Hydrogen Recovery by Pressure Swing Adsorption
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Introduction.

The experience.
The use of the Pressure Swing Adsorption (PSA) process has seen tremendous growth during the last decades mainly due to its simplicity and low operating costs. Major applications have been the recovery of high purity hydrogen, methane and carbon dioxide as well as the generation of nitrogen and oxygen. In addition, it has gained significance for the bulk removal of carbon dioxide from direct reduction top-gases.

Linde as the world leader in adsorption technology has designed and supplied more than 500 PSA plants – including the world’s largest units and units with highest availability.

The Linde hydrogen PSA units
The well proven Linde High Performance Pressure Swing Adsorption (PSA) units are designed for the recovery and purification of pure hydrogen from different hydrogen-rich streams, such as synthesis gases from steam reforming or gaseification processes, or from various off-gases in refinery or petrochemical plants.

Capacities range from a few hundred Nm³/h to large scale plants with more than 400,000 Nm³/h. The hydrogen product meets every purity requirement up to 99.9999 mol-% and is achieved at highest recovery rates.

Main hydrogen consumers are refineries requiring this valuable gas for example for their hydrocracking, deaeromatization or desulphurization processes.

As a second group of users the petrochemical industry has a considerable demand for hydrogen for its processes (e.g. methanol and ammonia synthesis). Additionally, Linde provides PSA solutions to a variety of other consumers like the electronics, biomass, and steel industries.

Linde’s PSA systems have proven to be successful in cases where performance, flexibility, availability and reliability are the determining factors. High quality and easy accessibility to all components minimize and facilitate maintenance to the maximum extent.
The process.

Separation by adsorption
The Pressure Swing Adsorption (PSA) technology is based on a physical binding of gas molecules to adsorbent material. The respective force acting between the gas molecules and the adsorbent material depends on the gas component, type of adsorbent material, partial pressure of the gas component and operating temperature. A qualitative ranking of the adsorption forces is shown in the figure below.

The separation effect is based on differences in binding forces to the adsorbent material. Highly volatile components with low polarity, such as hydrogen, are practically non-adsorbable as opposed to molecules like N₂, CO, CO₂, hydrocarbons and water vapour. Consequently, these impurities can be adsorbed from a hydrogen-containing stream and high purity hydrogen is recovered.

Adsorption and regeneration
The PSA process works at basically constant temperature and uses the effect of alternating pressure and partial pressure to perform adsorption and desorption. Since heating or cooling is not required, short cycles within the range of minutes are achieved. The PSA process consequently allows the economical removal of large amounts of impurities.

Thefigure on page 5 illustrates the pressure swing adsorption process. It shows the adsorption isotherms describing the relation between partial pressure of a component and its equilibrium loading on the adsorbent material for a given temperature.

Adsorption is carried out at high pressure (and hence high respective partial pressure) typically in the range of 10 to 40 bar until the equilibrium loading is reached. At this point in time, no further adsorption capacity is available and the adsorbent material must be regenerated. This regeneration is done by lowering the pressure to slightly above atmospheric pressure resulting in a respective decrease in equilibrium loading. As a result, the impurities on the adsorbent material are desorbed and the adsorbent material is regenerated. The amount of impurities removed from a gas stream within one cycle corresponds to the difference of adsorption to desorption loading.

After termination of regeneration, pressure is increased back to adsorption pressure level and the process starts again from the beginning.

Qualitative ranking of adsorption forces

<table>
<thead>
<tr>
<th>Component</th>
<th>Binding Force</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>weak</td>
</tr>
<tr>
<td>Oxygen</td>
<td></td>
</tr>
<tr>
<td>Argon</td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td></td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td></td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td></td>
</tr>
<tr>
<td>Ethane</td>
<td></td>
</tr>
<tr>
<td>Ethylene</td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td></td>
</tr>
<tr>
<td>Butane</td>
<td></td>
</tr>
<tr>
<td>Propylene</td>
<td></td>
</tr>
<tr>
<td>Ammonia</td>
<td></td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td></td>
</tr>
<tr>
<td>Mercaptanes</td>
<td></td>
</tr>
<tr>
<td>BTX</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>strong</td>
</tr>
</tbody>
</table>
A PSA plant consists basically of the adsorber vessels containing the adsorbent material, tail gas drum(s), valve skid(s) with interconnecting piping, control valves and instrumentation as well as a control system for control of the unit. The pressure swing adsorption process has four basic process steps:

- Adsorption
- Depressurization
- Regeneration
- Repressurization

To provide continuous hydrogen supply, minimum 4 adsorber vessels are required. The figure on page 6 shows the combination of the sequences of four adsorber vessels as a pressure-time-diagram.

**Adsorption**
Adsorption of impurities is carried out at high pressure being determined by the pressure of the feed gas. The feed gas flows through the adsorber vessels in an upward direction. Impurities such as water, heavy hydrocarbons, light hydrocarbons, CO₂, CO and nitrogen are selectively adsorbed on the surface of the adsorbent material. Highly pure hydrogen exits the adsorber vessel at the top. After a defined time, the adsorption phase of this vessel stops and regeneration starts. Another adsorber takes over the task of adsorption to ensure continuous hydrogen supply.

**Regeneration**
The regeneration phase consists of basically five consecutive steps:
- Pressure equalization
- Provide purge
- Dump
- Purging
- Repressurization

The steps are combined so as to minimize hydrogen losses and consequently to maximize the hydrogen recovery rate of the PSA system.

**Pressure equalization (step E1)**
Depressurization starts in the co-current direction from bottom to top. The hydrogen still stored in the void space of the adsorbent material is used to pressurize another adsorber having just terminated its regeneration. Depending on the total number of adsorbers and the process conditions, one to four of these so-called pressure equalization steps are performed. Each additional pressure equalization step minimizes hydrogen losses and increases the hydrogen recovery rate.

**Provide purge (step PP)**
This is the final depressurization step in co-current direction providing pure hydrogen to purge or regenerate another adsorber.

**Dump (step D)**
At a certain point of time, the remaining pressure must be released in counter-current direction to prevent break-through of impurities at the top of the adsorber. This is the first step of the regeneration phase when desorbed impurities leave the adsorber at the bottom and flow to the tail gas system of the PSA plant.
Purging (regeneration)
Final desorption and regeneration is performed at the lowest pressure of the PSA sequence. Highly pure hydrogen obtained from an adsorber in the provide purge step, is used to purge the desorbed impurities into the tail gas system.

The residual loading on the adsorbent material is reduced to a minimum to achieve high efficiency of the PSA cycle.

Repressurization (steps R1/R0)
Before restarting adsorption, the regenerated adsorber must be pressurized again. This is accomplished in the pressure equalization step by using pure hydrogen from adsorbers presently under depressurization. Since final adsorption pressure cannot be reached with pressure equalization steps, repressurization to adsorption pressure is carried out with a split stream from the hydrogen product line.

Having reached the required pressure level again, this regenerated adsorber takes over the task of adsorption from another vessel having just terminated its adsorption phase.

The typical scope of supply of Linde’s PSA units includes:
- Prefabricated valve skid
- Adsorber vessels
- Specially selected adsorbent material
- Tail gas drum
- Process control system

The scope can be altered to best suit client’s needs. Based on the customer’s requirements, feed gas compressor or tail gas compressor systems can be offered through Linde as an integrated PSA solution.

Scope of supply.

![Pressure time diagram](image1)

![PSA valve skid](image2)
The Linde High Performance PSA units provide remarkable advantages such as:

**Linde’s 30 years of expertise in adsorption technology**
Based on specific customer requirements, Linde specialists select the optimal PSA system for distinct purification tasks in order to achieve a perfect balance between plant performance and investment costs.

**Quality and reliability**
PSA process requirements make an informed selection of specially proven plant components (e.g. switching valves and related instrumentation) necessary. Linde only uses suitable and thoroughly selected, tested and approved plant components. This guarantees highest reliability of Linde’s PSA systems.

**Outstanding availability**
Linde PSA systems are characterized by an outstanding availability of hydrogen supply. With its special features such as operation with reduced number of adsorbers, adsorber group isolation and redundant control system, Linde PSA systems achieve virtually 100% on-stream performance and availability.

**Excellent flexibility**
Linde PSA systems achieve excellent flexibility in coping with varying feed gas conditions and hydrogen demands to match individual client needs.

**Modular design and prefabricated equipment**
Linde High Performance PSA systems are prefabricated to the maximum extent. The valve skid containing switching and control valves, instrumentation and interconnecting piping is completely prefabricated, preassembled and tested prior to delivery. This design philosophy reduces time and costs for erection and commissioning on site to the absolute minimum.

**Easy maintenance**
Maintenance necessity is limited to routine actions, which can be carried out by the operators on site. Linde pays highest attention to proper accessibility of all valves and instruments inside the valve skid. Hence, maintenance assistance from Linde is normally not required, but is certainly available at any time.
Linde’s Engineering Division continuously develops extensive process engineering know-how in the planning, project management and construction of turnkey industrial plants.

The range of products comprises:
- Petrochemical plants
- LNG and natural gas processing plants
- Synthesis gas plants
- Hydrogen plants
- Gas processing plants
- Adsorption plants
- Air separation plants
- Cryogenic plants
- Biotechnology plants
- Furnaces for petrochemical plants and refineries

The Engineering Division and its subsidiaries manufacture:
- Packaged units, cold boxes
- Coil-wound heat exchangers
- Plate-fin heat exchangers
- Cryogenic standard tanks
- Air heated vaporizers
- Spiral-welded aluminium pipes

More than 4,000 plants worldwide document the leading position of the Engineering Division in international plant construction.