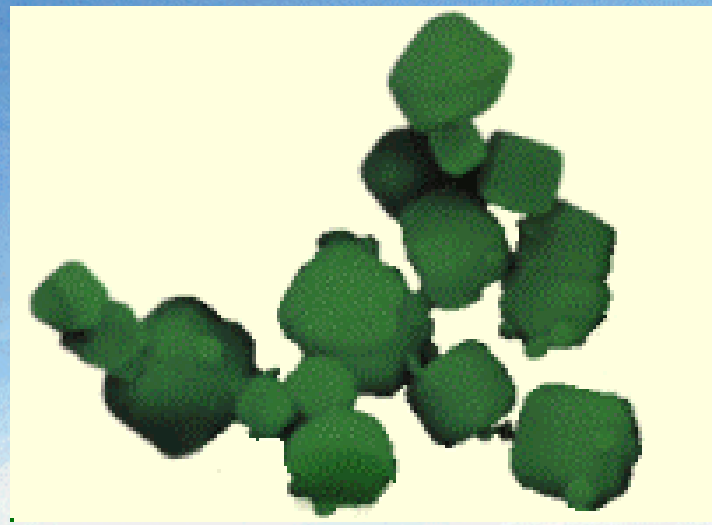
Outlines

- 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 alumino silicate 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

Sodium Silicate

Caustic Soda

Sodium Aluminate

Synthesis

Ion Exchange

Binder

Mixing

Extrusion

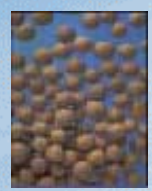
Granulation

Activation

Activation

Activation

Activated Powder



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 a 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_O 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

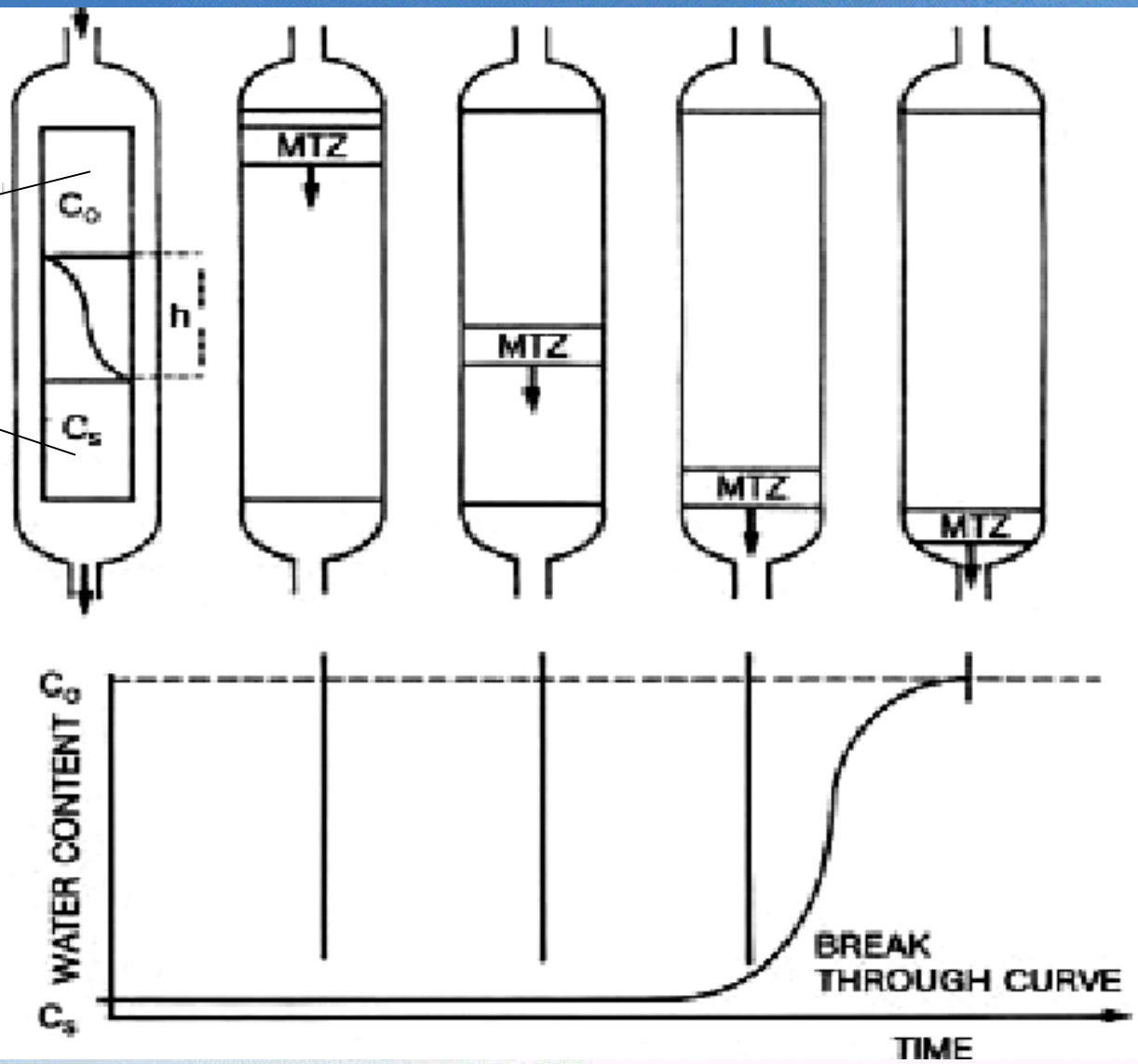
"Dynamic" Adsorption

- 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

Saturated mol sieve (no adsorption)

Fresh or regenerated mol sieve



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

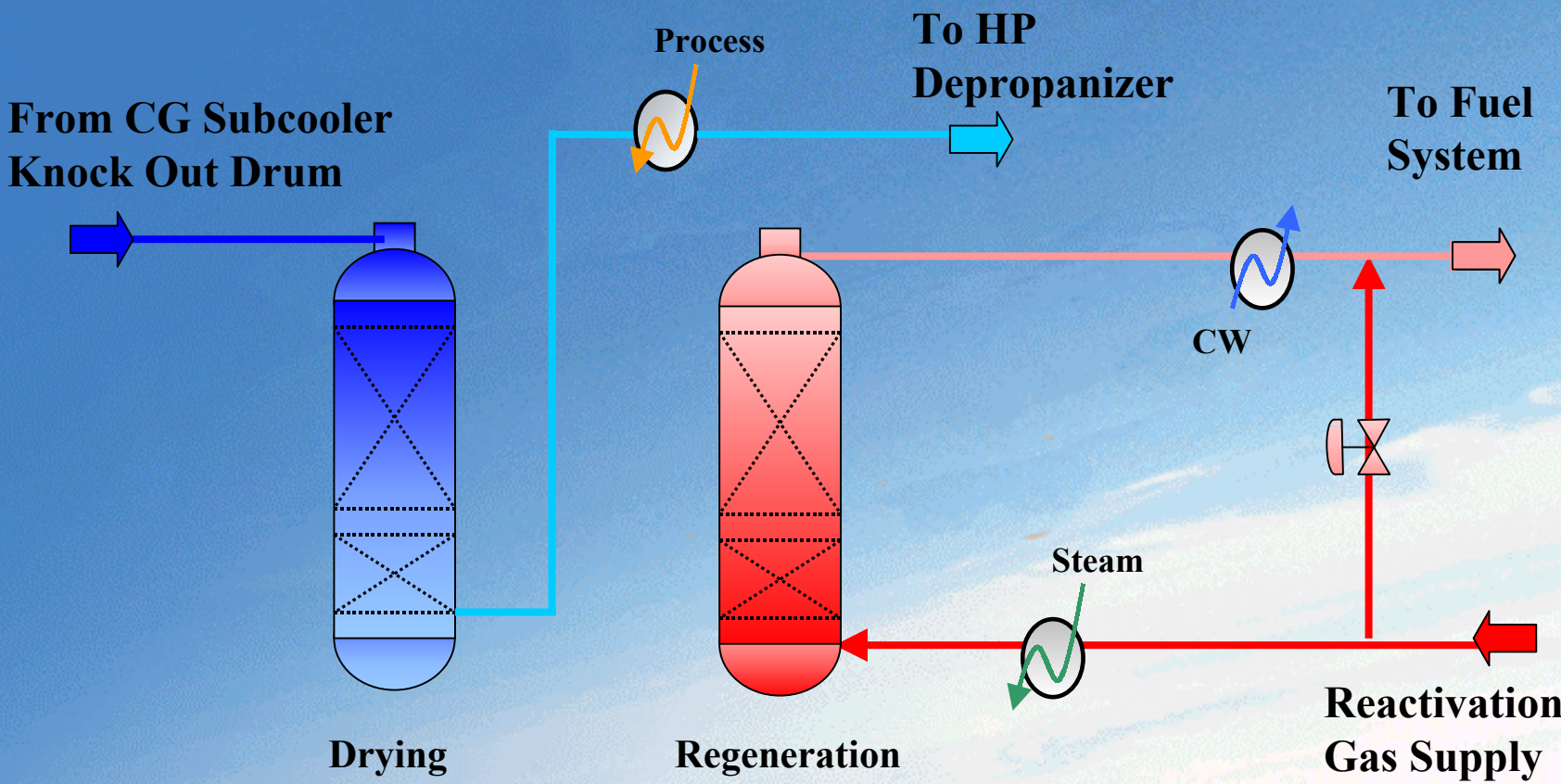
- The necessity of water removal is to prevent any hydrates in subsequent low temperature equipment.

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 ~ 10.5°C
* Pressure ~ 15 kg/cm^2g
* Flow rate ~ 76 ton/h
* Water content ~ 886 ppmv

Cracked Gas Dryers

- Comparison of Breakthrough Test

Parameter	*Vessel A* *Mol Sieve X*	*Vessel S* *Mol Sieve Y*
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 gH_2O/100g mol sieve	13.92 gH_2O/100g mol sieve
Mol sieve life	42 months to date	18 months to date

Cracked Gas Dryers

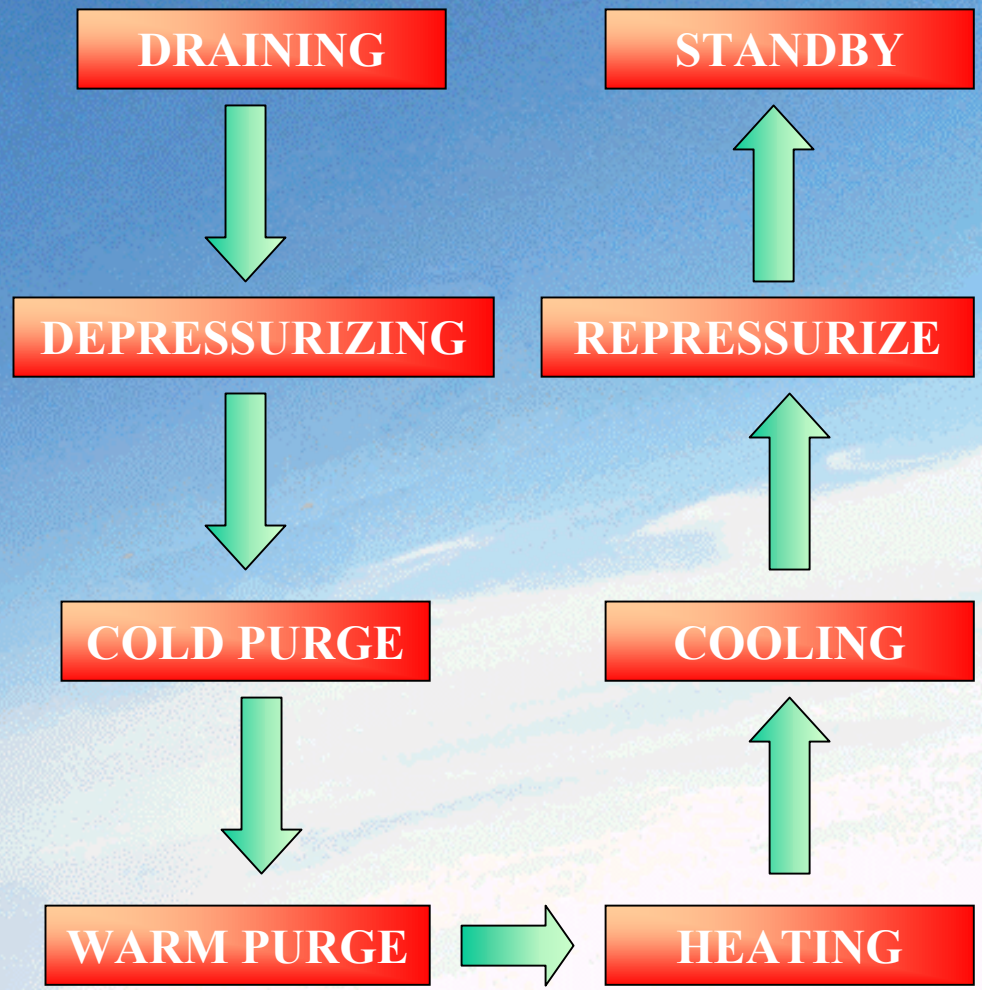
◆ Operating Conditions (Regeneration Step)

- Regeneration period of 48 hours
- Design regeneration conditions are:

* Depressurised to 4 kg/cm^2g

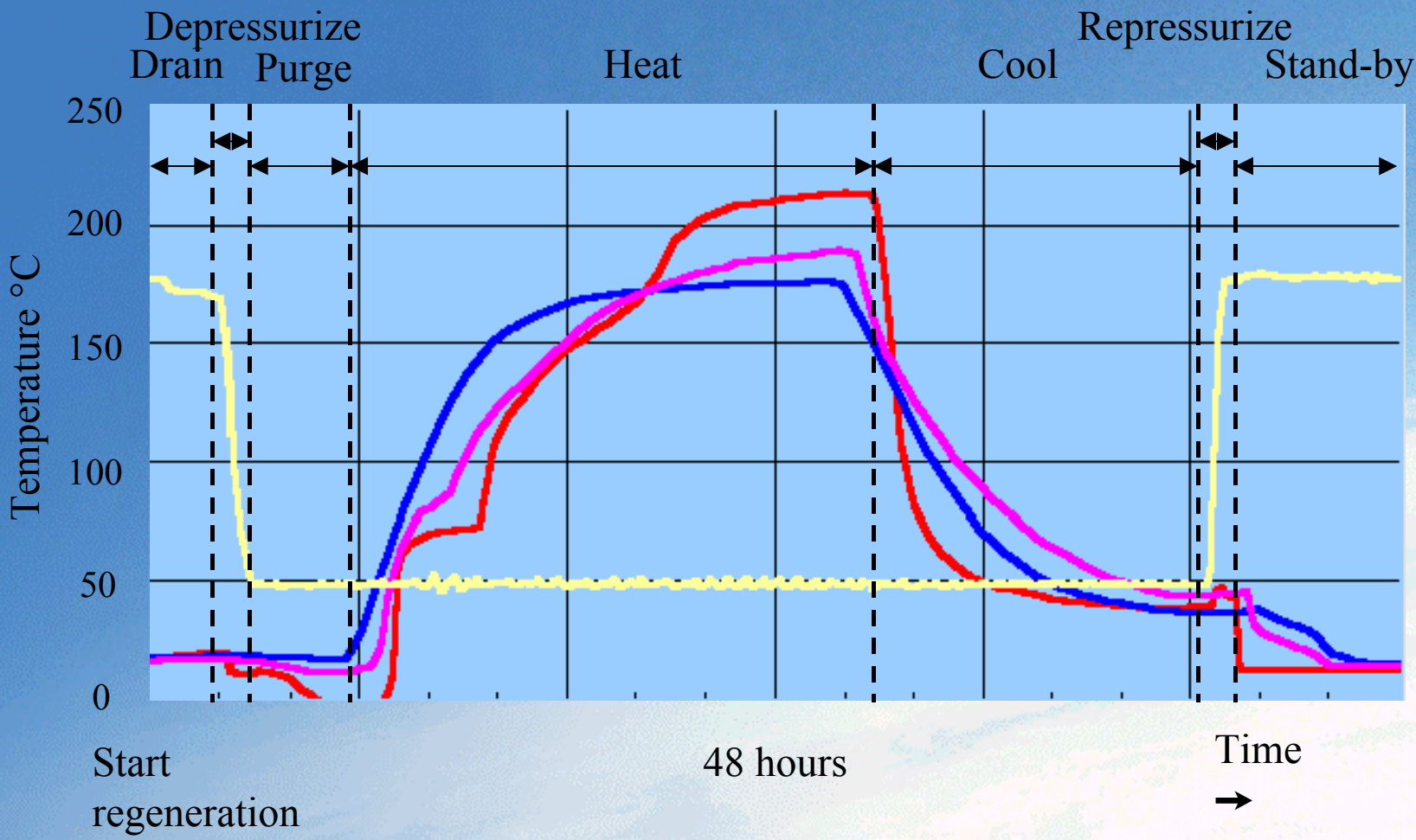
* Heat to bed temperature of 200°C

* Regen gas flow rate is 6 tons/h



Cracked Gas Dryers

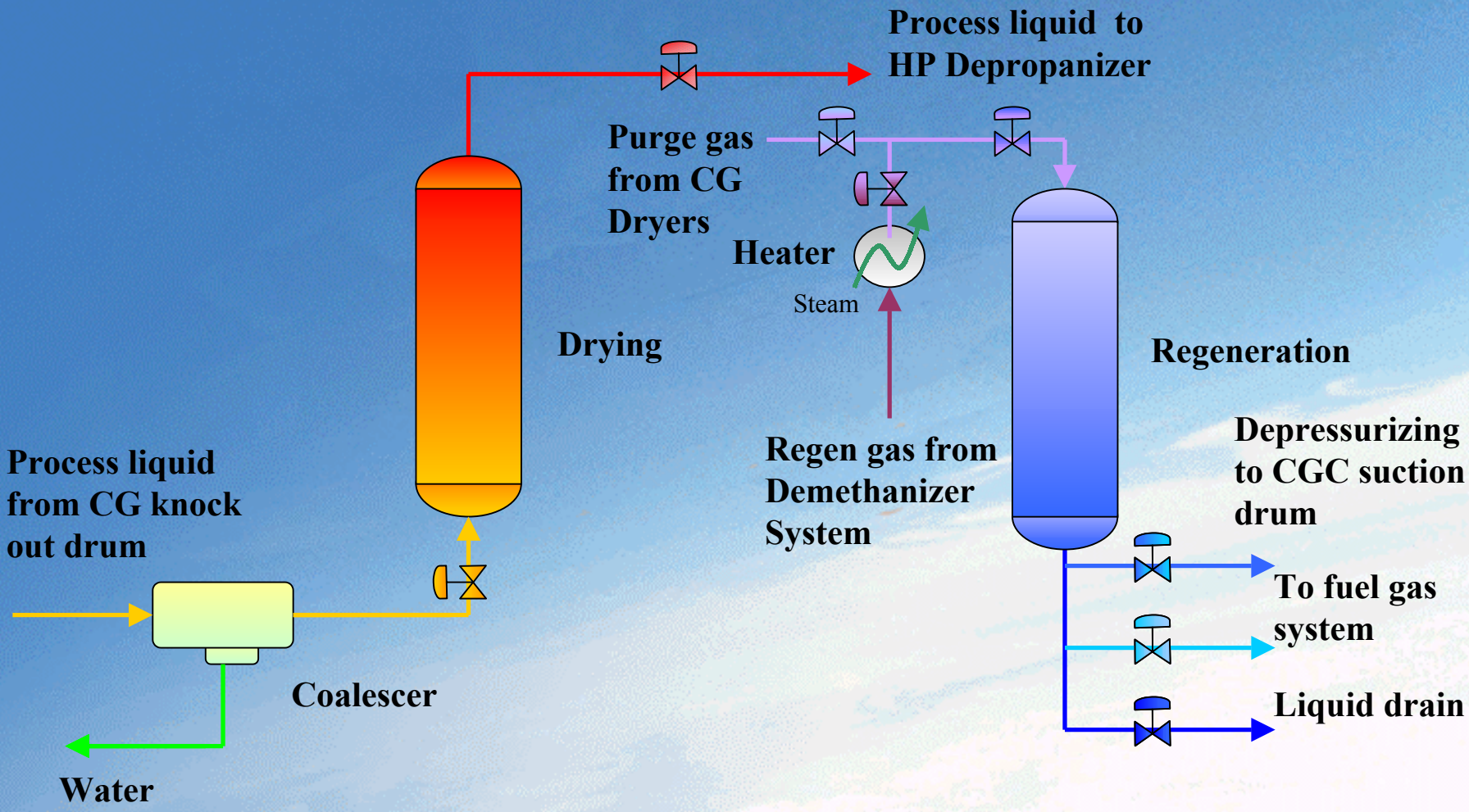
- *Typical Regeneration Curve (Mol Sieve Y)*



- **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 ~ 10.5°C
* Pressure ~ 18.6 kg/cm^2g
* Flow rate ~ 7736 kg/h
* Water content ~ 420 ppmw

Liquid Dryers

- Comparison of Breakthrough Test

Parameter	*Mol Sieve X*	*Mol Sieve Y*
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 gH_2O/100g mol sieve	14.58 gH_2O/100g mol sieve
Mol sieve life	35 months	24 months *

* Short run life due to different regeneration conditions

Liquid Dryers

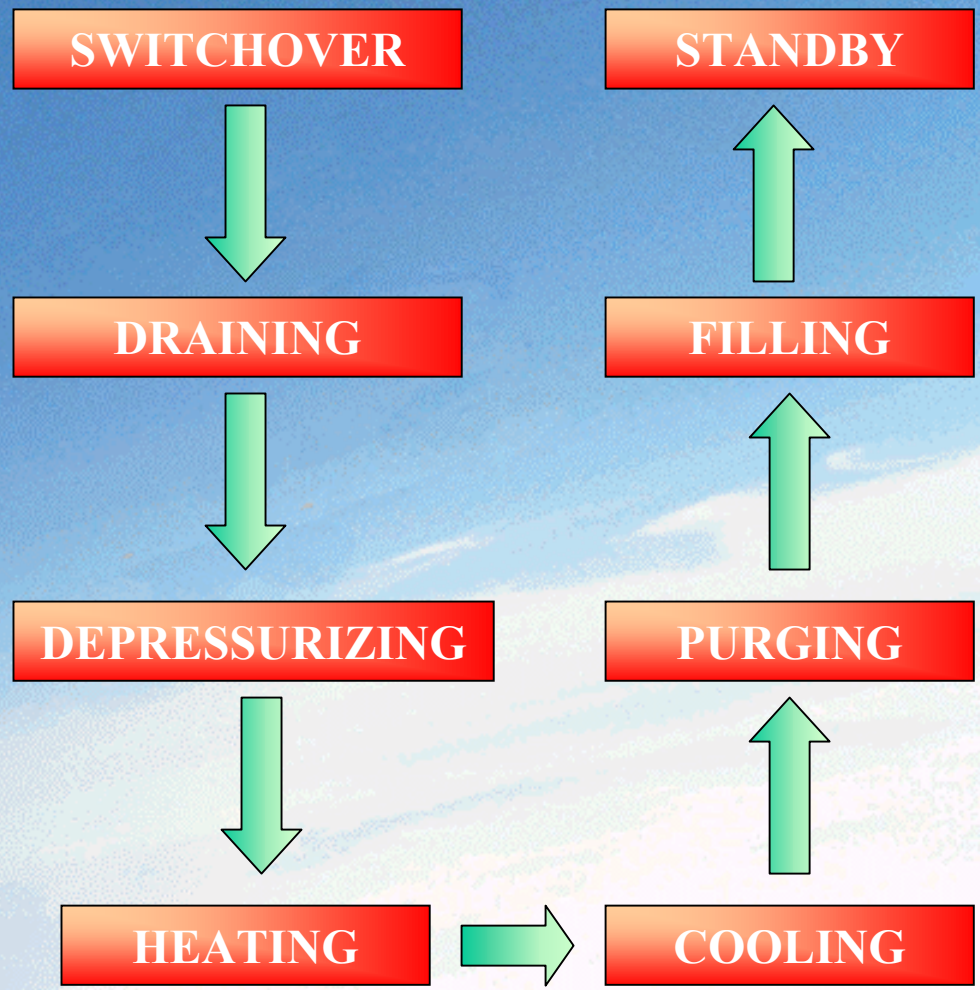
◆ Operating Conditions (Regeneration Step)

- Regeneration period is 24 hours
- The typical operating conditions are:

* Depressurised to 4 kg/cm^2g

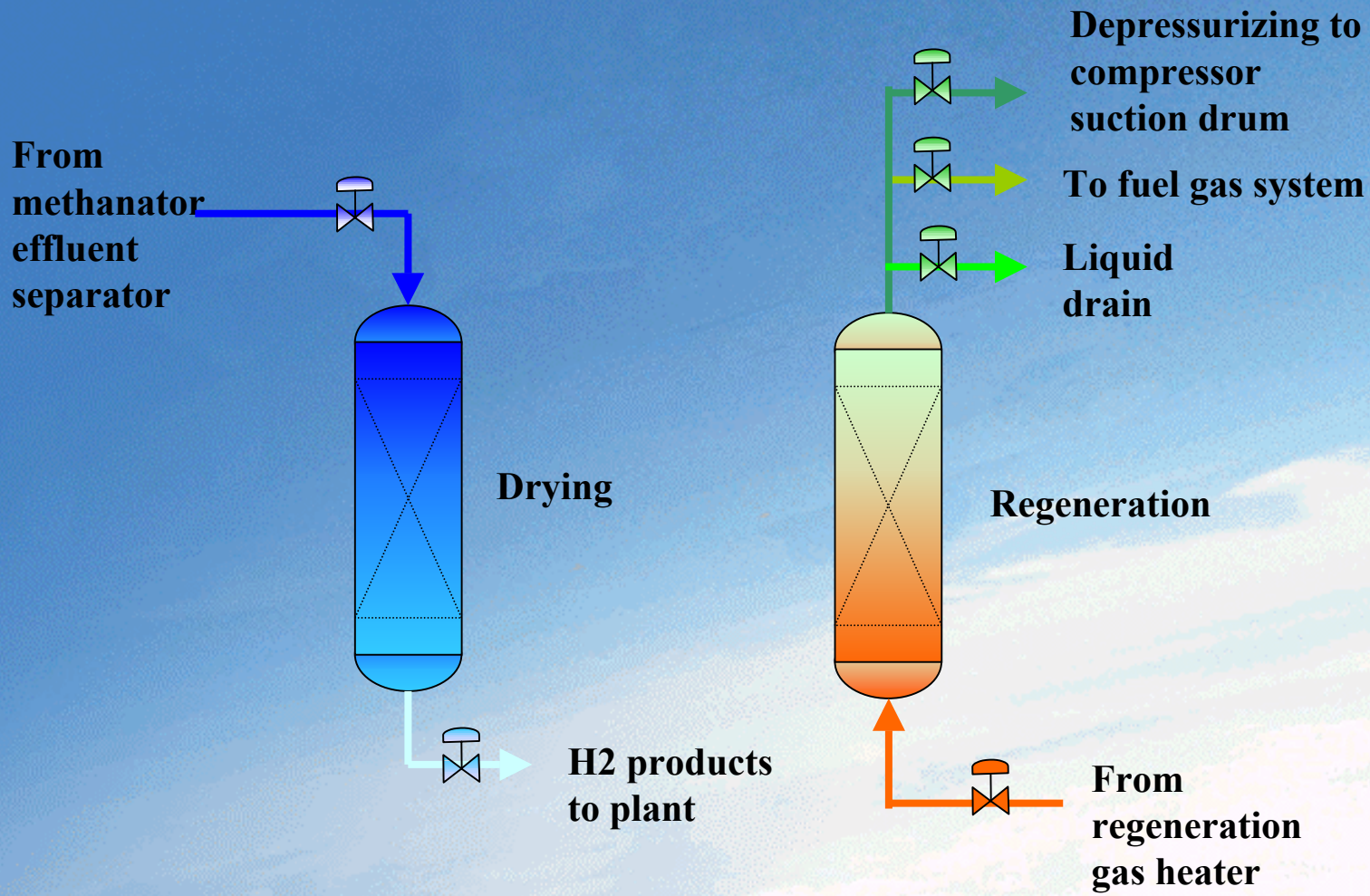
* Heat to bed temperature of 200°C

* 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 ~ 12°C
* Pressure ~ 30 kg/cm^{2}g
* Flow rate ~ 1226 kg/h
* Water content ~ 475 ppmv

Hydrogen Dryers

- Performance

Parameter	*Vessel A/S*
Mol sieve type	1/8” 3 Å
Flow rate	1300 kg/h
Water content	475 ppmv
Adsorption time	48 hours
Adsorption capacity	7.59 gH_2O/100g mol sieve
Mol sieve life	31 months to date

Hydrogen Dryers

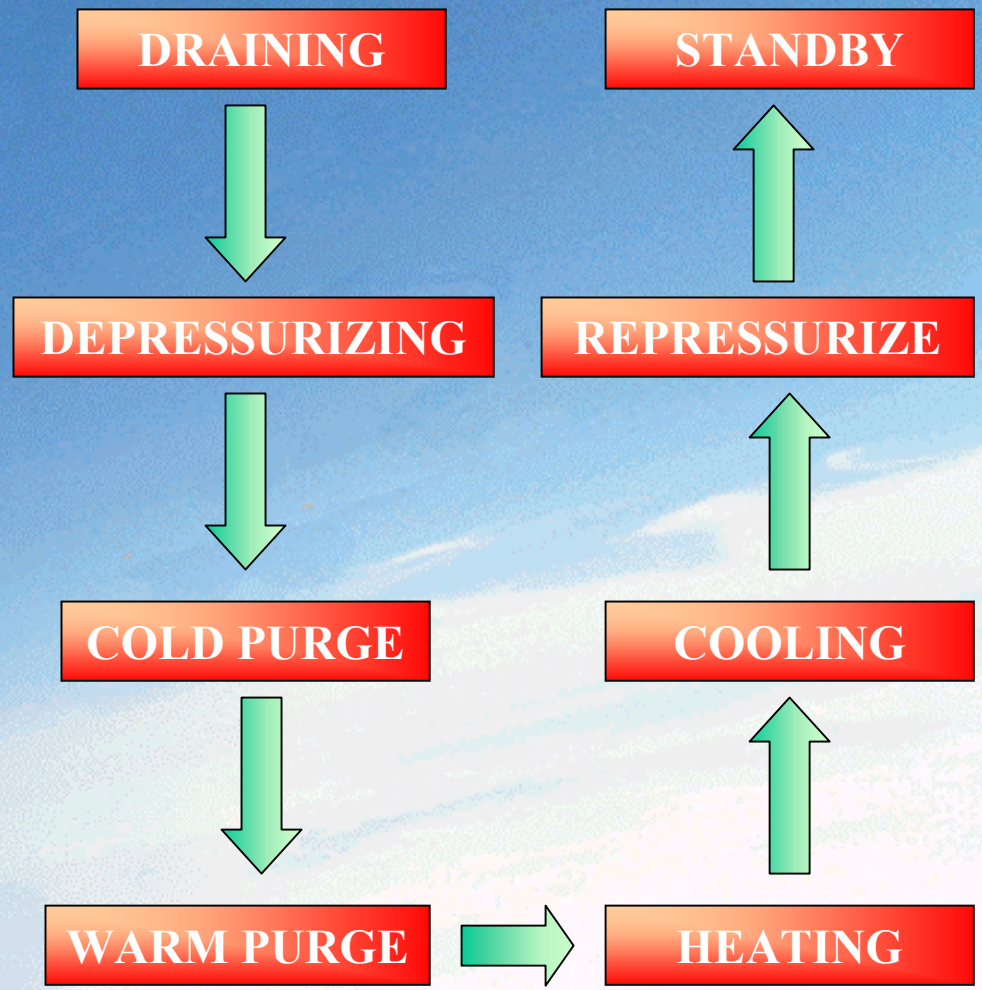
◆ Operating Conditions (Regeneration Step)

- Regeneration period of 48 hours
- Design regeneration conditions are:

* Depressurised to 4 kg/cm^2g

* 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