MOLECULAR SIEVES: IS YOUR REGENERATION PROCEDURE OPTIMIZED?

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Abstract

The paper treats the different aspects to be taken into account for a good regeneration of molecular sieves used in the Natural Gas Processing Industry and more particular for the drying of Natural Gas.
Different problems during regeneration are mentioned: wall effect (umbrella effect) and hydrothermal damaging due to refluxing. Then detailed aspects of the regeneration steps are treated including regeneration at low and high pressure. The influence of pressure and temperature during the regeneration is discussed with an example of a Natural Gas Drying unit. Finally solutions of how to regenerate the molecular sieve best by insuring a complete regeneration and reducing hydrothermal damaging are shown. An example using the proprietary software SIMATEP for optimization of regeneration procedures is included.

Introduction

People may ask why to optimize the regeneration procedure of molecular sieve units?
Usually they are just working. Changing from one vessel to another. No need to take care about?

This is the very short term view! Indeed, if the regeneration procedure of molecular sieves units is not optimized this may lead to harm the adsorbent and reduce significantly its life time.
For new units, plants under construction, it is important to take into account the good regeneration procedure in order to reach the requested life time of the adsorbent and even more important to design the equipment such as regeneration gas compressor, air cooler etc correctly.
For existing units the knowledge of how to optimize the regeneration procedure can help to give indications how to debottleneck existing units.

The present paper will focus on the molecular sieve application of Natural Gas drying, the most common application in the Gas Processing Industry.

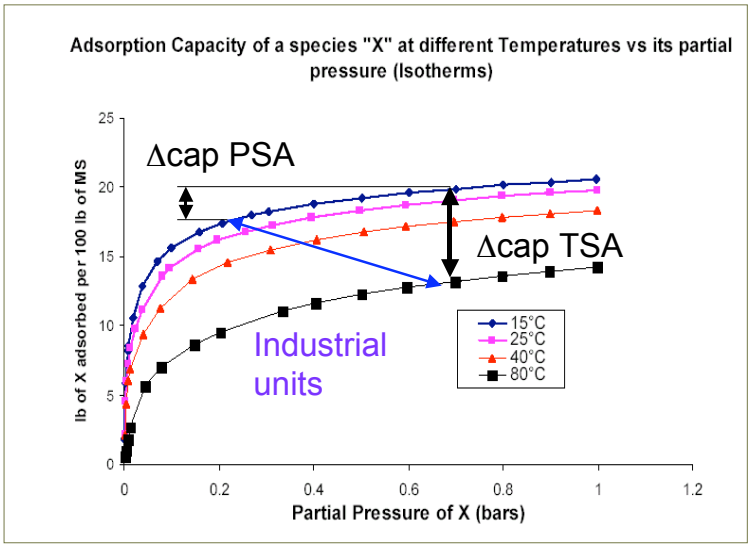
Development

First of all: how does it work the regeneration of molecular sieves? In industrial units two possibilities for regeneration are possible, either by PSA, Pressure Swing Adsorption, or by TSA, Thermal Swing Adsorption.

The PSA relies on the fact that the partial pressure of the molecule to be adsorbed is reduced thus reducing the adsorption capacity and desorbing the adsorbed molecule. There is no change in temperature, only change in absolute pressure conducting to a change of partial pressure of the molecule to be adsorbed. Except some small air drying units this PSA regeneration is not applied for drying due to the low dynamic adsorption capacity and the loss of treated gas used for the regeneration.

The TSA regeneration is done by increasing the temperature thus moving the adsorption equilibrium from the adsorbed phase to the gas phase. Taking into account the huge difference in adsorption capacity and the easy possibility to use it for a continuous process this is the commonly used regeneration mode.
In an industrial unit very often a TPSA regeneration is used as the gas used for the regeneration is a very dry gas.

Regeneration: how does it work?



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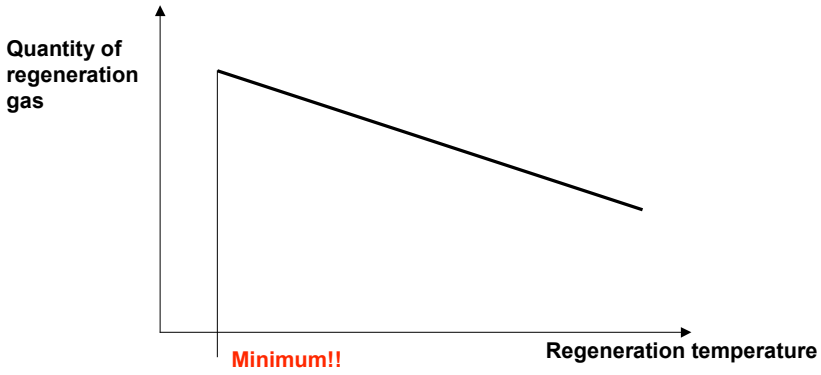
The standard regeneration procedure for a drying unit consists of the following steps:

1) Switch from one adsorber to another having been regenerated with possibly pressure change. When switching from one adsorber to another very often both adsorbers remain in adsorption for a certain time (range of some minutes) on order to allow smooth change over without any pressure variations.
2) A heating step, most often done in counter current to adsorption, probably including an intermediate heating step or heating ramp, to remove the adsorbed molecules and recover adsorption capacity.
3) A cooling step to get the adsorbent down to adsorption temperature. If this is done with wet gas it has to be done in the co current direction to adsorption to prevent a water peak when changing from regeneration to adsorption and to insure to reach the requested water dew point.
4) Switch from regeneration to adsorption possibly including a preliminary repressurization step.

The quantity of gas needed during the heating step depends on the quantity of adsorbent, the vessel weight, the quantity and type of molecules to be desorbed.

The heating temperature level influences the quantity of regeneration gas needed. The higher the temperature the lower the quantity of regeneration gas needed. This is shown in the graph below.

Regeneration: temperature influence



The quantity of regeneration gas depends on the inlet temperature during the heating. Below a minimum temperature the water dew point spec could not be reached (too high residual water content), the maximum temperature depends on the type of molecular sieve.

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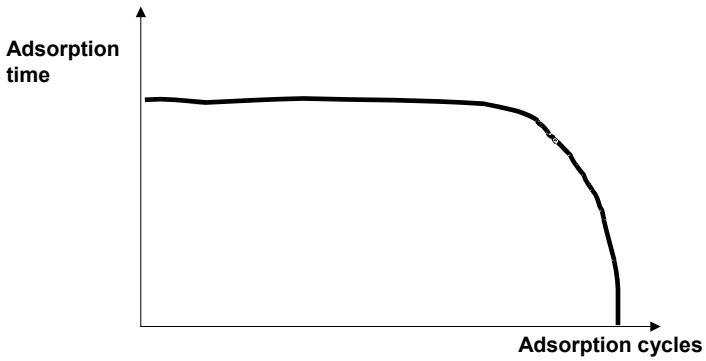
But the temperature should be within a certain range. If the temperature is too low the residual water content could be too high to reach the requested outlet specifications, if the temperature is too high the molecular sieve will face premature aging due to hydrothermal damaging of the crystal structure.

Insufficient heating (temperature level or regeneration quantity) or channelling during the heating step leading to an incomplete regeneration and water accumulation leading to premature water breakthrough can easily be detected as it occurs very often shortly after the start up of a new unit and leads to a sudden decrease of adsorption.

Regeneration: uncomplete regeneration



A sudden decrease of adsorption time is the sign for a bad regeneration (accumulation of water) ⇒ happens very often shortly after start up, possibility to recover sieves

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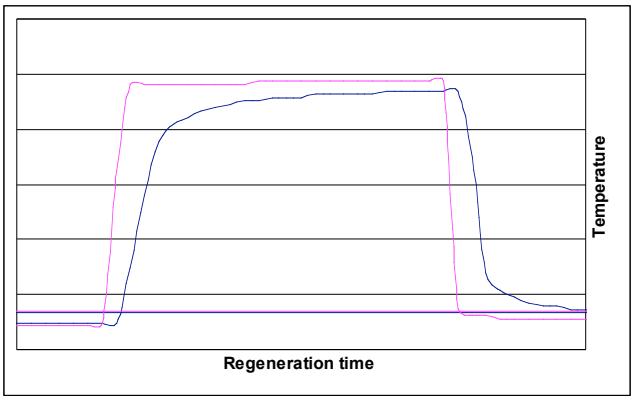
Very often it is easily possible to recover the adsorption capacity of the adsorbent by applying an accurate regeneration gas flow and duration especially during the heating step.

In order to be sure to well regenerate the adsorbent it is important to respect the following points:

- correct level of maximum heating temperature: high enough the well remove the adsorbed molecular, but low enough not to shorten the life time of the adsorbent due to thermal damaging of the crystal structure of the zeolite
- temperature difference during the heating between inlet and outlet of the vessel below a certain range (max 20°C). This indicates the quality of the heat insulation.
- At the end of the heating step the outlet temperature should remain almost constant during a certain time (depending on the vessel size between 30 and 90 minutes) in order to make sure to well heat up the vessel the most homogeneously possible. See graph below.

Regeneration: uncomplete regeneration



Make sure to have a plateau at the outlet during heating.

Make sure to have a small temperature difference between inlet and outlet during heating.

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In order to prevent premature aging due to hydrothermal attack of the crystal structure it is recommended to respect the maximum regeneration temperature (inlet adsorber) that are shown below.

Regeneration: Maximum temperature

3A: 230°C (446°F) for saturated gases, up to 260°C (500°F) for unsaturated gases

4A: normally 250°C (482°F), up to 290°C (554°F) with precautions

For information

5A/13X: 300°C (572°F) in case of sweetening, but if there is NO water on the sieves

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The pressure influence on the regeneration, particularly for drying units should not be underestimated. The pressure range can roughly be divided in two ranges. Above approx. 30 bars (435 psi) or below.

If the regeneration pressure is below 30 bars the boiling temperature of water at regeneration pressure is below the regeneration temperature. This case is commonly called heating limited as it is sufficient to bring sufficient energy with the regeneration gas in order to well remove the water.

If the regeneration pressure is above 30 bars the boiling temperature of water at regeneration pressure is above the regeneration temperature. This case is commonly called stripping limited and there is more regeneration gas necessary to remove the water from the adsorbent as the gas is limited in water saturation. Depending on the regeneration pressure 25-50% more regeneration gas might be necessary than for regeneration at low pressure.

The influence of regeneration pressure is shown in the following case study.

CASE STUDY

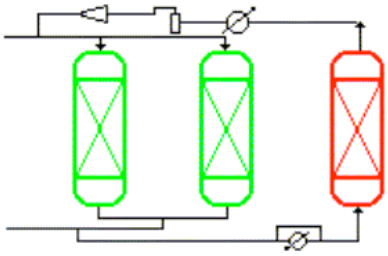
3 adsorber system, 2 in adsorption, 1 in regeneration

500 MMSCFD, 60 bar (870 psia), 30°C (86°F),

Saturated gas, 4A molecular sieve,

Adsorption time 16 hrs,

Regeneration recycled (air cooler sat. @ 55°C (131°F), 60 bar (870 psia))



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Let's take a standard Natural Gas Drying units with two adsorbers in adsorption and 1 adsorber in regeneration, drying a saturated gas, 16 hours adsorption time and recycling of the dried gas used as regeneration to the inlet of the adsorbers.

The first case is done with an adsorption at 60 bars (870 psi) and a regeneration at 30 bars (435 psi). The regeneration temperature for this case is 250°C as a standard 4A sieve is used. This is the base case which is used a reference case for the other cases.

The regeneration has to include a depressurization and a repressurization step leading to a maximum available regeneration time (heating and cooling) of 7 hrs 30 minutes.

Changing the regeneration pressure from 30 bars (435 psi) to 60 bar (870 psi) leads to the following changes (case 2):

- more available regeneration time as no de-/repressurization step is necessary but
- an increase of 15% of the regeneration gas flow rate (versus the base case = case 1)
- an increase of the total regeneration gas quantity of 23%
- and increase of the adsorbent volume of 4% as more regeneration gas is recycled.

In this case more time is available which makes it possible to increase regeneration flow rate less than the total quantity needed to well regenerate the adsorbents. The heating time will be relatively higher than the heating time of the case 1.

This case shows that if ever the pressure influence hasn't been taken into account there could be problems leading to malfunction of the drying system. The regeneration gas compressor (and air cooler) will have to treat the higher flow rate and the adsorbent bed will have to adsorb more water. If the regeneration compressor can not process the necessary regeneration flow there will be accumulation of water and premature breakthrough due to incomplete regeneration. As the adsorbent quantity is not sufficient to treat the recycled regeneration gas quantity the life time of the total adsorbent bed will be lower.

Supposing the regeneration temperature will be increased from 250°C to 290°C (case 3) in order to counter the possibly not available regeneration gas flow rate. The following changes will occur versus the case 1:

- more available regeneration time as no de-/repressurization step is necessary but

- an increase of 8% of the regeneration gas flow rate (versus the base case = case 1)
- an increase of the total regeneration gas quantity of 15%
- and increase of the asdorbent volume of 2% as more regeneration gas is recycled.

Except the question of the compressor and air cooler capacity the question here is if the material of the vessels can stand the higher temperature.

The slide below resumes the three cases:

CASE STUDY

	MS Quantity	Regengas quantity	Regen flow rate
CASE 1	100%	100%	100% F_{R1}
CASE 2	104%	115%	123% F_{R1}
CASE 3	102%	108%	115% F_{R1}

Case 1: Regeneration at 250°C, 482°F and 30 bar, 435 psia

Case 2: Regeneration at 250°C, 482°F and 60 bar, 870 psia

Case 3: Regeneration at 290°C, 555°F and 60 bar, 870 psia
(possibility to reach lower dew point)

Case 4: ???

HYDROTHERMAL DAMAGING

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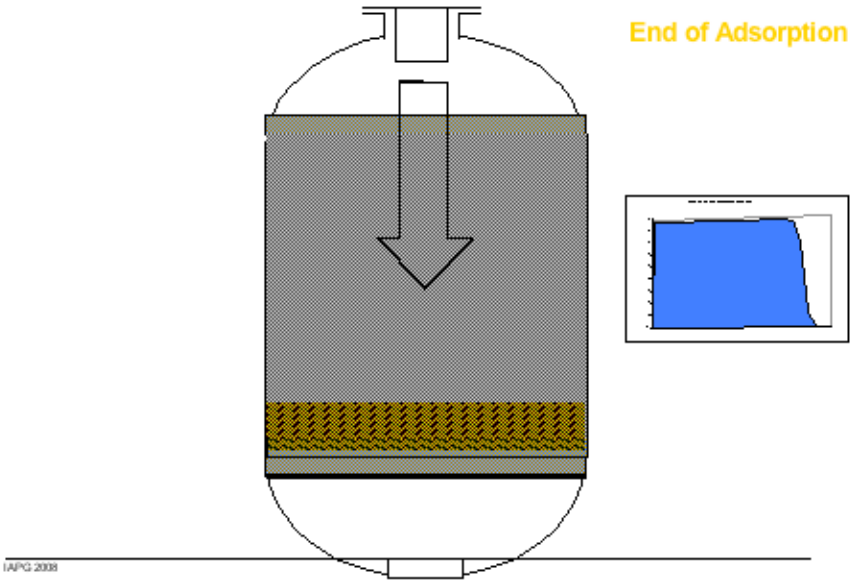
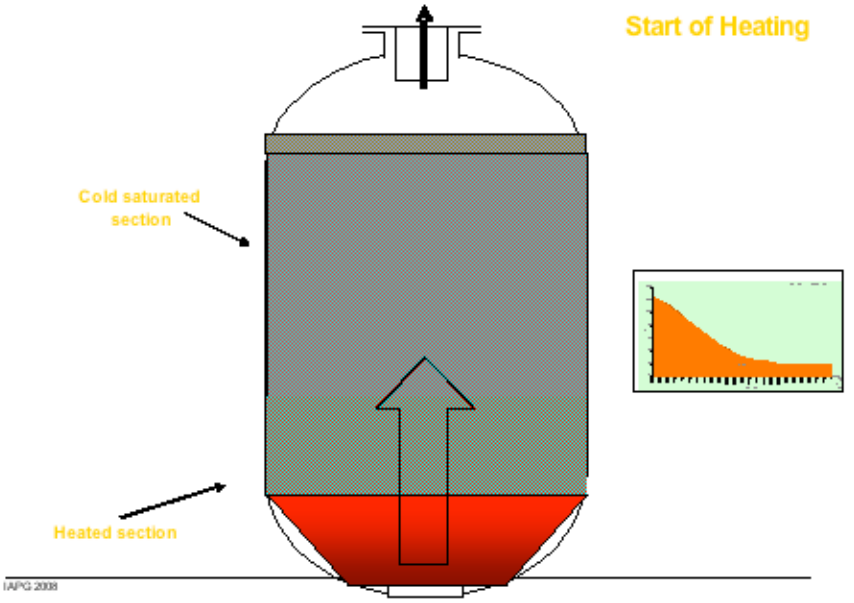
Case 3 seems to be a solution if ever the pressure influence of the regeneration has not been taken into account and if the question of material resistance is solved. But it is only a short term solution.
When regenerating the sieves with a high temperature regeneration gas attention should be paid to hydrothermal damaging.

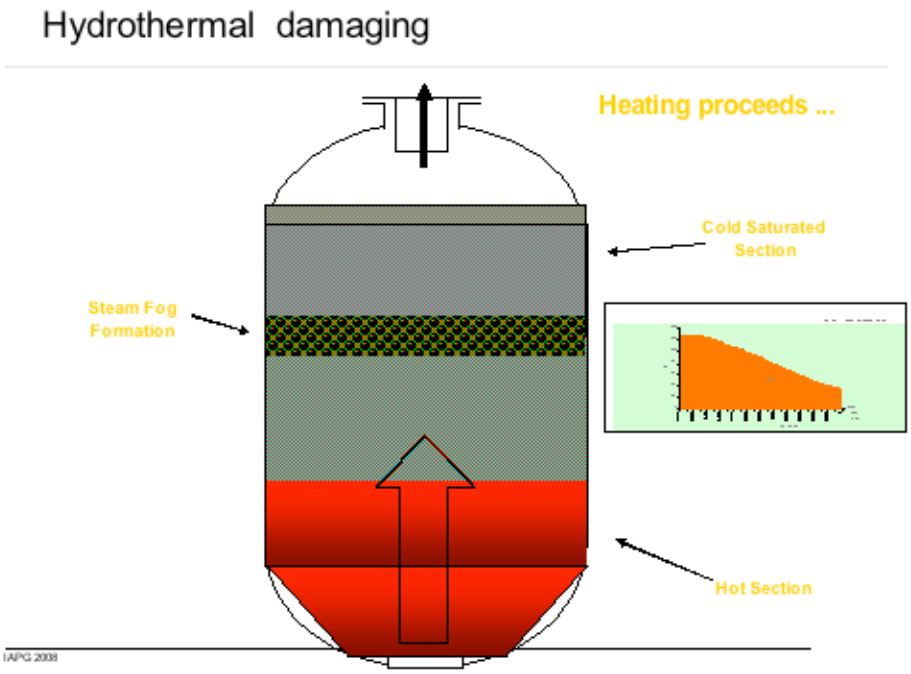
Hydrothermal damaging occurs when water saturated molecular sieves bed is heated up to fast. In this case the bottom layers of the bed desorbs water which is condensed at the top layers of the bed leading to boiling of the sieve in liquid water, especially at the top layers of the bed.
The consequence is destruction of the crystal structure of the zeolites and loss of adsorption capacity. It may lead to formation of fines depending on the binder formulation of the molecular sieve. The result is a significantly shorter life time of the adsorbent due to low adsorbent capacity and/or too high pressure drop.

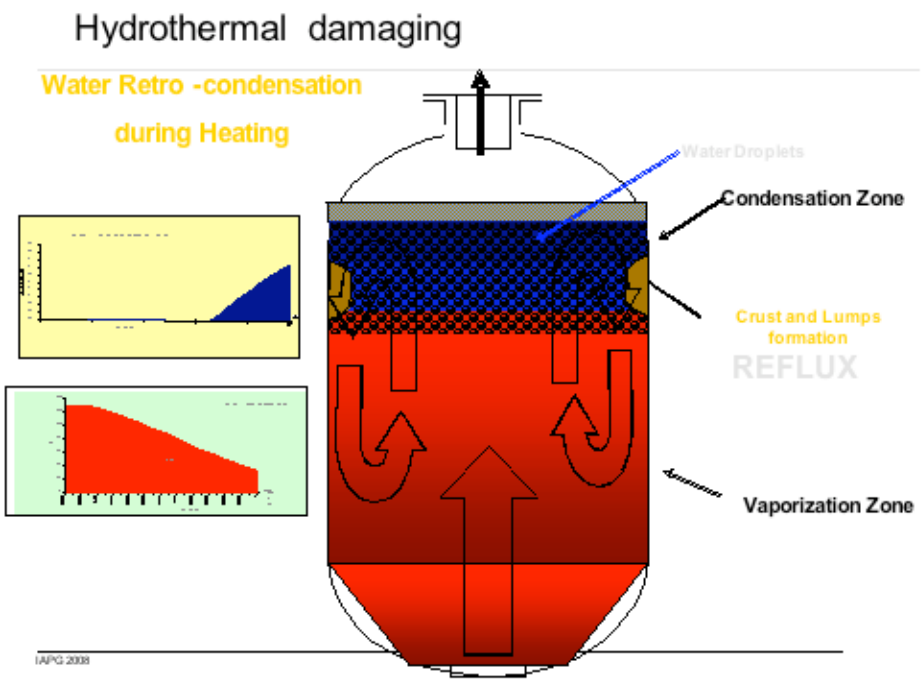
Hydrothermal damaging



Hydrothermal damaging







In order to prevent hydrothermal damaging it is recommended to heat up the whole bed smoothly to a certain temperature level to prevent water condensation but to prevent significant water desorption at the same time.

Case 4 describes such a regeneration procedure. It includes an intermediate heating step at a temperature of around 120°C of a duration of 30 minutes.

The differences between case 1 and case 4 are the following:

- Same heating and cooling time available (7 hrs 30 minutes) as the intermediate heating step takes 30 minutes

- Regeneration gas flow rate 115% at high pressure and high temperature
- Total regeneration gas quantity of 123% versus case 1
- Adsorbent quantity 102% versus case 1

The regeneration gas quantity and flow are similar to the case 2 but the advantage of case 4 is that the water dew point of the dried gas is lower than in case 2 as the regeneration gas temperature is lower resulting in a lower residual water content.

The table below resumes the four cases:

CASE STUDY

	MS Quantity	Regengas quantity	Regen flow rate
CASE 1	100%	100%	100% F_{R1}
CASE 2	104%	115%	123% F_{R1}
CASE 3	102%	108%	115% F_{R1}
CASE 4	102%	115%	123% F_{R1}

Case 1: Regeneration at 250°C, 482°F and 30 bar, 435 psia

Case 2: Regeneration at 250°C, 482°F and 60 bar, 870 psia

Case 3: Regeneration at 290°C, 555°F and 60 bar, 870 psia

Case 4: Regeneration at 290°C, 555°F and 60 bar, 870 psia, interm. heating

Case 5: keep regeneration gas flow rate and MS height of case 2, internal heat insulation , diameter 3.5 m, increase feed flow rate, decrease adsorption time

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Let us look at a possible debottlenecking of case 2. Case 2 was chosen as in most of the Natural Gas drying unit the regeneration gas pressure is close to the adsorption pressure in order to limit energy consumption for recompression.

Supposing the regeneration gas recycle is limited to a certain flow rate but the plant should be debottlenecked to a higher capacity.

Treating a higher flow rate by keeping the same adsorbent volume could be possible by decreasing the adsorption time. This would result in a higher regeneration gas flow rate as less regeneration time is available which was excluded in this study due to the supposed limitation of the regeneration gas recycle.

A possibility could be to install an internal heat insulation. This decreases the energy necessary to heat up the vessel steel and makes more regeneration gas available to desorb water. If there is margin in adsorption pressure drop in the plant this is an interesting solution.

The feed gas flow rate could be in this case increased to 140% of the flow rate of case 2. The vessel diameter would be approximately 95% (internal heat insulation) leading to a pressure drop of 0.7 bar (EOR of case 2). The regeneration gas flow rate would be identical and the regeneration gas quantity even only 61%. Taking into account the lower volume available for the adsorbent the adsorbent quantity is reduced to 88% and the adsorption time decreased from 16 hrs to 9 hrs.
As the cycle time is shorter the adsorbent life time would be lower.

CASE STUDY

	MS Quantity	Regengas quantity	Regen flow rate
CASE 2	100%	100%	100% F_{R2}
CASE 5	88%	61%	100% F_{R2}

Internal insulation, 3.7m ⇒ 3.5 m internal diameter

Higher feed flow rate : 140%

Higher pressure drop during adsorption : 233%

Adsorption time down from 16hrs to 9hrs (shorter life time)

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How to prevent hydrothermal damaging?

Heating up the adsorber without using a heating ramp leads to a strong temperature difference in the vessel. At the bottom, the molecular sieve will be very hot and will desorb from the beginning of the regeneration the adsorbed water while the layers at the top of the adsorber will still be at adsorption temperature. The water desorbed from the bottom layer will condense in the top layer. This phenomena is called refluxing or retro condensation.
The heating going on will heat up the liquid water and boil the molecular sieves in liquid water. Hydrothermal damaging will appear in consequence.
The binder of the zeolite might be attacked or weakened leading to dust formation or formation of agglomerates.

Hydrothermal damaging is different depending on the type of molecular sieve:

- X type molecular sieves (10 A or 13X): a loss of crystalline structure occurs with a roughly proportional loss in adsorption capacity
- A type molecular sieve (3A, 4A, 5A): the external crystal surface is attacked resulting in a “pore closure” effect that affects the kinetics of adsorption. Nevertheless, the substantial adsorption capacity persists. In general, 3 A molecular sieves (potassium A type) are more sensitive to hydrothermal damaging than 4A (sodium type) and 4A type more than 5A (calcium A type).

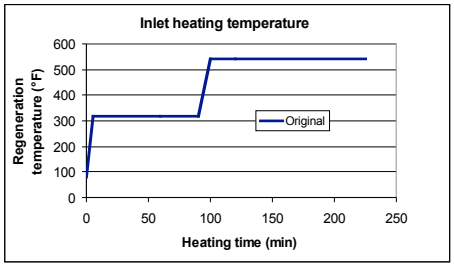
The higher the regeneration temperature the more severe the damaging of the molecular sieves.

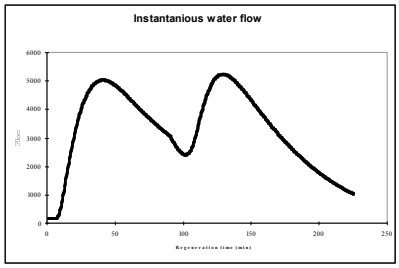
The SIMATEP simulation program determines for a given unit the quantity of liquid water, the section of the molecular sieves and the temperature when it appears for a given regeneration procedure.

The slide below shows a case of an existing unit with a regeneration procedure with an intermediate heating step. The initial intermediate heating step is at a relatively high level.
This leads to a water desorption in two peaks.

The outlet temperature shows that a significant amount of the water desorbed during the first peak is condensed on the top layers as there is a temperature plateau showing that the energy put in the adsorber is used to evaporate water instead of heating up the whole system.

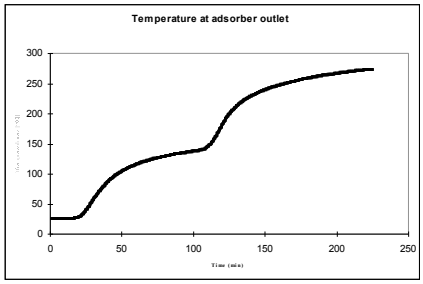
How to prevent hydrothermal damaging?





Original procedure:

- int. temperature too high, too much water desorbed
- plateau of outlet temperature showing water re-vaporization



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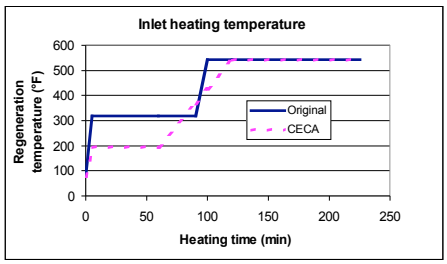
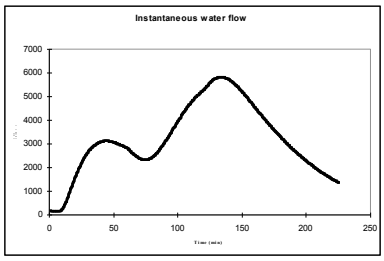
In order to limit the hydrothermal damaging the temperature level of the intermediate heating step was decreased and the ramp smoothened. The consequence is that the first water peak is lower, the whole bed is heated up more smoothly by limiting the water desorption.
The outlet temperature shows a less significant plateau and a more constant increase of temperature at the outlet.

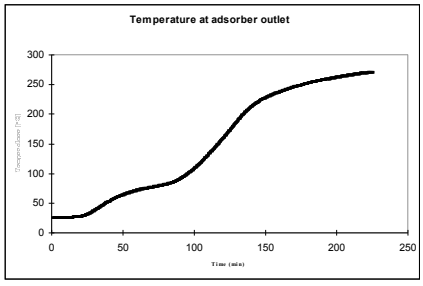
How to prevent hydrothermal damaging?





New procedure:

- int. temperature lower
- smoother increase of outlet temperature



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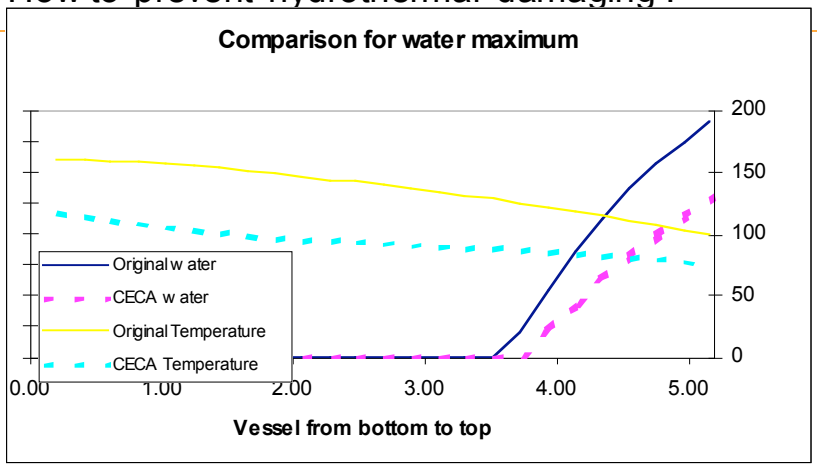
Looking at the moment when the maximum liquid water quantity appears on the sieves and the corresponding temperature profile the new regeneration procedure allows to decrease the total quantity of liquid water appearing on the adsorbent and the temperature level thus decreasing the hydrothermal attack.

How to prevent hydrothermal damaging?



Conclusion

When looking at your molecular sieve unit and its regeneration procedure:

- Don't underestimate the pressure influence on the regeneration gas quantity

- Think about hydrothermal damaging

- Optimization does not cost a lot but lengthens the life time of the molecular sieves

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Biography of the Authors

Peter Bernd Christian MEYER is Business Manager Dynamic Applications and head of the Dynamic Applications department for the molecular sieves of CECA in the headquarter in Paris. Dynamic Applications covering adsorbent applications for Natural Gas, Petrochemistry, Refinery and Industrial Gases. He has more than 7 years experience in the adsorbent business. He worked previously 5 years as Process and Project Engineer in an engineering company Salzgitter Anlagenbau in Germany and in a process department of a ARKEMA (ancient name ATOFINA). He holds a diploma of the Technical University of Karlsruhe, Germany in Chemical Engineering and a second diploma from the Ecole National Supérieure du Pétrole et des Moteurs (known as IFP school), France in Refinery, Engineering and Gas Technology.
He has already given several presentations about molecular sieves at the GPA Europe.

Bob A. DAVENPORT is employed by ARKEMA Inc. as the Sales and Marketing Manager for Ceca Molecular Sieves Dynamic Applications in the Western Hemisphere. Experience includes 25 years selling and servicing adsorbent applications in the natural gas, refining and petrochemical industries. The last 13 years were with molecular sieve manufacturers. He holds a B.S in Environmental Science from Lamar University.