



Critical Adsorption Techniques for Cryogenic

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Abstract

This article focuses mainly on the critical adsorption methods in especially oil and gas industries describing various phenomenon to be used based on the critical applications so that desired product is achieved with efficiency. These are different technologies per different licensors owning the catalyst wherever applicable.

Keywords: Purification; CO₂; Critical Adsorption; Diameter

Introduction

Purification is a process that separates unwanted particles from the desired product. The unwanted particles are of wide range that can be harmful environmentally and also effect the yield of the product for desirable purity. The same purifications are termed as adsorption, absorption in terms of distillation. Also condensation and solidification are considered to be the other process of purification.

Critical adsorption phenomenon

It is important to distinguish adsorption from absorption:

Adsorption = fixation on the surface by a solid (adsorbent) of molecules of a gas or a liquid

Absorption = fixation in volume of the molecule of a gas or a liquid (picture of a sponge).

As adsorption is a surface phenomenon, it will be reversible. All solid bodies have a more or less important adsorbent power,

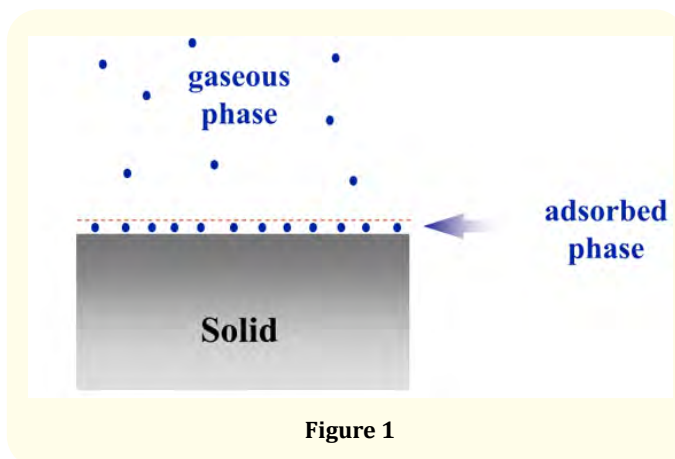


Figure 1

depending on their nature, their surface finish (porosities), and the nature of the adsorbed body.

Once the surface of the adsorbent body is covered with a molecules coat of the adsorbed body, fixation stops. Then, the bigger the adsorbent body surface, the higher the adsorbed quantity, which leads to look for porous adsorbent materials (characterisation: specific surface in m²/g, porous volume in cm³/g and distribution of pores average diameter of a few hundreds of angstroms).

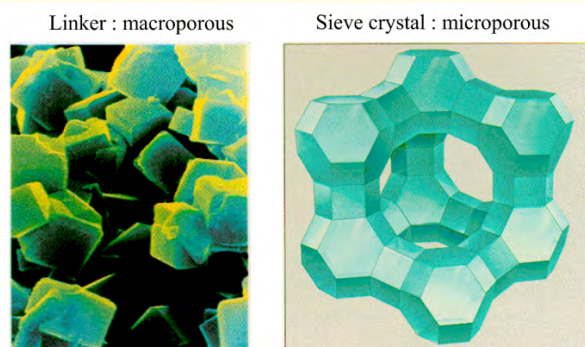


Figure 2

An important characteristic of adsorption phenomenon is that it is exothermic.

Adsorbed molecules on the surface are then in a physical state closed to liquid phase, which is strengthened by the fact that adsorption heat is much closed to the condensation latent heat one.

In order to make adsorption occur, there must be some attraction between the body molecules or impurities to adsorb, and the adsorbent surface must be; it is weak dipolar attraction forces called *VAN DER WAALS's* forces.

Moreover, the diameter of adsorbed impurities must be lower than the adsorbent pores one, which stands for a molecules trap.

Then, depending on the adsorbent nature and the nature of the impurity to adsorb, an adsorbent selectivity is defined.

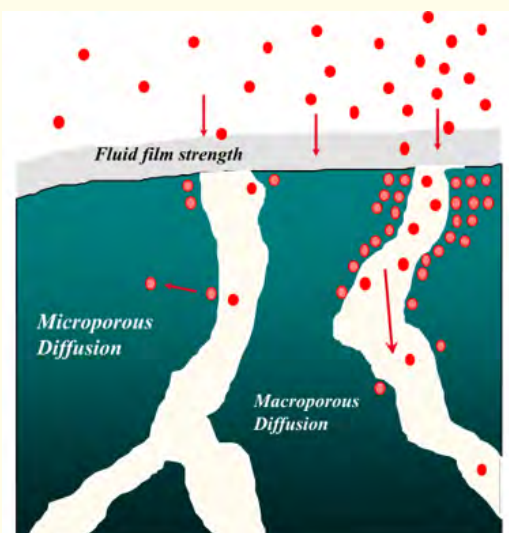


Figure 3

Methane and ethane are very badly adsorbed, but on the other hand, acetylene (molecule much unsaturated) is very well stopped. Starting from propane, other hydrocarbons are all quite well stopped.

As they have, at atomic level, a crystalline structure which is able to "trap" molecules, the adsorbents structure is made of macro porous between which molecules that are wanted to be stopped can insert.

Then general structure of adsorbents can be visualised as a gallery in which molecules diffuse, as selection is made on the compared size of these ones and the pores ones.

Adsorption isotherm is an important diagram to understand the operation of adsorption mechanism.

It is generally made of a curves network at different temperatures and it represents the adsorbed quantity of the considered component in function of its partial pressure [5,6].

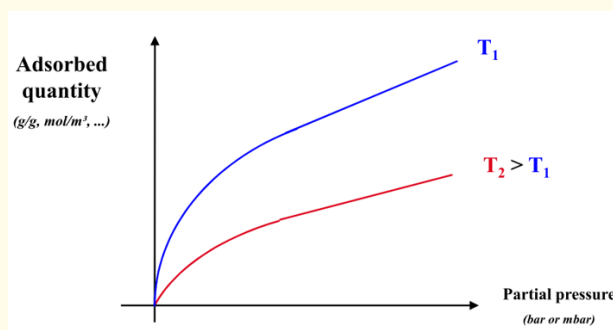


Figure 4

Thus it is characteristic of adsorption of a set specie on a set adsorbent.

Each point of the curve is the equilibrium expression of gaseous phase and adsorbed phase at a set temperature.

It is noticeable that adsorbed quantity is inversely proportional to temperature. Then, adsorption is all the better since temperature is low. Adsorbed quantity is also higher if partial pressure of the component, or total pressure of the mixture, is high.

Adsorption phenomenon will thus be improved by following factors:

	Chemical formula	Specific surface (m ² /g)	Relative density (kg/m ³)	Porous volume (cm ³ /g)	Pore diameter (Å)	Max. regulation temperature (°C)
Amorphous structure	Coals	C	800 to 1500	500	0.5 to 0.7	100 to 150°C
	Silica gels micro or macroporous	Si O ₂	600 to 800	700	0.4 to 0.5 10 to 1000	200 to 250°C
	Aluminas	Al ₂ O ₃	300 to 350	800	0.35 to 0.4 10 to 40	150 to 200°C
Crystalline structure	Zeolites or Molecular sieve					
	Type A	3A K ₂			» 3 Å	
		4A Na ₂	800	700	» 4 Å	
		5A Ca O			» 5 Å	
	Type X	13X	900	600	» 10 Å	300 to 350°C
	Mordenite		500	800	0.17 4 à 7	

Figure 5

- A low temperature,
- A high pressure,

But also sharp adsorbents granulometry and a long switch time between gases and adsorbents, that is to say a low gas speed in adsorption cylinder.

Water isothermal on alumina, molecular sieve 13X, silica gel

If water is better adsorbed on 13X than on other adsorbents, reactivation temperature needed is comparatively higher than for the other ones (300°C in place of 120 to 150°C).

That is why water adsorption is performed on an alumina bed, before the CO₂ one on a molecular sieve 13X.

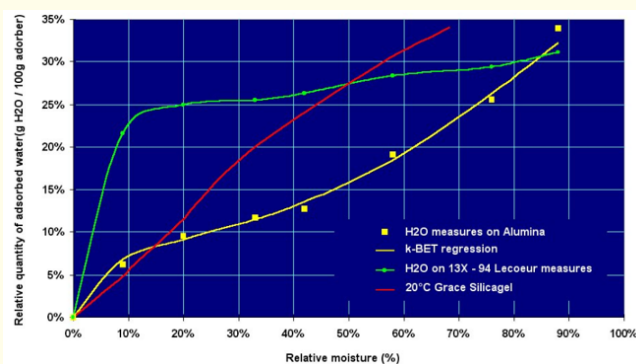


Figure 6

Water, CO₂ and nitrogen isotherms on molecular sieve 13X

The X axes represents partial pressure of the adsorbed component.

Water is adsorbed preferentially to CO₂ on the molecular sieve 13X, but requires a higher desorption temperature. However,

nitrogen and CO₂ are equally adsorbed but with a comparable evolution up to 6 abs bar.

Important note: the X axes is in abs bars for nitrogen, not in mbars.

Nota concerning nitrogen co-adsorption: in classic conditions of a front end purification, air is under ~ 6 abs bars.

Partial pressure of N₂ is:

$$P_{N_2} = 6 \text{ abs. bar} \times 78\% = 6 \times 0.78 = 4.7 \text{ bar abs} \Rightarrow Q_{\text{ads}} \sim 6\%/100 \text{ g 13X}$$

In the case of a GOK, purification pressure is higher, up to 30 bars. Partial pressure of N₂ is then:

$$P_{N_2} = 30 \text{ abs. bar} \times 78\% = 30 \times 0.78 = 23.4 \text{ bar abs} \Rightarrow Q_{\text{ads}} \sim 16\%/100 \text{ g 13X}$$

Then we note that the higher air partial pressure is in purification conditions, the more preferentially nitrogen will be adsorbed. In the case of GOK, we are in front of the phenomenon of preferential adsorption of nitrogen, which leads to an important increase of temperature due to adsorption heat. Then, to avoid to send a too important heat front just when cylinders are inverted after repressurization, there is no other choice than lengthening the parallel operation step of cylinders in order to smooth as much as possible in the time the corresponding heat peak.

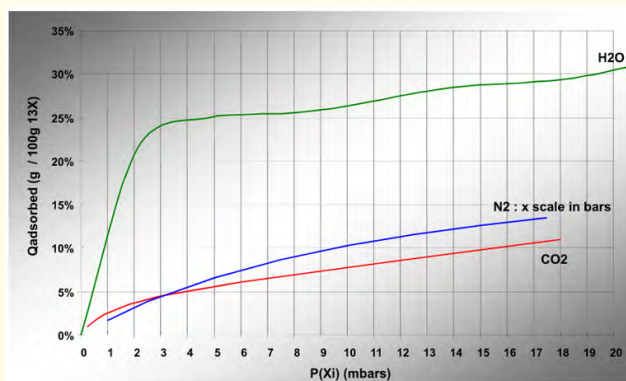


Figure 7

Adsorption kinetics

A specie adsorbed quantity in the time, at set pressure and temperature, follows an asymptotic evolution at the value called "at the equilibrium".

Then for a set gas speed in adsorbent (or switch time on adsorbent), the equilibrium value is never perfectly reached.

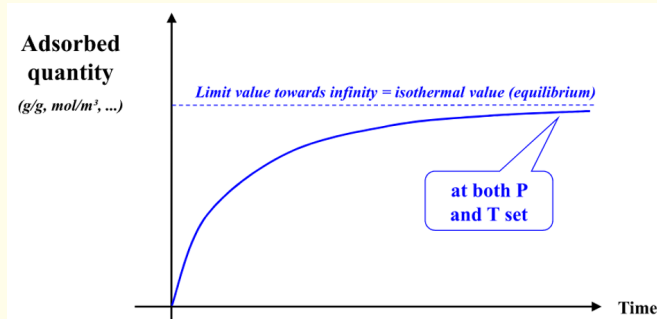


Figure 8

Adsorption cycle and reactivation

Here is an analogy in order to visualise adsorption evolution in the purification cylinder: as gas is purified in the adsorbent bed, an adsorption front moves forward in the same direction than purified gas. When this front reaches the cylinder end, this one is saturated and the adsorbent phase must be stopped, in order to prevent the purified component from “drilling” at the cylinder end [4].

Thus a reactivation is made in opposite direction thanks to a purified gas that will assure the desorption of precedent purified components in adsorption phase.

Then, as adsorbent reactivates, this dry gas charges in water and CO_2 .

At the end of reactivation, there is a small residual quantity of water and CO_2 left in the cylinder because reactivation is not perfectly systematic. In order to prevent this residual quantity to change in the time, and moreover in case of an operational accident, an exceptional reactivation can be made at a high temperature.

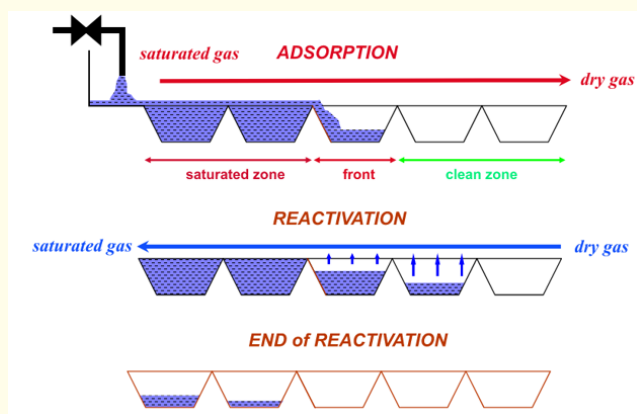
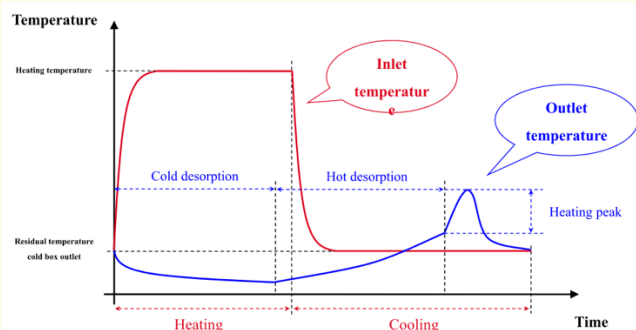


Figure 9

In adsorption step

In adsorbents beds, adsorption front changes in the time from the inlet to the outlet of the cylinder, as air, charged with water and CO_2 passes through it.

However, at every moment, adsorbed quantity in the cylinder is not the one which is reached at the equilibrium, at least on a adsorption front level. It is a phenomenon of slow that is all the more important since gas speed is high, or since switching time is low (inverse value).

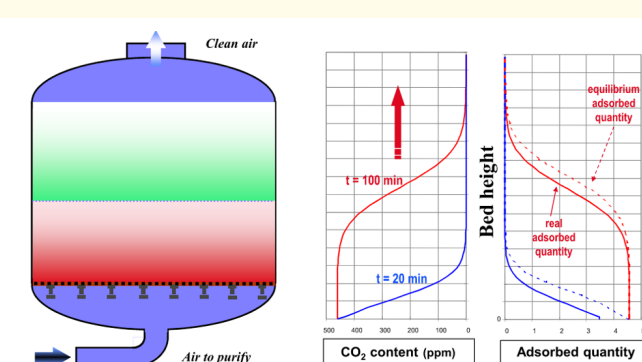


Figure 10

In reactivation step

For the same reason than before, the same shift between real and equilibrium adsorbed quantity appears in reactivation phase.

At the end of reactivation a residual front of impurities is thus obtained, that must be taken into account in order to prevent it from changing in the time and from consuming a little more adsorption capacity at each cycle [1].

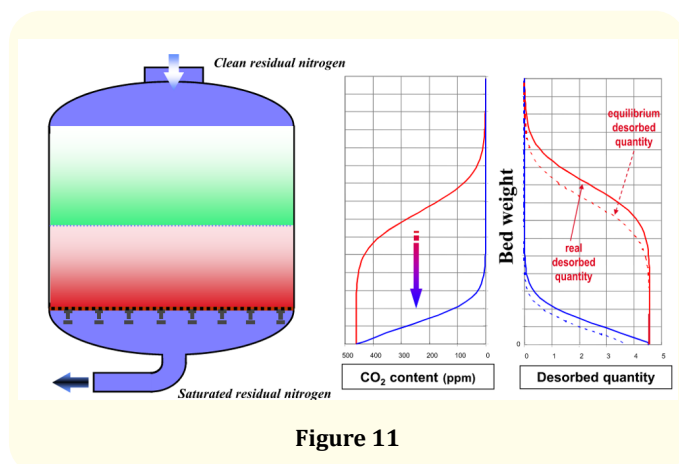


Figure 11

Moreover, the reactivation flow, which is a part of the remaining nitrogen in the cold box, thus dry and without CO_2 , is lower than the flow of air that is wished to be purified. Hence it is necessary to have, as much as possible, favourable reactivation conditions to desorption, that is to say lower pressure and higher temperature.

Two very different effects favourable to desorption are in fact used for the adsorber reactivation itself:

- A first desorption called “cold” by depressurization effect (point 1 to 2 of diagram).
- A second desorption called “hot” by heating effect (point 2 to 3 of diagram).

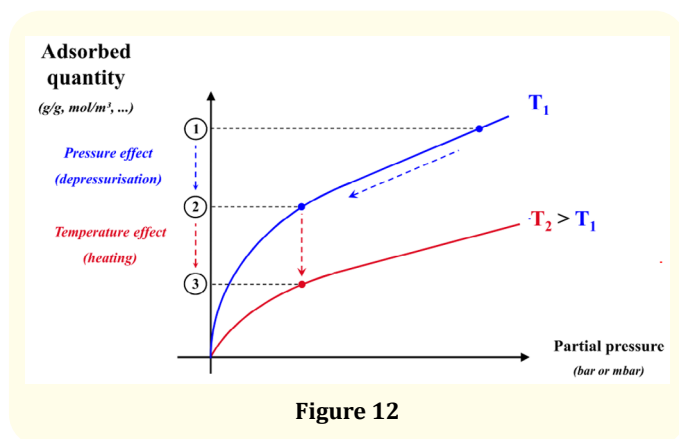


Figure 12

Thus point 3 represents the residual quantity of impurities at the end of the reactivation.

The technology of adsorbers with horizontal beds is used for flows up to $100\,000\text{ Nm}^3/\text{h}$ under medium pressure.

This is an economical limit because the phenomenon of attrition or fluidisation of adsorbents balls bed on the surface limits us

in case of excessive gas speed. Actually, adsorbents balls will be moved on against each other and will come into fire.

A limit speed is thus set to fix minimal section of bed hence adsorbers diameter.

The cylinder size is also limited by the maximal size of transport.

Up to a capacity of about $100\,000\text{ Nm}^3/\text{h}$, an other configuration is taken.

The technology of adsorbers with horizontal beds is recommended for air flows higher than $100\,000\text{ Nm}^3/\text{h}$ under medium pressure.

In order to have the possibility of doing every step necessary to whole cycle of each reactivation cylinder - adsorption then reactivation, it is imperative first to have two adsorbers available, thus a cylinder will be in reactivation while the other is in adsorption - and conversely -, and also a valves and pipes layout to enable the air flow to pass from one to the other without stopping the cold box feed in air [3].

Hence, we will have a valves gap for air inlet and outlet, for reactivation residual nitrogen inlet and outlet, and for the balancing cylinders pressures.

Adsorbers have two adsorbents beds: alumina, for water adsorption and molecular sieve for CO_2 adsorption.

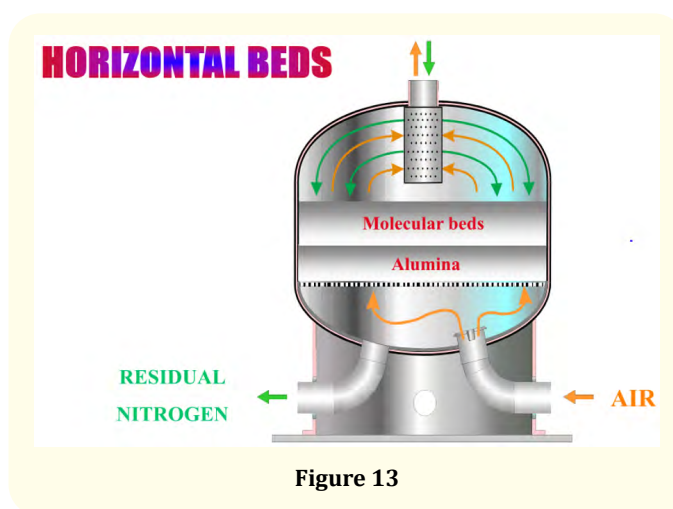
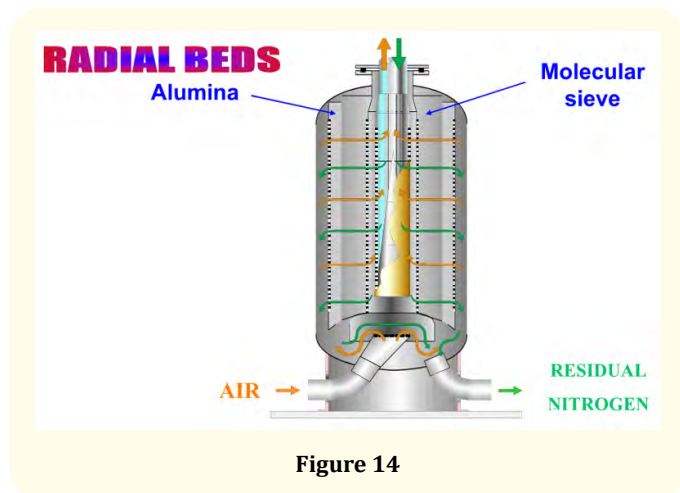


Figure 13

In practice alumina is always used for holding water, whereas the molecular sieve, in classic exploitation conditions, is more grasping of water. The reason is that alumina requires a water

desorption energy lower than the sieve one (about 800 kcal per gram of water, 1000 for the molecular sieve). Then, after having passed through the alumina bed, air reaches the molecular sieve bed purified in water but not in CO_2 because alumina holds it very badly [2].



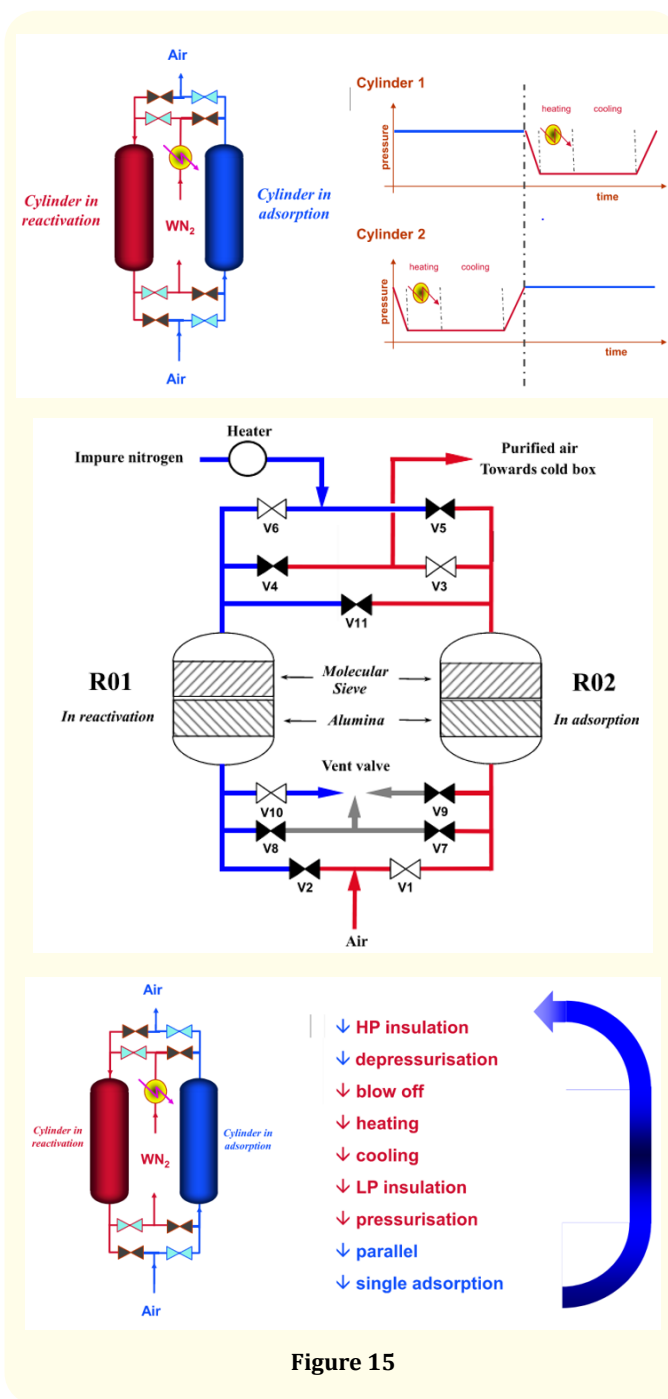
Classic functioning conditions are:

- Air in purification phase at a temperature closed to the ambient one, under 5 to 6 abs bar (cold box inlet pressure),
- Remaining impure nitrogen in reactivation between 80 and 150°C in heating and at the same temperature than the cold box inlet air (except for the difference in temperature at the warm end of the main exchanger), under nearly 1.2 abs bar (residual cold box outlet pressure).

Note: a temperature of about 300°C would be needed to do water desorption on molecular sieve. It is temperature that will be needed during an exceptional reactivation in case of operational incidents like water drilling of alumina bed (thus water adsorption on molecular sieve), drive of little water drops from air/water pre-cooling tower downstream adsorbers, leakage of reactivation heating tube vapour to impure nitrogen, or merely during the adsorbers fulling while facility is settled (adsorption of ambient moisture).

The whole cycle sequence is made of 9 steps, a detailed description of which can be found in the appendices.

These 9 steps enable to pass from principal adsorption steps to reactivation (heating and cooling), and conversely. The other



steps are called inversions, as they prepare cylinders to new pressure conditions in passages from adsorption to reactivation, and conversely.

Temperature profiles in function of time, in adsorber inlet and outlet, represent a good indication of the reactivation efficiency.

Temperature profile in inlet proves that a heat front enters the cylinder at the beginning of the reactivation during the heating step.

The outlet profile is characteristic of this reactivation quality. It is made of 3 main phases:

- **Desorption (cold level):** Temperature decreases because of the endothermic effect of first desorption, whereas heat front has not ever migrated to the cylinder outlet. It is the image of desorption under cylinder depressurization effect during the precedent step.
- **Desorption (hot level):** When the heat front has reached the end of the cylinder, this one has been consumed by complete desorption of water and CO₂. The result is a little temperature increase.
- **Heat peak:** As all impurities have been desorbed, a little heat excess in comparison to exact heat quantity needed to reactivation, and given during the heating phase, will cause an outlet peak that will not have been consumed by desorption. It represents the proof that reactivation did occur. However, this peak must be limited in order to not lead, in the end of cooling, to a temperature higher than the temperature of cold box inlet ; this would actually involve sending, via air after the cylinder inversion in adsorption, a heat front to the cold box that would thermally disturb the hot end of the main exchanger and also its exchange diagram (see influence of air inlet temperature at the hot end in exchanger part). So this heat peak is necessary but has to be controlled by the heating time.

Conclusion

Its very important to choose the different types of critical adsorption methods for various applications for better productivity with atmost efficienciency in terms of operation and cost. Also very critical to chose the licensor suitable for the relevant process again cost effective and design effective.

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