Pressure Swing Adsorption

Fundamentals

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• Pressure Swing Adsorption – a brief introduction;
• Historical perspective;
• Adsorbent main properties;
• Adsorbent regeneration;
• Equilibrium-controlled separation;
• Kinetic-controlled separation;
• PSA steps;
• Modelling, simulation and optimization of PSA units;
• Model example.
How does Pressure Swing Adsorption work?
Pressure Swing Adsorption – a brief introduction

How can we obtain B from a mixture of A+B?

If we have an adsorbent that adsorbs more A than B, we can separate them.

How?
How can we obtain B from a mixture of A+B?

Let’s choose an operating pressure considering:

- Acceptable capacity and selectivity;
- Maximum pressure allowed by the adsorbent and unit/equipment;
- Energy consumption;
- Product requirements.
How can we obtain B from a mixture of A+B?

If we pass a stream containing A+B at the operating pressure, through a bed packed with this adsorbent:

- A will be preferentially adsorbed (retained by the adsorbent);
- B will move through the bed and leave it at the top.

This will happen until the adsorbent is saturated with A.

What should we do next?
How can we obtain B from a mixture of A+B?

Now we have to clean the adsorbent.

How?
How can we obtain B from a mixture of A+B?

If we decrease the pressure the adsorption capacity also decreases.

For example, if we open the bed to the atmosphere and let the gas out, the final pressure will be 1 bar.
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Is this enough?
How can we obtain B from a mixture of A+B?

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For example, if we open the bed to the atmosphere and let the gas out, the final pressure will be 1 bar.

Is this enough?

No
How can we obtain B from a mixture of A+B?

What else can we do?
How can we obtain B from a mixture of A+B?

What else can we do?

- Use vacuum to decrease the pressure (the power consumption increases);
- Pass the product through the bed to decrease the partial pressure of the undesired component (some of the product is lost).
How can we obtain B from a mixture of A+B?

After this swing of the pressure the column is cleaned and ready to be fed again.

This is Pressure Swing Adsorption.
The first single bed Pressure Swing Adsorption (PSA) process was patented in 1932 by Finlayson and Sharp, from the company British Celanese.
Twenty years later, Khale, from Linde, patented a two bed PSA process
PSA units are usually composed by two or more columns packed with one or more adsorbents
The main properties of the adsorbents are:

- Adsorption capacity;
- Adsorption kinetics;
- Selectivity;
- Mechanical stability;
- Thermal stability;
- Chemical stability.
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Amount of each species that is retained by the adsorbent
The main properties of the adsorbents are:

- Adsorption capacity;
- Adsorption kinetics;
- Selectivity;
- Mechanical stability;
- Thermal stability;
- Chemical stability.

Speed at which each species is retained by the adsorbent.
The main properties of the adsorbents are:

- Adsorption capacity;
- Adsorption kinetics;
- Selectivity;
- Mechanical stability;
- Thermal stability;
- Chemical stability.

**Equilibrium selectivity** – ratio between the adsorption capacities of the more adsorbed species and the less adsorbed species;

**Kinetic selectivity** – ratio between the kinetic parameter of the more adsorbed species and the less adsorbed species;
The main properties of the adsorbents are:

- Adsorption capacity;
- Adsorption kinetics;
- Selectivity;
- Mechanical stability;
- Thermal stability;
- Chemical stability.

Resistance of the adsorbent – the formation of dust may damage the valves and contaminate the product.

It also limits the height of the columns.
The main properties of the adsorbents are:

- Adsorption capacity;
- Adsorption kinetics;
- Selectivity;
- Mechanical stability;
- Thermal stability;
- Chemical stability.

It is important to know how the adsorbent reacts to temperature increase. Some adsorbent can be damaged when increasing the temperature.
The main properties of the adsorbents are:

- Adsorption capacity;
- Adsorption kinetics;
- Selectivity;
- Mechanical stability;
- Thermal stability;
- Chemical stability.

Some adsorbents can be damaged in the presence of some species such as water vapour or ammonia. It is important to know if these species are in the feed streams and if so, take measures to avoid the degradation of the adsorbent.
Adsorbent regeneration

- PSA;
- TSA;
- CSA.
Adsorbent regeneration

- PSA;
- TSA;
- CSA.

**Pressure Swing Adsorption**

The adsorbent is regenerated by lowering the pressure.

**Diagram:**

- X-axis: Pressure (bar)
- Y-axis: Loading (mol/kg)
- Line starts at 0 pressure, 0 loading, and ends at 8 bar, 4 loading.
- Marker at 30°C.
Adsorbent regeneration

- PSA;
- TSA;
- CSA.

Temperature Swing Adsorption

The adsorbent is regenerated by increasing the temperature.
Adsorbent regeneration

- PSA;
- TSA;
- CSA.

Concentration Swing Adsorption

The adsorbent is regenerated by lowering the concentration.
As we can see, there is a significant difference between the H$_2$ and CO$_2$ adsorption capacities. This difference in the adsorption capacity allows the separation of these two gases. This is an equilibrium-controlled separation.

Equilibrium-controlled separation

Oxygen separation from air

Applications:

- Fishing farms;
- Medical applications;
- Pulp bleaching;
- Steelmaking and metal-cutting;
- …

Source: www.sequal.com

Source: www.oxymat.dk
Carbon molecular sieves are commonly used for nitrogen production from air by PSA.

How can the separation be possible if both gases adsorb almost the same?

As we can see, oxygen adsorbs faster than nitrogen.

This difference in the adsorption kinetics allow the separation of these two gases.

This is a kinetic-controlled separation

Nitrogen separation from air

Applications:

- Electronics industry;
- Metals industry;
- Food industry;
- Tire inflation;
- …

Source: www.ultrafill99.com
(Air Products)
The basic steps used in PSA are:

- Pressurization;
- Adsorption (production);
- Pressure equalization (provide and receive);
- Blowdown;
- Purge.
Pressurization

The column is pressurized with feed at high pressure.

By increasing the pressure we increase the working capacity.
Adsorption (production)

The outlet of the column is opened and the unit starts producing.

The more adsorbed species are retained by the adsorbent while the less adsorbed species continue moving along the column until they exit it.
Nature of fronts vs. isotherm shape

\[ q_i = f(c_i) \]

Favorable isotherms \( \rightarrow \) Compressive fronts

\[ u_{sh} = \frac{u_i}{1 + \frac{1 - \varepsilon}{\varepsilon} \frac{\Delta q_i}{\Delta c_i}} \]

Unfavorable isotherms \( \rightarrow \) Dispersive fronts

\[ u_{c_i} = \frac{u_i}{1 + \frac{1 - \varepsilon}{\varepsilon} f'(c)} \]
Pressure equalization - provide

Before the concentration wave reaches the end of the column, the production is stopped.

The column is then connected to other at low pressure to provide gas for a partial pressurization.

This step allows for significant energy cost reduction.
Blowdown

The column is evacuated.
By decreasing the pressure we decrease the working capacity.
The more retained component will be desorbed and leaves the column.
Purge

Some of the product from a column that is in the production step is introduced in this column.

This reduces the partial pressure allowing a further desorption of the more retained specie.

This step also cleans the voids.
Pressure equalization - receive

After the column is cleaned, it is ready for receiving more feed.

The column is connected to a column that ended the production step and receives gas for a partial pressurization.

Afterwards this column will be further pressurized with feed – production step.
For a two-bed PSA the steps may be organized as following:

<table>
<thead>
<tr>
<th>Press</th>
<th>Ads</th>
<th>PEQ</th>
<th>Blwd</th>
<th>Purge</th>
<th>REQ</th>
</tr>
</thead>
<tbody>
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</tbody>
</table>
An accurate process simulator is an important tool for learning, designing and optimization purposes
Prior to any simulation, necessary data must be gathered:

• Adsorption capacities;
• Adsorption kinetics;
• Heat of adsorption;
• Particle size;
• Adsorption bed hydrodynamic properties.
Modelling, Simulation and Optimization of PSA units

Magnetic suspension balance from Rubotherm
Fixed bed unit
The process is modelled at different scales:

- Equilibrium and kinetics of adsorption
- Convection and diffusion
- Mass and energy balances
The complexity of the model is dictated by the adsorbent.

Different “building blocks” may be used to construct the mathematical model.
Process modelling and simulation follow these steps:

1. **Experiments**
2. **Experimental Runs**
3. **Process Modelling**
4. **Process Simulation**
5. **Results agree?**
   - **Yes** -> **Process Optimization**
   - **No** -> **Refine the model**

The process ends with refinement or optimization based on the agreement of experimental and simulation results.
Process simulation can be used to predict:

- Product purity;
- Product recovery;
- Productivity;
- Energy consumption.
Model assumptions:

• Ideal gas behaviour

• No mass, heat or velocity gradients in the radial direction

• Axial dispersed plug flow

• External mass and heat transfer resistances (film model)

• Bidispersed adsorbent particle with macropore and micropore mass transfer resistances (LDF model)

• No temperature gradients inside each particle

• Constant porosity along the bed
Model Example

Balances to the gas phase

\[
\frac{\partial}{\partial z} \left( \varepsilon D_{ax} C_{g,T} \frac{\partial y_i}{\partial z} \right) - \frac{\partial}{\partial z} \left( u_0 C_{g,i} \right) - \varepsilon \frac{\partial C_{g,i}}{\partial t} - (1 - \varepsilon) a_p k_f \left( C_{g,i} - C_{s,i} \right) = 0
\]

\[
- \frac{\partial P}{\partial z} = \frac{150 \mu (1 - \varepsilon)^2}{\varepsilon^3 d_p^2} u_0 + \frac{1.75 (1 - \varepsilon) \rho}{\varepsilon^3 d_p} |u_0| u_0
\]

\[
\frac{\partial}{\partial z} \left( \lambda \frac{\partial T_g}{\partial z} \right) - u_0 C_{g,T} C_p \frac{\partial T_g}{\partial z} + \varepsilon R_g T_g \frac{\partial C_{g,T}}{\partial t} -
\]

\[
- (1 - \varepsilon) a_p h_f \left( T_g - T_p \right) - \frac{4 h_w}{d_{wi}} \left( T_g - T_w \right) - \varepsilon C_{g,T} C_V \frac{\partial T_g}{\partial t} = 0
\]
Balances to the solid phase

\[ \frac{\partial \overline{C_{p,i}}}{\partial t} = \frac{\Omega_M D_{p,i}}{R_p^2} \left( C_{s,i} - \overline{C_{p,i}} \right) - \frac{\rho_p}{\varepsilon_p} \frac{\partial \overline{q_i}}{\partial t} \]

\[ \frac{\partial \overline{q_i}}{\partial t} = \frac{\Omega_m D_{c,i}}{r_c^2} \left( \overline{q_i^*} - \overline{q_i} \right) \]

\[ (1 - \varepsilon) \left[ \varepsilon_p \sum_{i=1}^{n} \overline{C_{p,i}} C_{v,i} + \rho_p \sum_{i=1}^{n} \overline{q_i C_{v,ads,i}} + \rho_p \overline{C_{ps}} \right] \frac{\partial T_p}{\partial t} = \]

\[ = (1 - \varepsilon) \varepsilon_p R_g T_p \frac{\partial \overline{C_{p,T}}}{\partial t} + \rho_b \sum_{i=1}^{n} \left( - \Delta H_{ads} \right)_i \frac{\partial \overline{q_i}}{\partial t} + (1 - \varepsilon) a_p h_f (T_g - T_p) \]

\[ P_i = \frac{q_i}{K_{Hi}} \exp \left( \frac{2}{S} \sum_{j=1}^{N} A_{ij} q_j + \frac{3}{2 S^2} \sum_{j=1}^{N} \sum_{k=1}^{N} B_{ijk} q_j q_k \right) \]
Balance to the column wall

\[ \rho_w C_{p,w} \frac{\partial T_w}{\partial t} = \alpha_w h_w (T_g - T_w) - \alpha_{w\ell} U (T_w - T_\infty) \]

Initial conditions

\[ y_i = C_{p,i} = q_i = 0 \quad \text{for } i \neq \text{inert} \]

\[ y_{\text{inert}} = 1 \]

\[ C_{p,\text{inert}} = C_{g,T} \]

\[ T_g = T_p = T_w = T_{\text{inlet}} \]
This presentation is available at:

http://www.fe.up.pt/~jcsantos/PSA/