THE LINDE GROUP

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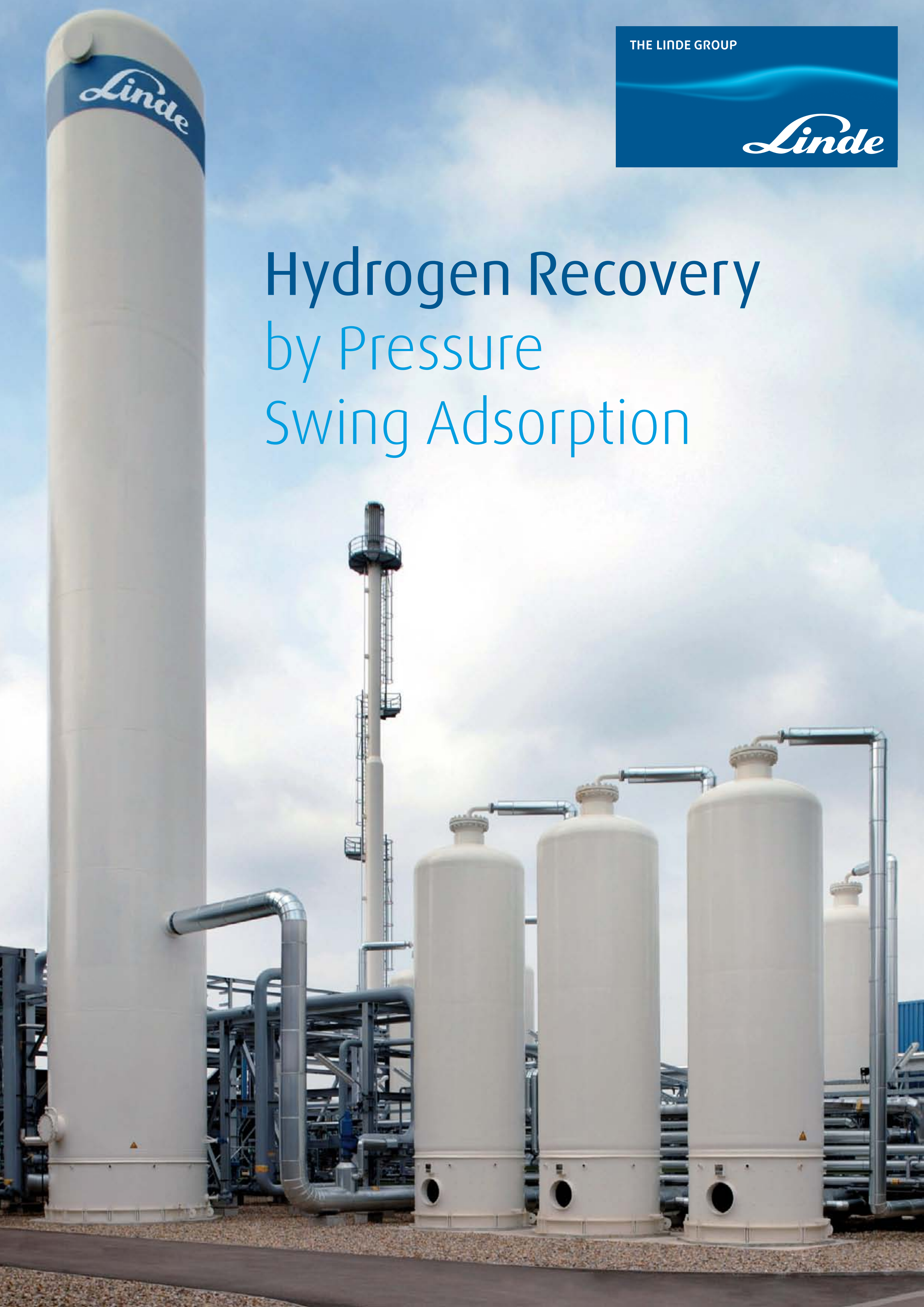
Hydrogen Recovery by Pressure Swing Adsorption



Contents.

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 PSA units are designed for the recovery and purification of pure hydrogen from different hydrogen-rich streams, such as synthesis gases from steam reforming process, partial oxidation or gasification, as well as from various off-gases in refineries or petrochemical processes, e.g. ethylene off-gas, coke oven gas, methanol and ammonia purge gas.

Capacities range from a few hundred Nm^3/h to large scale plants with more than 400,000 Nm^3/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 cracking, dearomatization or desulphurization processes.

As a second group of users in the petrochemical industry has a demand for hydrogen for its methanol and ammonia synthesis, MTBE processes, etc.

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 as N_2, CO, CO_2, 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.

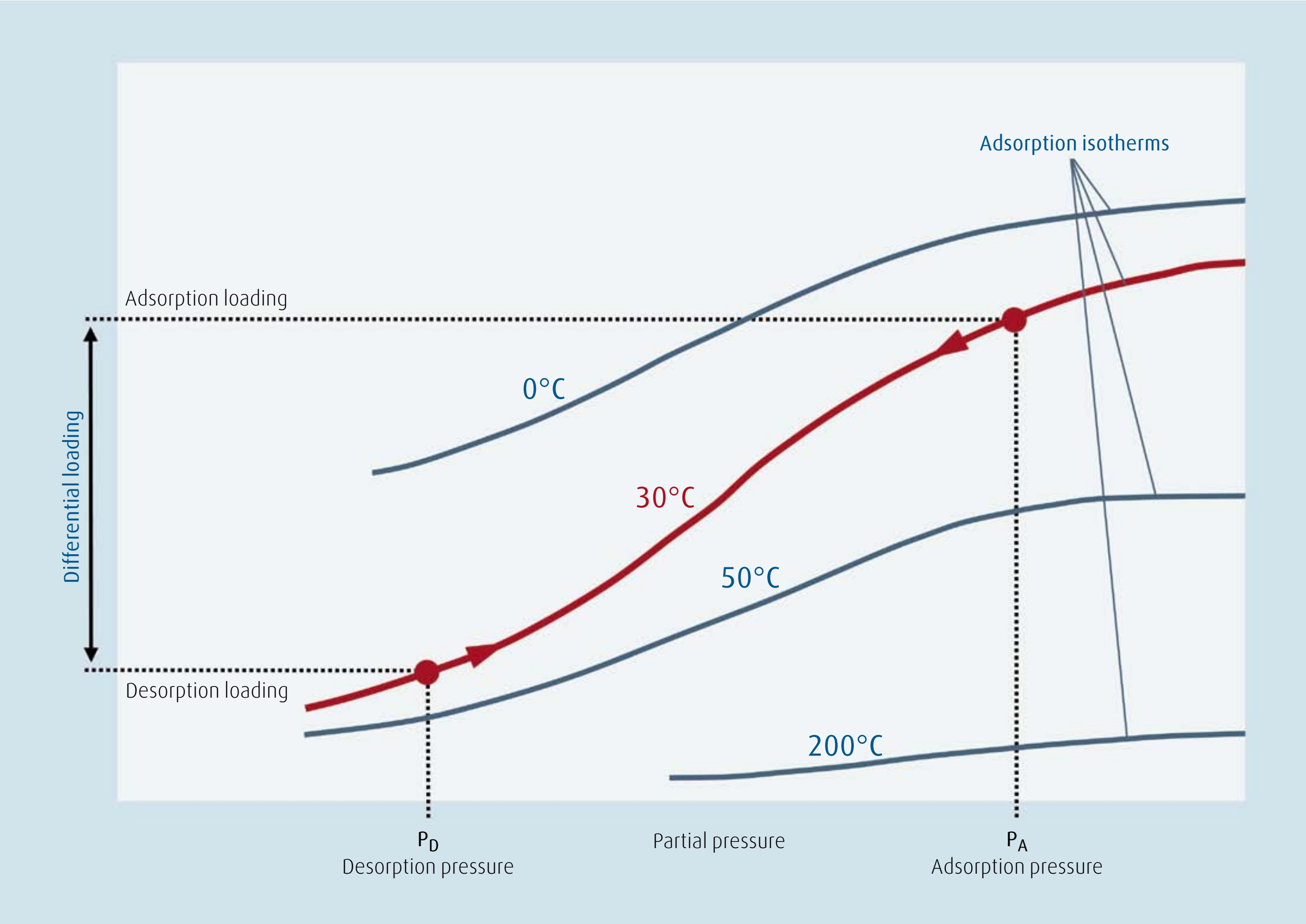
The figure on page 5 illustrates the pressure swing adsorption process. It shows the adsorption isotherms describing the relation between partial pressure of a component and its equilibrium loading on the adsorbent material for a given temperature.

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

Pressure swing adsorption plant in Leuna, Germany



Adsorption and regeneration by pressure swing

The PSA sequence.

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 and 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, CO_2, CO and nitrogen are selectively adsorbed on the surface of the adsorbent material. Highly pure hydrogen exits the adsorber vessel at 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.

Scope of work.

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.

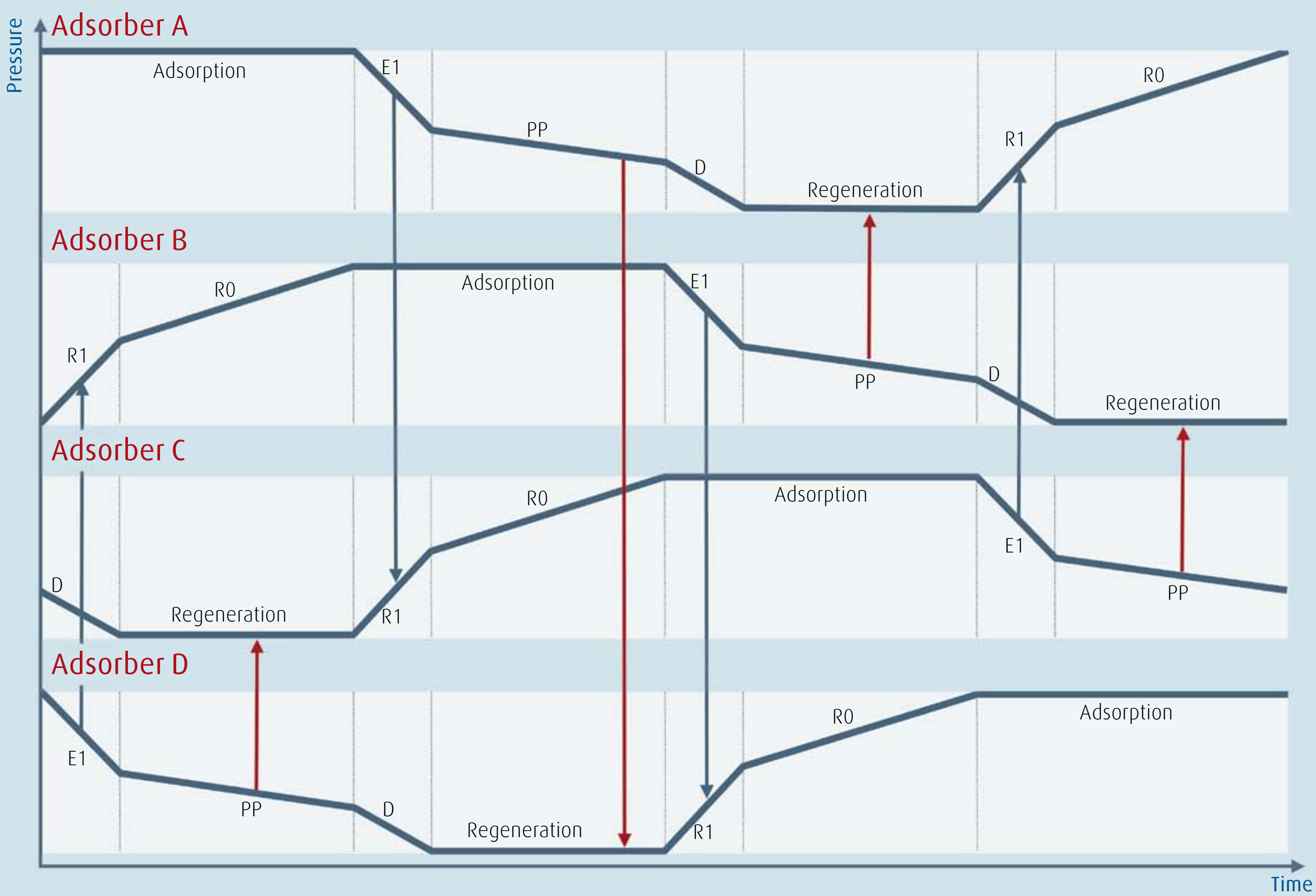
The typical scope of supply of Linde's PSA units includes:

- 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 a integrated PSA solution.

PSA valve skid

Pressure time diagram



Two pressure swing adsorption units in Canada

The advantages.

The Linde high performance PSA units provide remarkable advantages such as:

Linde's expertise in adsorption technology
Based on customer's requirements, the Linde PSA specialists will select the optimum PSA system for the specific purification task in terms of optimum ratio between plant performance and investment cost.

Quality
The high switching cycles of PSA units require special equipment distinguished by a high degree of durability. Linde only applies qualified components, which meet these demands perfectly and which are proven during many years of experience.

Reliability
The use of selected and suitable components implies the high reliability of Linde's PSA systems. Especially high performance switching valves are used in Linde's PSA process.

Availability
The 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's PSA units achieve virtually 100% on-stream performance and availability.

Flexibility
Excellent flexibility to match actual client's needs are achieved with Linde's PSA systems as they are capable of providing a high degree of flexibility to cope with feed gas conditions and varying hydrogen demand.

Modular design and prefabricated equipment
Linde's high performance PSA systems are prefabricated to a maximum extent. The valve skids containing switching and control valves, instrumentation and interconnecting piping are completely prefabricated, preassembled and tested prior to delivery. This design philosophy reduces time and costs for erection and commissioning on site to and absolute minimum.

Easy maintenance
Maintenance is limited to easy and quick routine actions which can be carried out by the operators on site. Highest attention is given to a proper accessibility of all valves and instruments inside the valve skid. Assistance from Linde is hence normally not required but is certainly available at any time convenient to client.

Collaborate. Innovate. Deliver.

Linde’s Engineering Division is a leading player in the international plant engineering business. Across the globe, we have delivered more than 4,000 plants and cover every step in the design, project management and construction of turnkey industrial facilities. Our proven process and technology know-how plays an indispensable role in the success of our customers across multiple industries – from crude oil, natural gas extraction and refining to chemical and metal processing.

At Linde, we value trusted, lasting business relationships with our customers. We listen carefully and collaborate closely with you to meet your needs. This connection inspires us to develop innovative process technologies and equipment at our high-tech R&D centres, labs and pilot plants – designed in close collaboration with our strategic partners and delivered with passion by our employees working in more than 100 countries worldwide.

From the desert to the Arctic, from small- to world-scale, from standardised to customised builds, our specialists develop plant solutions that operate reliably and cost-effectively under all conditions.
You can always rely on us to deliver the solutions and services that best fit your needs – anywhere in the world.

Discover how we can contribute to your success at www.linde-engineering.com

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Core competencies at a glance

Plant engineering
- Air separation plants
- LNG and natural gas processing plants
- Petrochemical plants
- Hydrogen and synthesis gas plants
- Adsorption plants
- Cryogenic plants
- Carbon capture and utilisation plants
- Furnaces, fired heaters, incinerators

Component manufacturing
- Coldboxes and modules
- Coil-wound heat exchangers
- Plate-fin heat exchangers
- Cryogenic columns
- Cryogenic storage tanks
- Liquefied helium tanks and containers
- Air-heated vaporisers
- Water bath vaporisers
- Spiral-welded aluminium pipes

Services
- Revamps and plant modifications
- Plant relocations
- Spare parts
- Operational support, troubleshooting and immediate repairs
- Long-term service contracts
- Expert reviews for plants, operations and spare part inventory
- Operator training

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