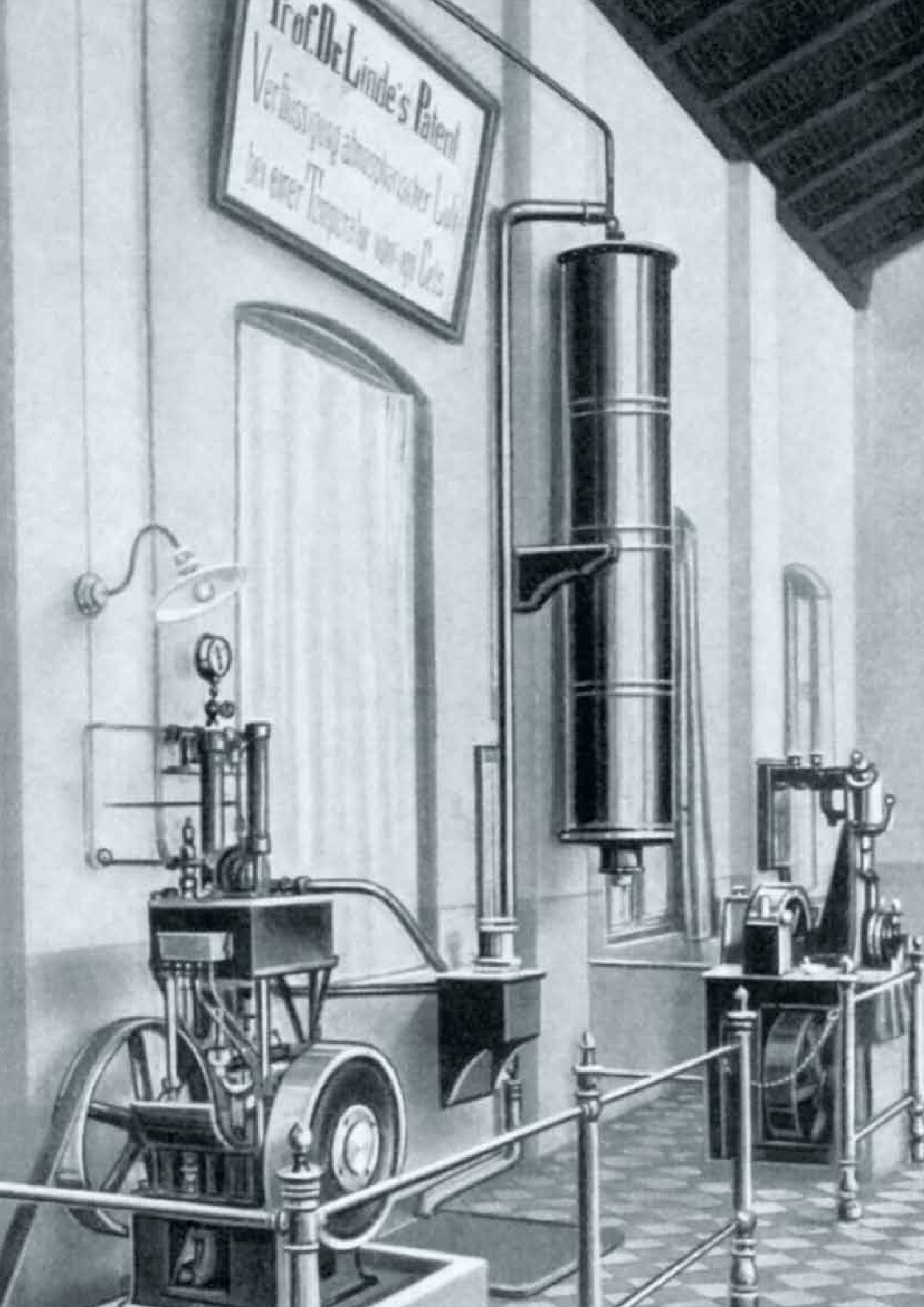
THE LINDE GROUP

Air separation plants.

History and technological progress in the course of time.

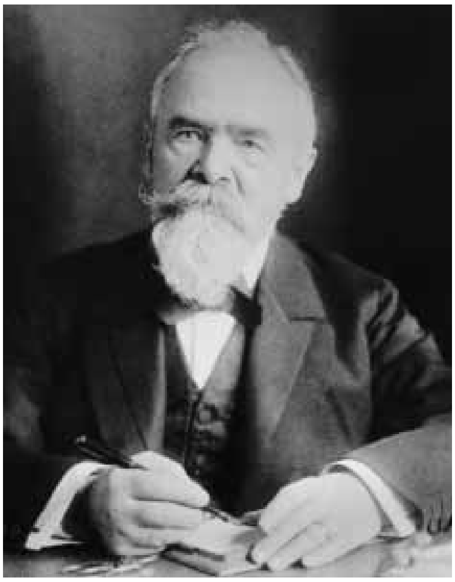

Prof. Dr. Linde's Patent
Verflüssigung atmosphärischer Luft
bei einer Temperatur von Cels.

When and how did air separation start?

In May 1895, Carl von Linde performed an experiment in his laboratory in Munich that led to his invention of the first continuous process for the liquefaction of air based on the Joule-Thomson refrigeration effect and the principle of countercurrent heat exchange. This marked the breakthrough for cryogenic air separation.

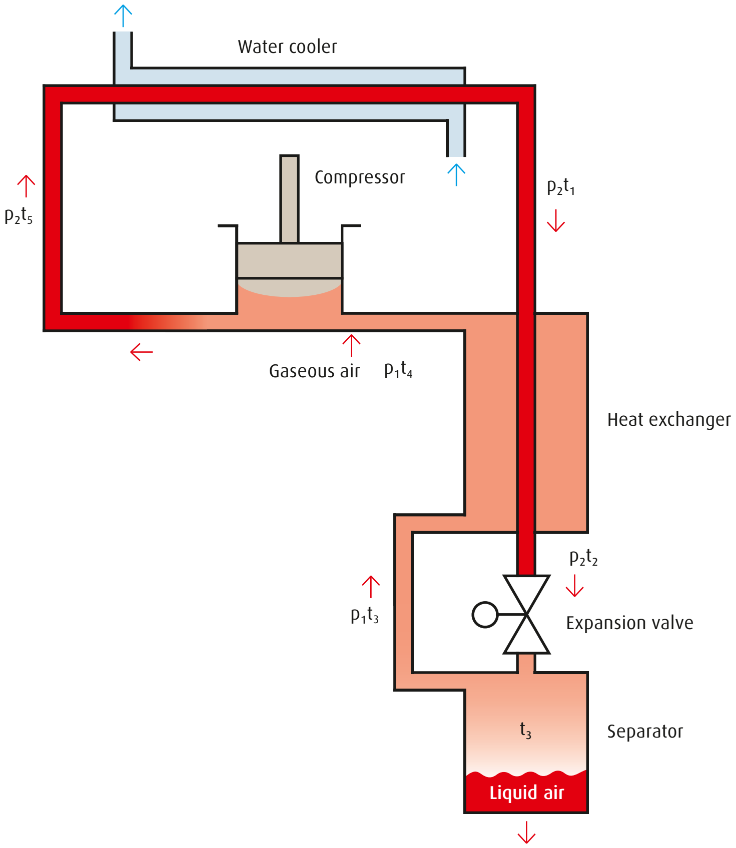
For his experiment, air was compressed from 20 bar $[p_1]$ $[t_4]$ to 60 bar $[p_2]$ $[t_5]$ in the compressor and cooled in the water cooler to ambient temperature $[t_1]$. The pre-cooled air was fed into the countercurrent heat exchanger, further cooled down $[t_2]$ and expanded in the expansion valve (Joule-Thomson valve) $[p_1]$ to liquefaction temperature $[t_3]$. The gaseous content of the air was then warmed up again $[t_4]$ in the heat exchanger and fed into the suction side of the compressor $[p_1]$. The hourly yield from this experiment was approx. three litres of liquid air.

Linde based his experiment on findings discovered by J. P. Joule and W. Thomson (1852). They found that compressed air expanded in a valve cooled down by approx. 0.25°C with each bar of pressure drop. This proved that real gases do not follow the Boyle-Mariotte principle, according to which no temperature decrease is to be expected from expansion. An explanation for this effect was given by J. K. van der Waals (1873), who discovered that the molecules in compressed gases are no longer freely movable and the interaction among them leads to a temperature decrease after decompression.



Carl von Linde in 1925.

Liquefaction process of air separation

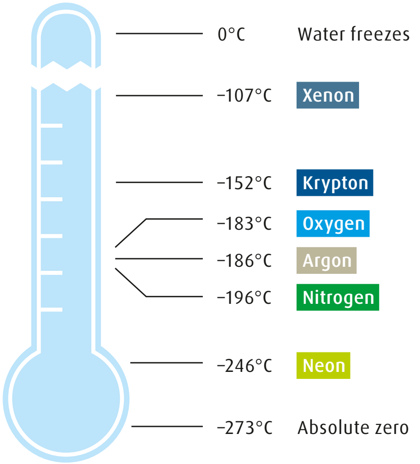


Composition of air

Nitrogen	78.08%
Oxygen	20.95%
Argon	0.93%
Neon	0.0018%
Helium	0.0005%
Krypton	0.00011%
Xenon	0.000009%

What are the physical properties of air required for liquefaction?

Boiling points



To enable air to be separated into its constituents by means of rectification – the actual separation process – a large part of the air volume used must be liquefied. A gas can only be transformed into a liquid state at temperature and pressure conditions below those of its critical point.

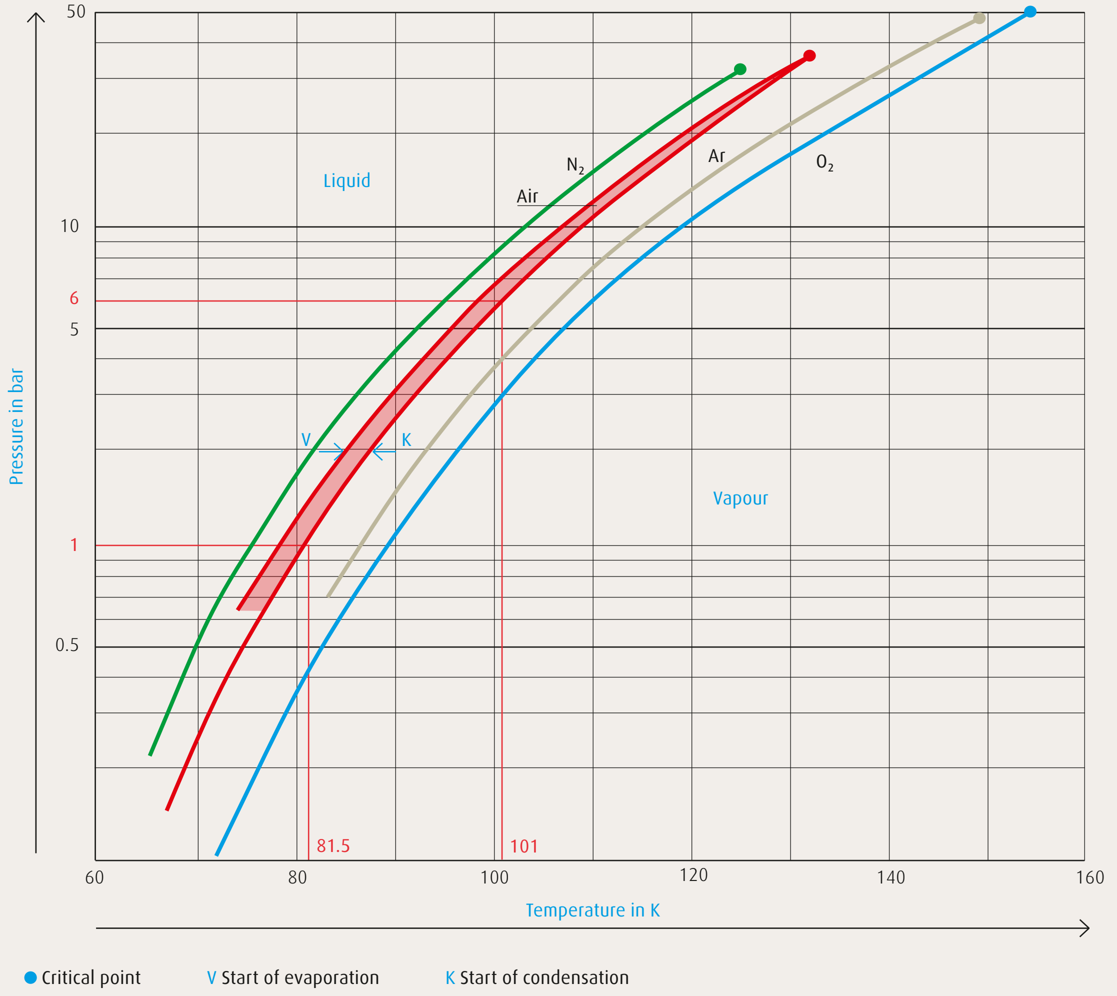
The critical point of air is T_{crit} = –140.7°C (132.5 K) and P_{crit} = 37.7 bar. In other words, air can be liquefied only at temperatures below –140.7°C (132.5 K).

The vapour pressure curve illustrates the temperatures and pressures at which a gas condenses or a liquid evaporates.

- → Air below atmospheric pressure (1 bar) must be chilled to –192°C (81.5 K) before it starts to condense
- → Air below a pressure of 6 bar must be chilled to –172°C (101 K) before it starts to condense

The boiling point and condensation conditions of gas mixtures such as air are not identical. A condensation line and a boiling point line delineate the boiling point range.

Vapour pressure curves of atmospheric gases



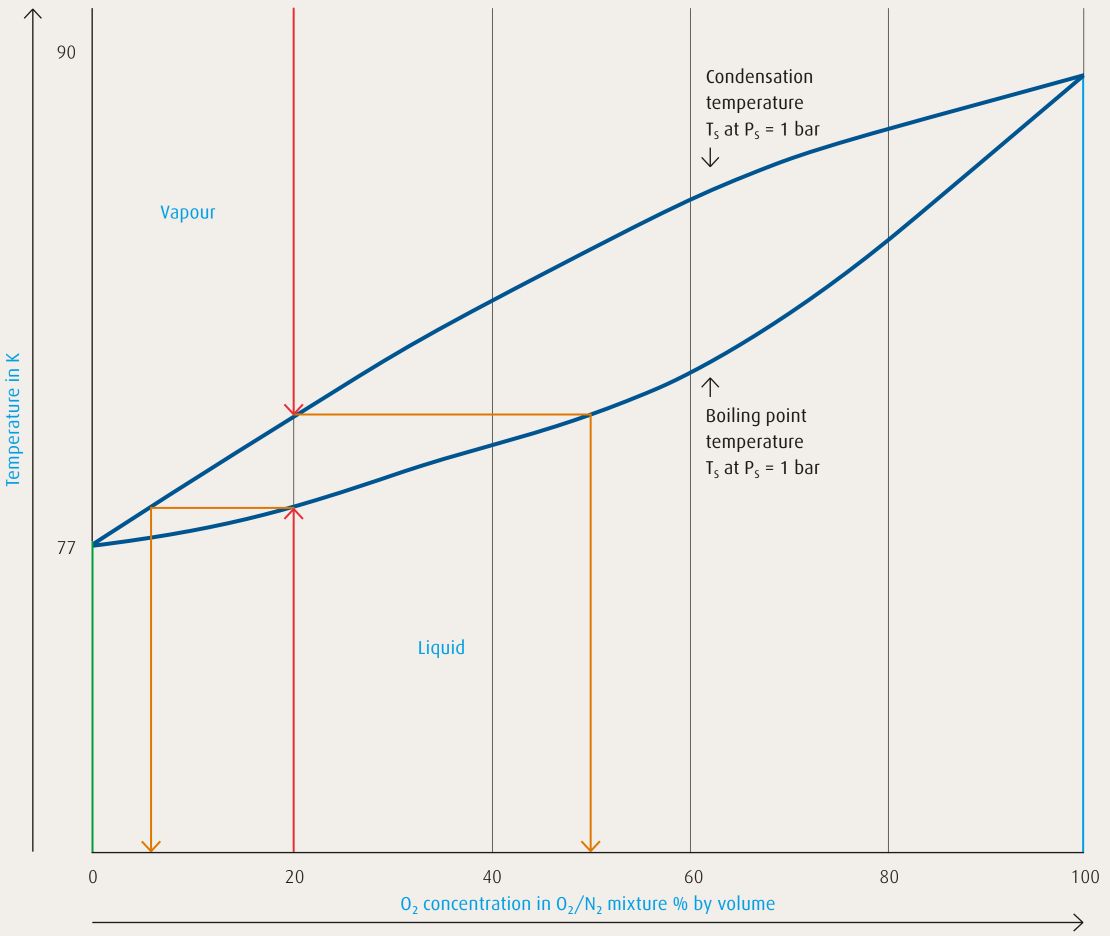
What is rectification of air?

Rectification is synonymous with countercurrent distillation. This special distillation separation process enables the individual components of a mixture to be separated with a high purity combined with a good yield, even when their boiling points are relatively close to each other.

As a result of the different vapour pressures of the individual components ($pN_2 > pO_2$), the composition of the vapour differs from that of the liquid mixture.

The vapour produced from a boiling liquid mixture of O_2/N_2 will thus have a higher N_2 concentration than the liquid mixture from which it originates.

Boiling point diagram of O_2/N_2 mixtures



What are the principles of air separation?

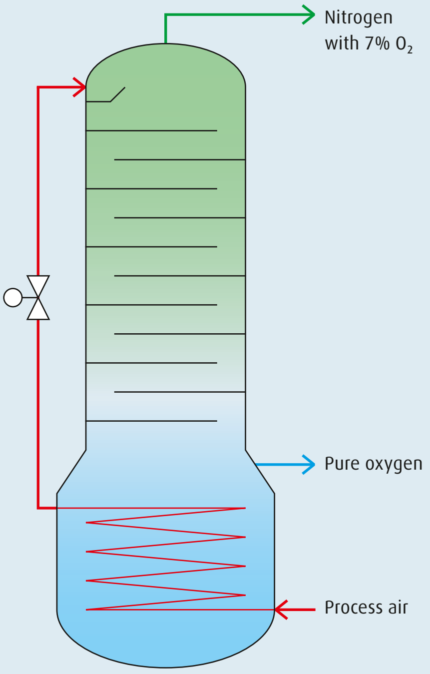
Air separation by rectification in a single/double column

Using his air liquefaction principle as a basis, Carl von Linde constructed the first air separation plant for oxygen production in 1902 using a single-column rectification system.

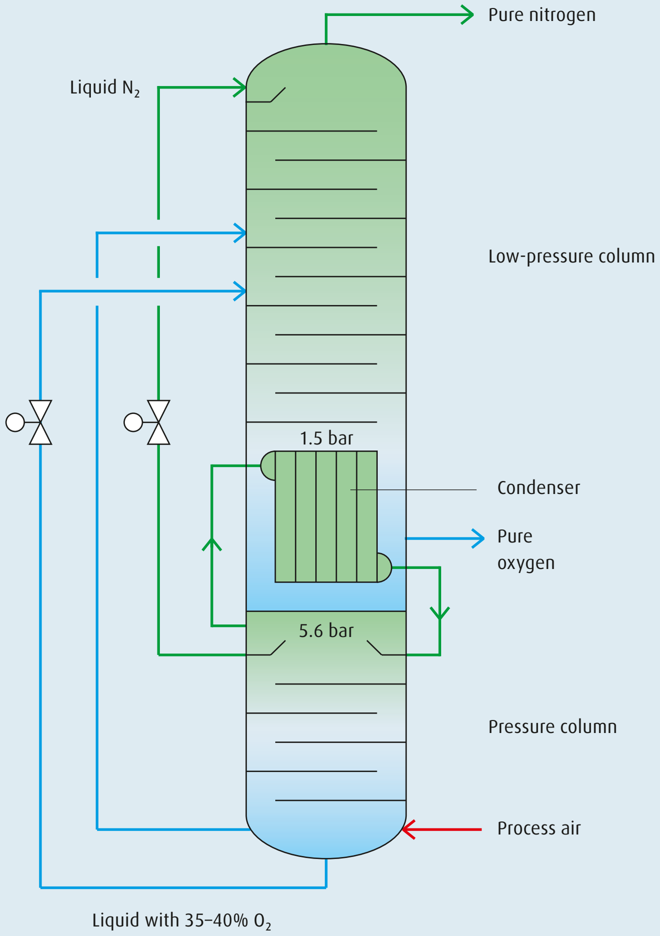
In 1910, he established the basis for cryogenic air separation with the development of a double-column rectification system. Now it was possible to produce pure oxygen and pure nitrogen simultaneously.

This involves installing a pressure column below the low-pressure column. At the top of this pressure column, pure nitrogen was drawn off, liquefied in a condenser and fed to the top low-pressure column as reflux. At the top of the low-pressure column, pure gaseous nitrogen was withdrawn, while liquid oxygen evaporated at the bottom of this column to deliver pure gaseous oxygen. This principle of double-column rectification combining the condenser and evaporator to form a heat exchanger unit is still used today.

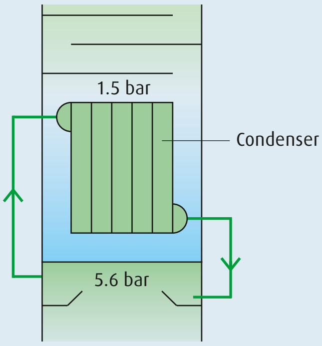
Single column



Double column



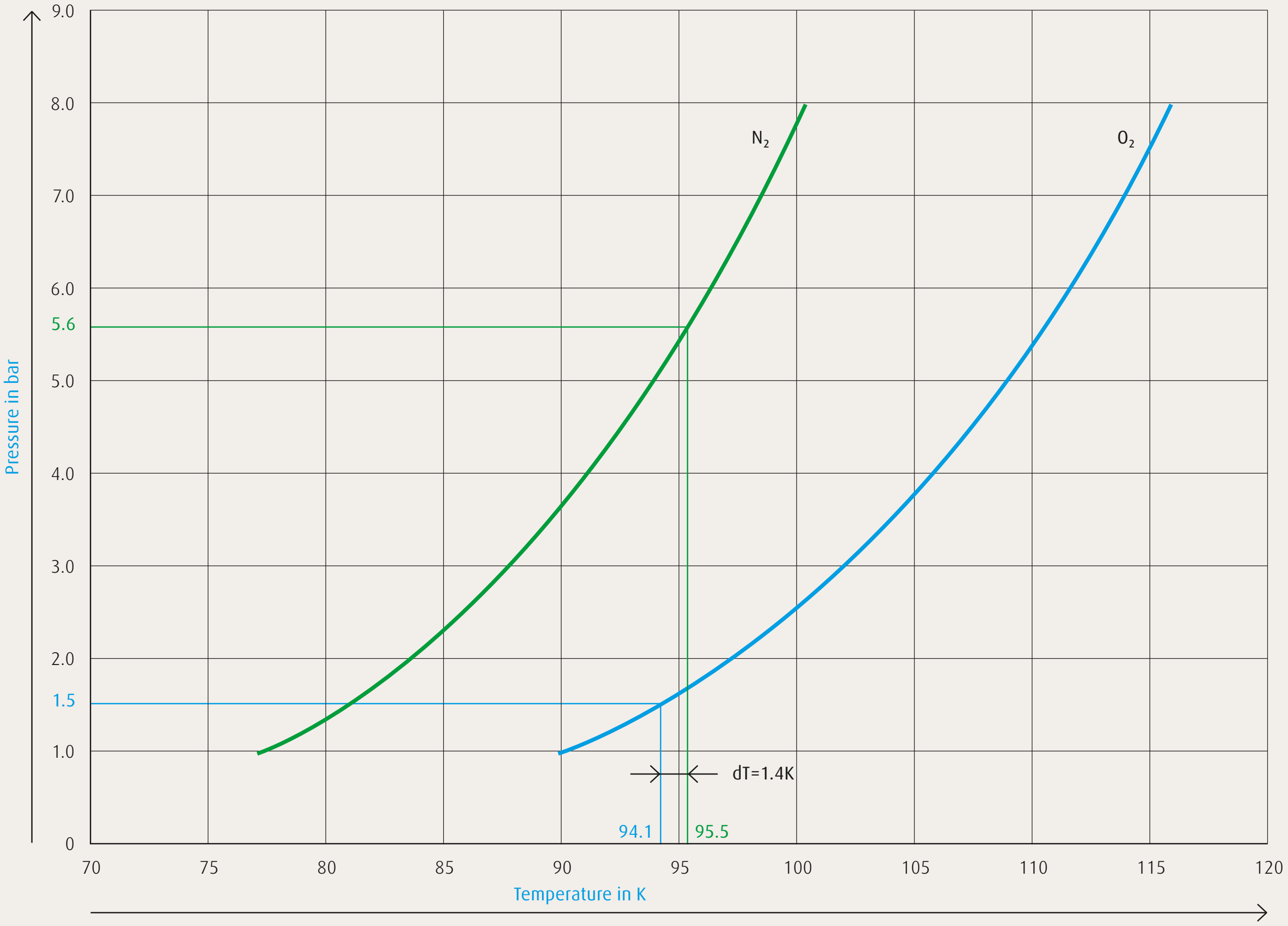
Condenser



Condenser/reboiler

The principle of double-column rectification is characterised by the combination of condenser and evaporator to form a common heat exchanger unit. This divides the rectification into two separate areas with different pressures.

Vapour pressure of N_2 and O_2



Fabrication of sieve tray column.

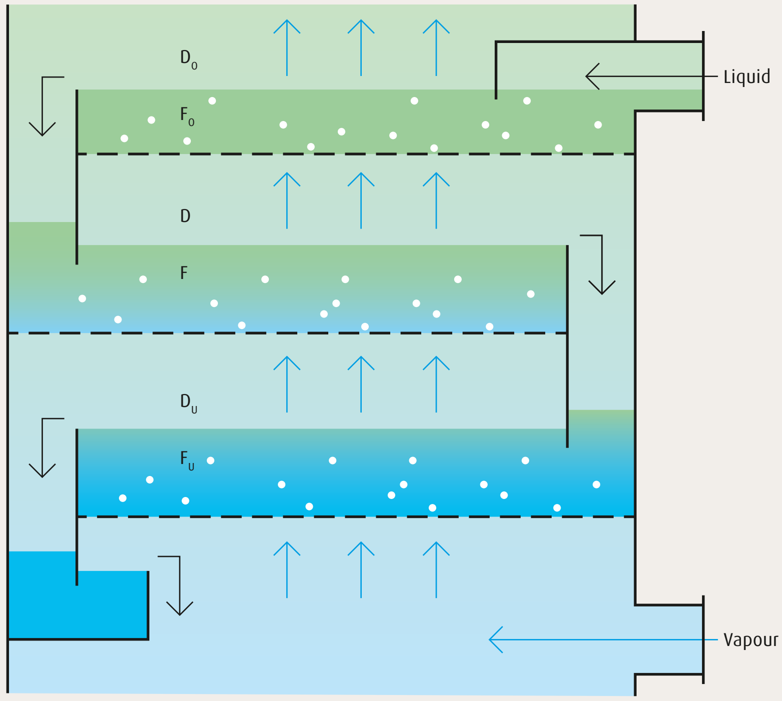
What happens inside a column?

Any tray of the rectification column follows the same principle:
The O_2 concentration of the boiling O_2/N_2 liquid mixture F is greater than the O_2 concentration of the vapour D. A certain volume of liquid corresponding to the same volume of reflux constantly flows from the tray above into the liquid mixture below with an equivalent volume flowing down over a weir onto the tray below.

The vapour D_u coming from the bottom tray penetrates the liquid mixture F and has a higher O_2 content than the vapour mixture D.

The O_2 concentration of the vapour D_o rising from the upper tray is in turn less than that of the vapour D. Thus a gas rich in nitrogen is obtained in the head of the column and a liquid rich in oxygen is obtained in the sump of the column.

Principle of sieve trays



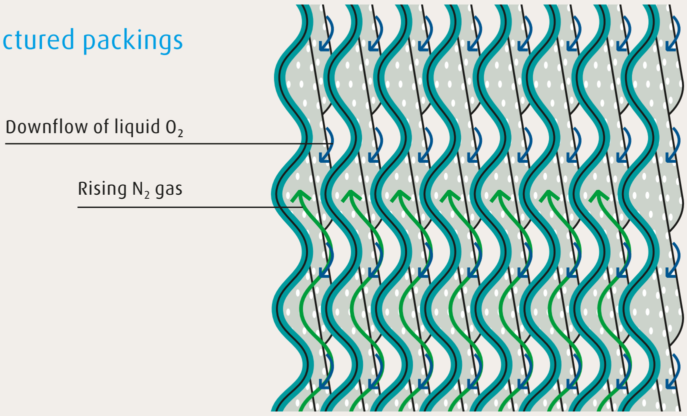
Structured packings

1991

World's largest air separation plant with packed columns

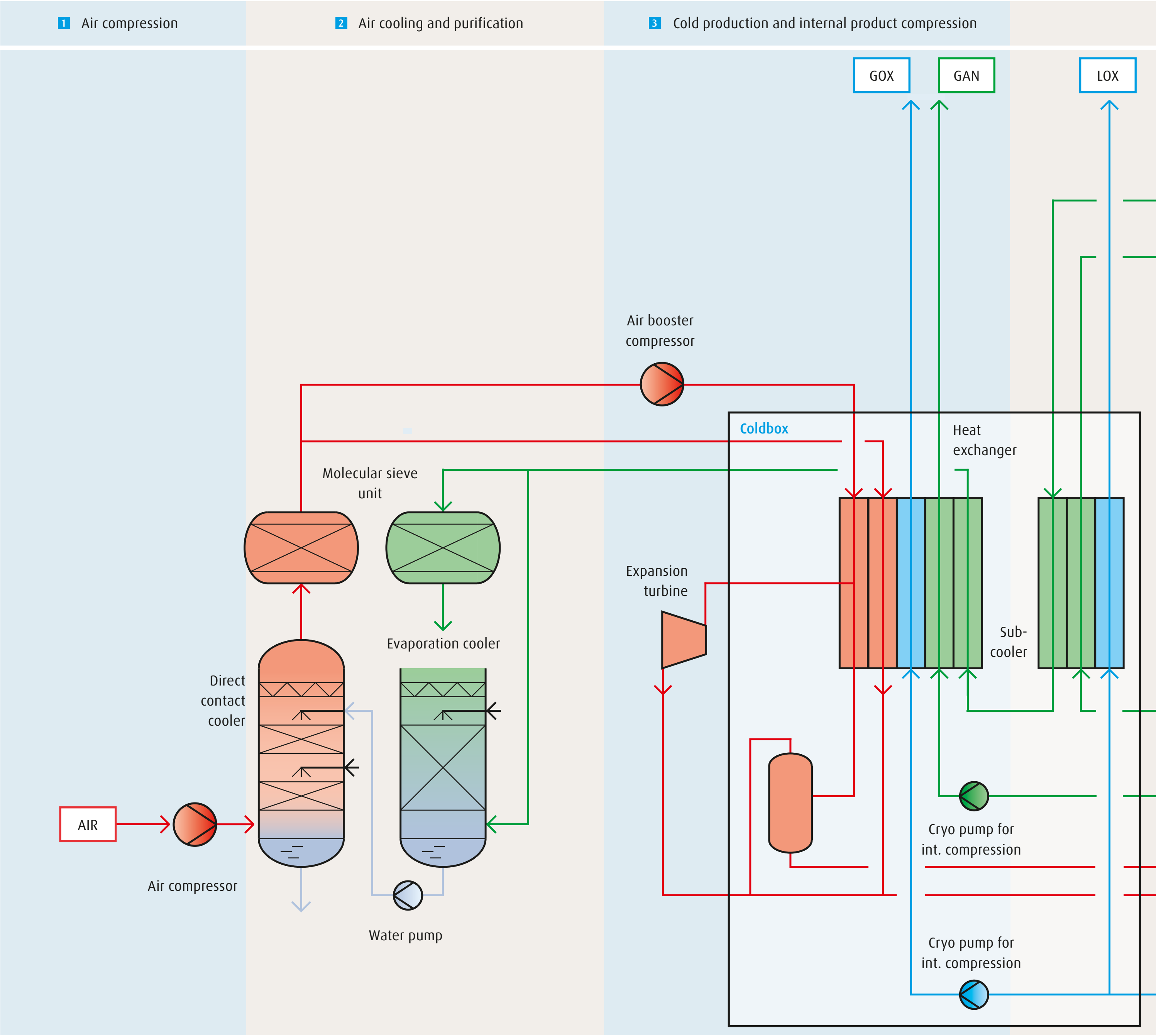
Significant progress in air separation technology was made in the mid-1980s. For the first time, structured packings were used in cryogenic rectification. Packed columns work in a similar way to sieve trays. The intensive contact between liquid and vapour required for the rectification takes place on the huge surface area of the packing material. Liquid flowing down becomes increasingly richer in oxygen, whereby the ascending vapour is enriched with nitrogen. The main benefits of packed columns compared with sieve trays are a lower pressure drop and consequently a lower power consumption for the air separation process. Another important advantage of packed columns is the possible loading range including a very high turn down to nearly 30%. This also forms the basis for a new process for argon separation.

Principle of structured packings



Packed column.

What does a typical cryogenic air separation process look like?



1 Air compression

- → Compression of ambient air by a multi-stage turbo compressor with intercoolers at a supply pressure of approx. 6 bar.
- → Removal of dust particles by a mechanical air filter at the inlet of the compressor.

2 Air cooling and purification

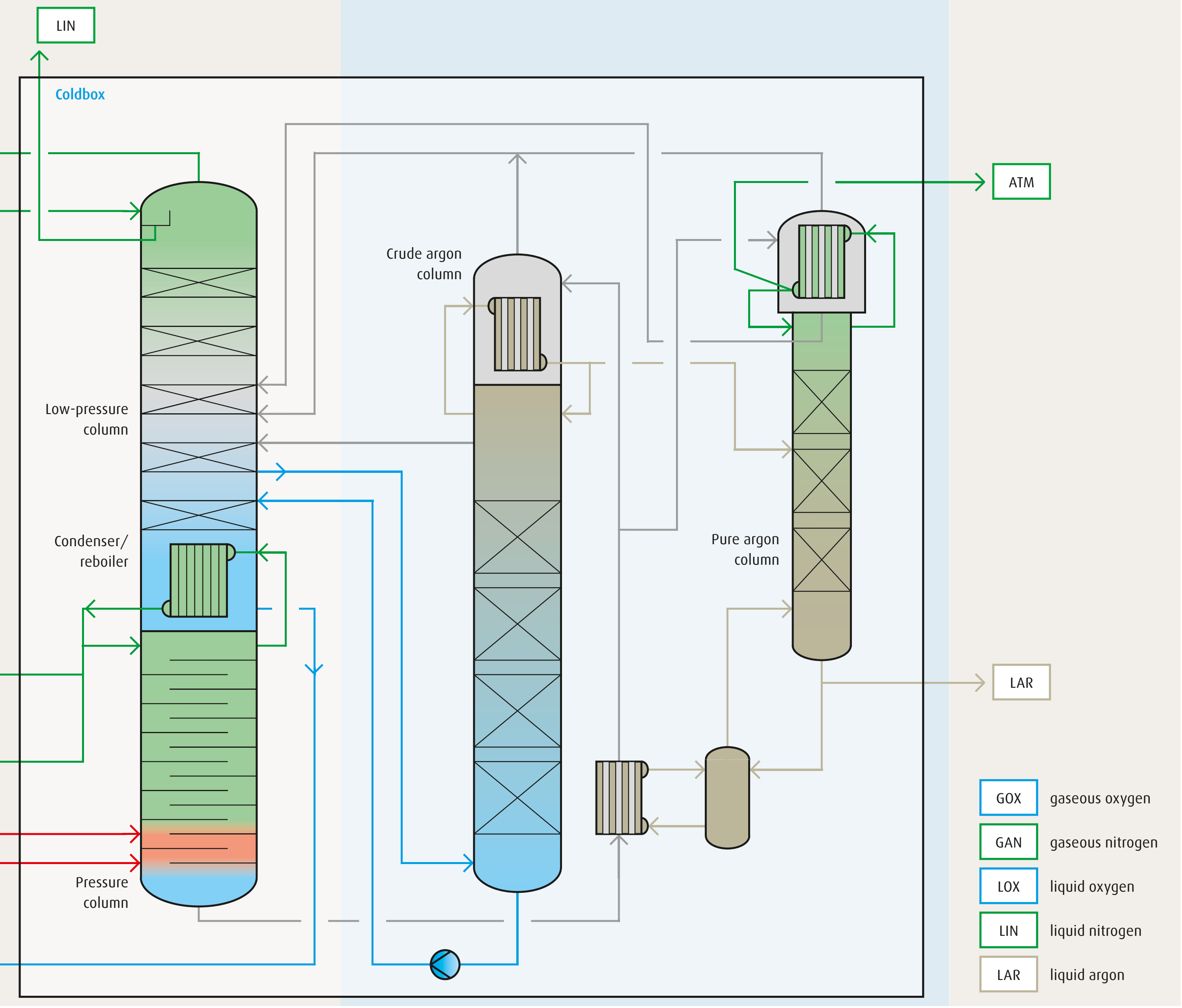
- → Cooling of process air with water in a direct contact cooler and removal of water soluble air impurities.
- → Chilling of cooling water in an evaporation cooler against dry nitrogen waste gas from the rectification process.
- → Removal of CO_2, water and hydrocarbons from the process air in periodically loaded/regenerated molecular sieve adsorbers.

3 Cold production and internal product compression

- → Cooling of process air in heat exchangers down to nearly liquefaction temperature by means of countercurrent with gas streams from the rectification process.
- → Further compression of a sidestream of process air by an air booster compressor. Expansion and cold production of the boosted air stream in an expansion turbine.
- → Expansion and liquefaction of a sidestream of the boosted air in a liquid separator.
- → Evaporation and warming to ambient temperature of the pumped oxygen and nitrogen product in high-pressure heat exchangers.

4 Cryogenic rectification of air

5 Cryogenic rectification of argon



4 Cryogenic rectification of air

- Pre-separation of the cooled and liquefied air within the pressure column into oxygen-enriched liquid in the column sump and pure nitrogen gas at the column top.
- Liquefaction of the pure nitrogen gas in the condenser/reboiler against boiling oxygen in the sump of the low-pressure column. Liquefied nitrogen provides the reflux for the pressure column and (after sub-cooling) for the low-pressure column.
- Different types of condenser are described in detail on page 16.
- Further separation of the oxygen-enriched liquid within the low-pressure column into pure oxygen in the sump and nitrogen waste gas at the top.

5 Cryogenic rectification of argon

- Argon-enriched gas from the low-pressure column is transformed into oxygen-free crude argon by means of separation within the crude argon column.
- Pumping back liquid oxygen from the crude argon column sump into the low-pressure column. Removal of the remaining nitrogen in the pure argon column.

Milestones in air separation.

1902 – World’s first air separation unit (ASU) for oxygen production

1904 – World’s first air separation plant for the recovery of nitrogen

1910 – World’s first air separation plant using the double-column rectification process

1930 – Development of the Linde-Fränkl process for air separation

1950 – First Linde-Fränkl oxygen plant without pressure recycling and stone-filled reactors

1954 – World’s first air separation plant with air purification by means of adsorbers

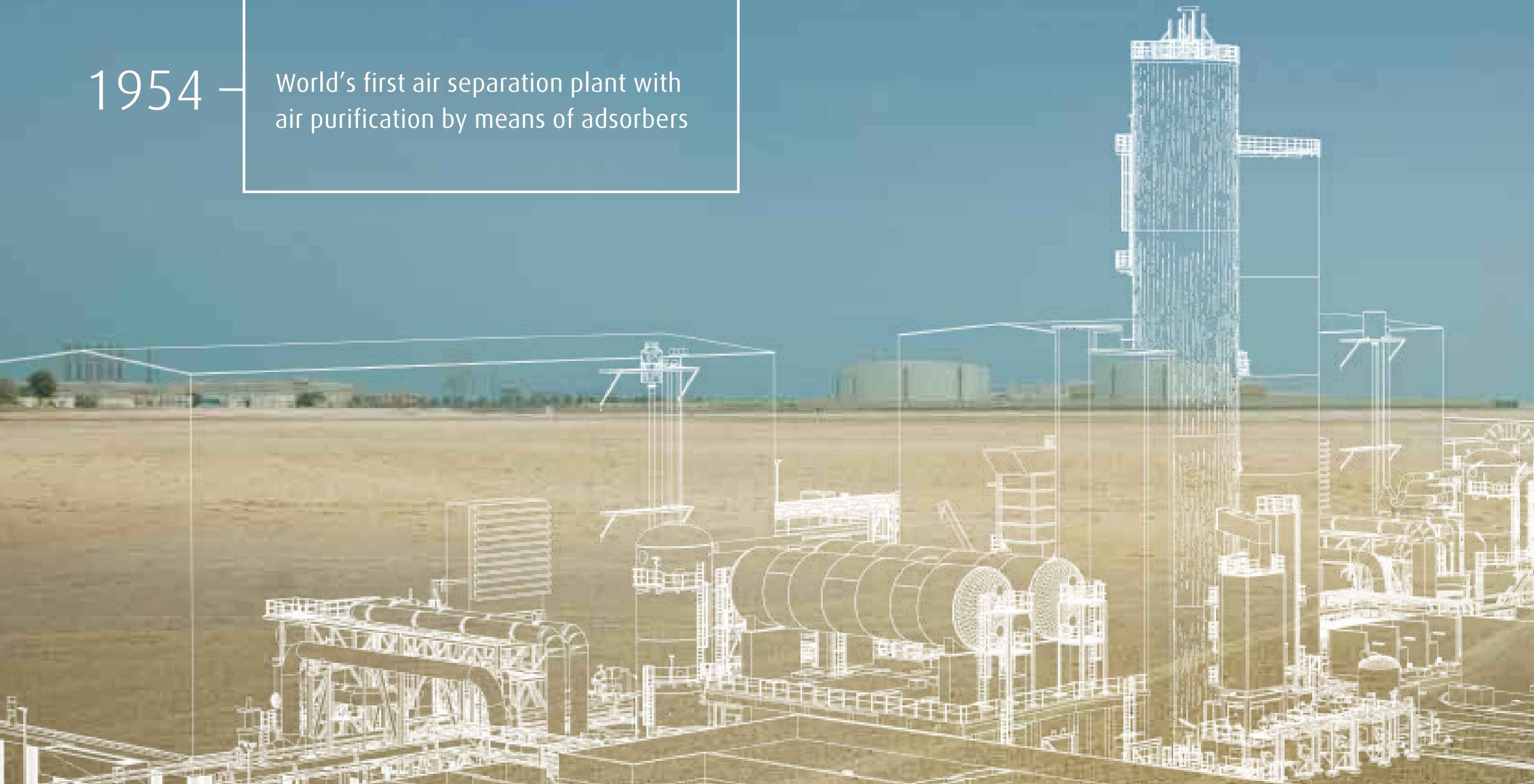
1968 – Introduction of the molecular sieve technology for pre-purification of air

1978 – **Internal compression of oxygen applied to tonnage air separation plants, p. 14**

1981 – Introduction of the elevated pressure process

1984 – World’s largest VAROX air separation plant with variable oxygen flow adjustment

1988 – First columns with structured packings

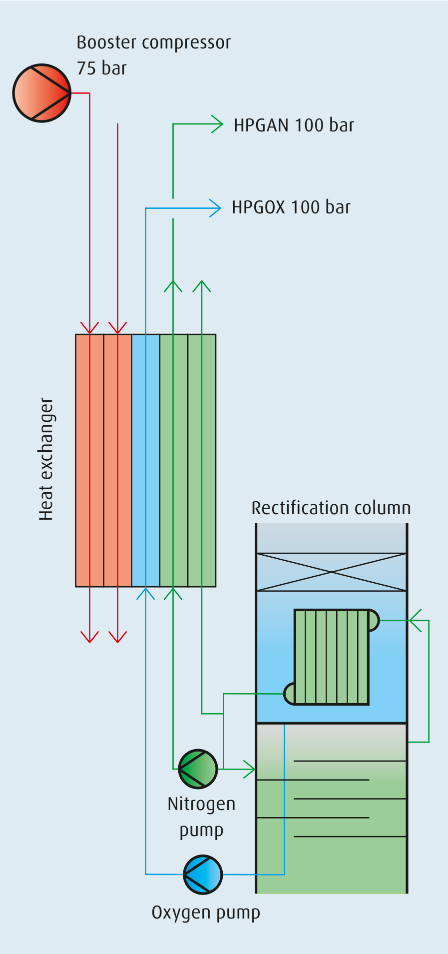


1990	**Linde introduced argon production by rectification, p. 15** World's first remotely controlled air separation plant with unmanned operation
1991	World's largest air separation plant with packed columns
1992	Ultra-pure gases production in air separation plants
1993	First world-scale radial adsorbers in large air separation plants
1997	**Largest air separation plant built for N_2 with capacity of 5 x 10,000 tpd, fifth train added in 2004, p. 18–19**
2000	**Development of the advanced multi-stage bath-type condenser, p. 16**
2006	**Largest EPC contract in history of air separation with 8 x 3,800 tpd O_2, p. 20–21**
2008	**Reflux condenser in crude argon column, p. 16**
2010	Advanced cryogenic process, efficiency optimised for CCS application (oxyfuel, IGCC)
2011	**Argon production without pure argon system, p. 15**
2012	**Flexible high air pressure process, p. 14**
2015	Simple filling of dual-bed radial adsorber
2016	Optimised fins for high-pressure PFHEs in ASUs **Trouble-free start-up of largest ASU complex in the world 6 x 3,600 tpd of oxygen , p. 22–23**
2017	**Start-up of world's largest air separation plant 5 x 5,250 tpd of oxygen, p. 24–25**

1978

Internal compression of oxygen

Internal compression



The internal compression (or liquid pumping) process allows for oxygen, nitrogen as well as argon to be compressed within the coldbox by means of liquid pumps, to be evaporated and warmed up in heat exchangers, and finally to be supplied to the end user at the required pressure.

In order to evaporate and warm up the compressed liquid, a countercurrent stream of air with a higher pressure than the liquid is required for thermodynamic reasons.

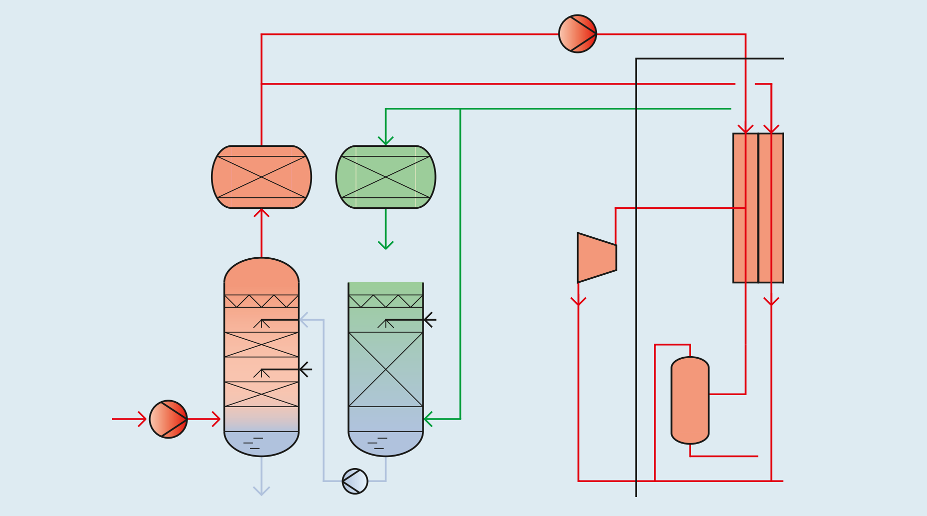
For plants that produce pressurised nitrogen, the booster and/or recycle nitrogen compressor also provide the countercurrent stream for evaporation. With this method, complex external oxygen compression is no longer required, thus plant operation and maintenance have become considerably easier and more reliable. Furthermore, the risk of dangerous hydrocarbon enrichment in the condenser is avoided because liquid oxygen is continuously withdrawn from the condenser and pumped into the heat exchanger, where it evaporates. Compared with the external compression system, a considerably higher level of safety has been achieved.

2012

Flexible high air pressure process used in ASUs

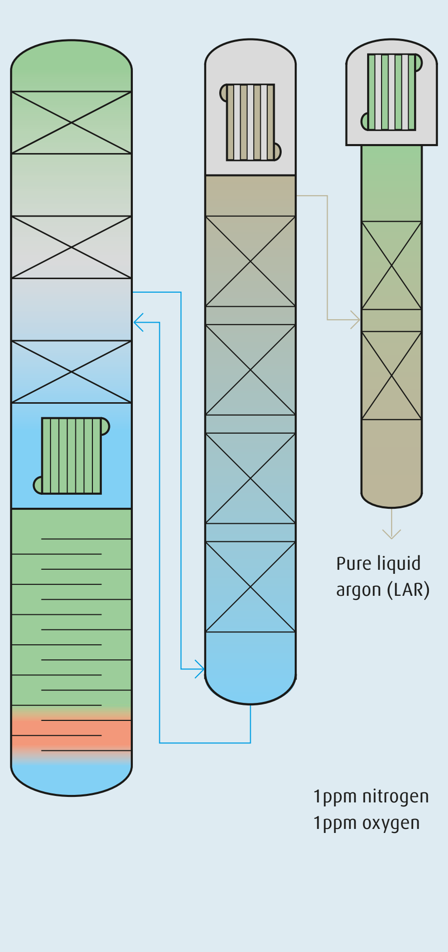
High air pressure process

The ambient air is compressed by a state-of-the-art multi-stage turbo compressor with intercoolers at a supply pressure of approx. 20 bar. A booster air compressor is no longer required with this process design, leading to a reduction of investment cost. A further advantage is the improved energy efficiency of the main air compressor for small plants.



Pure argon production by rectification

Conventional process
The area in the low-pressure column where the argon concentration is at a maximum (approx. 10%) is known as the argon belly. From there, the gas stream is fed into the raw argon column for further rectification. The remaining oxygen in this gas stream is completely removed in the packed raw argon column. Due to the very low pressure drop in the packings, it is possible to install a sufficient number of "theoretical trays" required for the rectification. In the adjoining pure argon column, the remaining nitrogen is removed by rectification and the pure argon is liquefied.

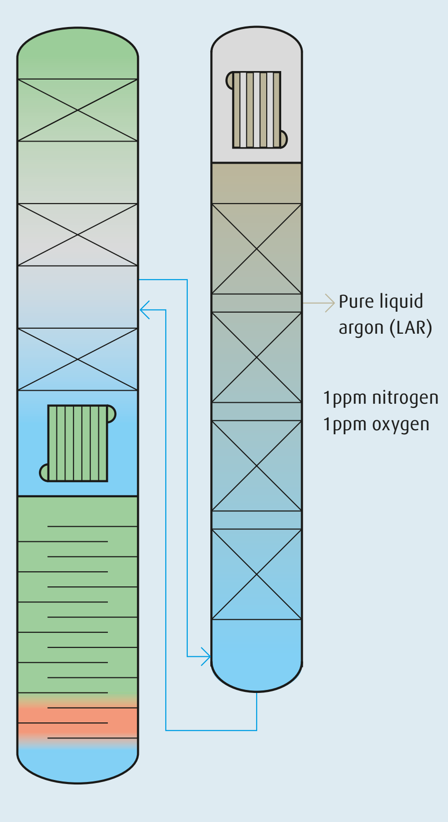


1990

Pure argon production by rectification

Cost-optimised process for small- and medium-sized air separation plants
As in the conventional process, a gas stream from the low-pressure column is fed into the raw argon system. Due to optimised packing types, the gas stream is already free of nitrogen. Therefore, only the remaining oxygen needs to be removed in the argon system.

The argon purity and recovery can be kept at the same level as in the conventional process. The additional pure argon column is no longer required.



2011

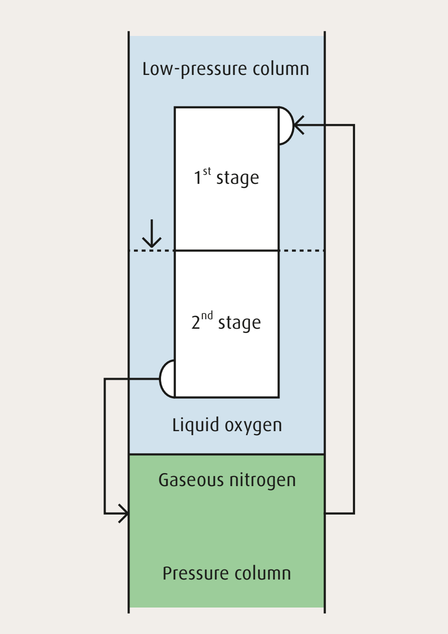
Pure argon production by rectification without pure argon system

Condenser

2000
Development of cascade condenser

Cascade condenser

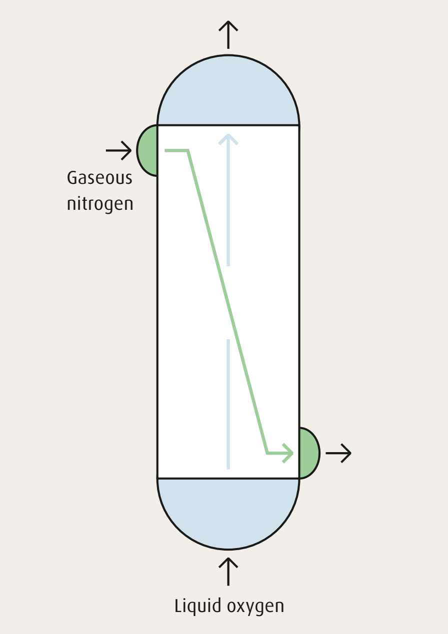
- → Multi-stage bath-type condenser
- → Suitable for medium-sized and large ASUs
- → Suitable for ASUs with internal oxygen compression
- → Integration of large heat transfer area into low-pressure column compared to conventional bath-type condenser
- → No oxygen pipework
- → Energy-saving solution
- → Safe operation



2006
Forced flow condenser

Forced flow condenser

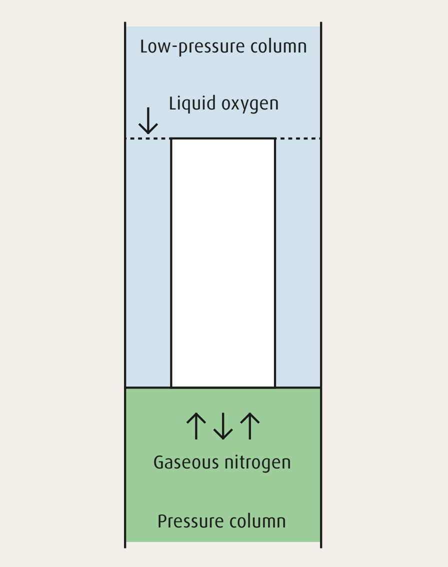
- → No condenser vessel required
- → Less space necessary
- → Specially designed for total evaporation
- → Energy-saving solution



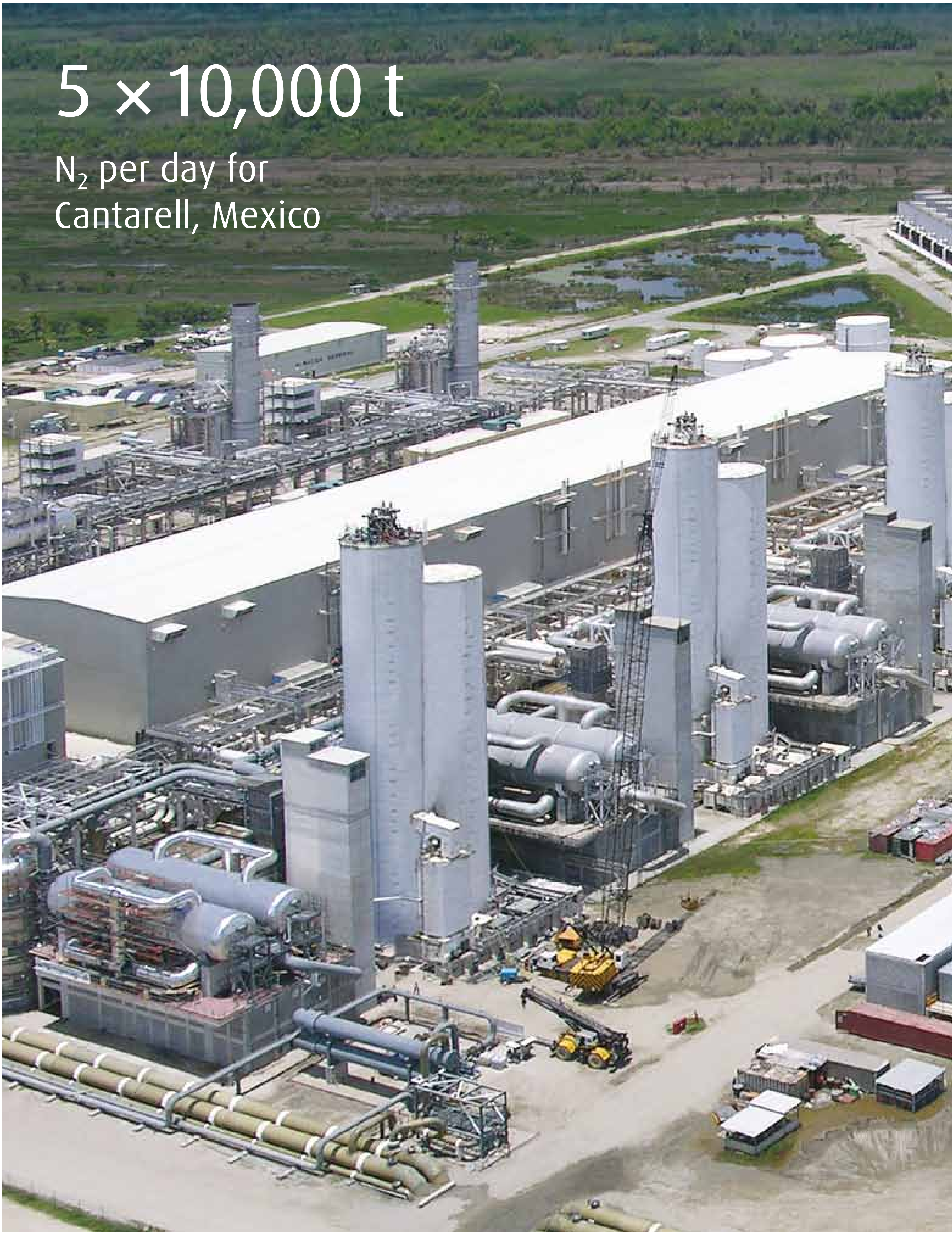
2008
Reflux condenser for argon rectification

Reflux condenser

- → Used instead of conventional bath-type condenser
- → No oxygen and no nitrogen pipework necessary
- → Space-saving design compared to bath-type condenser
- → Very simple and stable mode of operation
- → Cost-efficient design



Condenser fabrication.



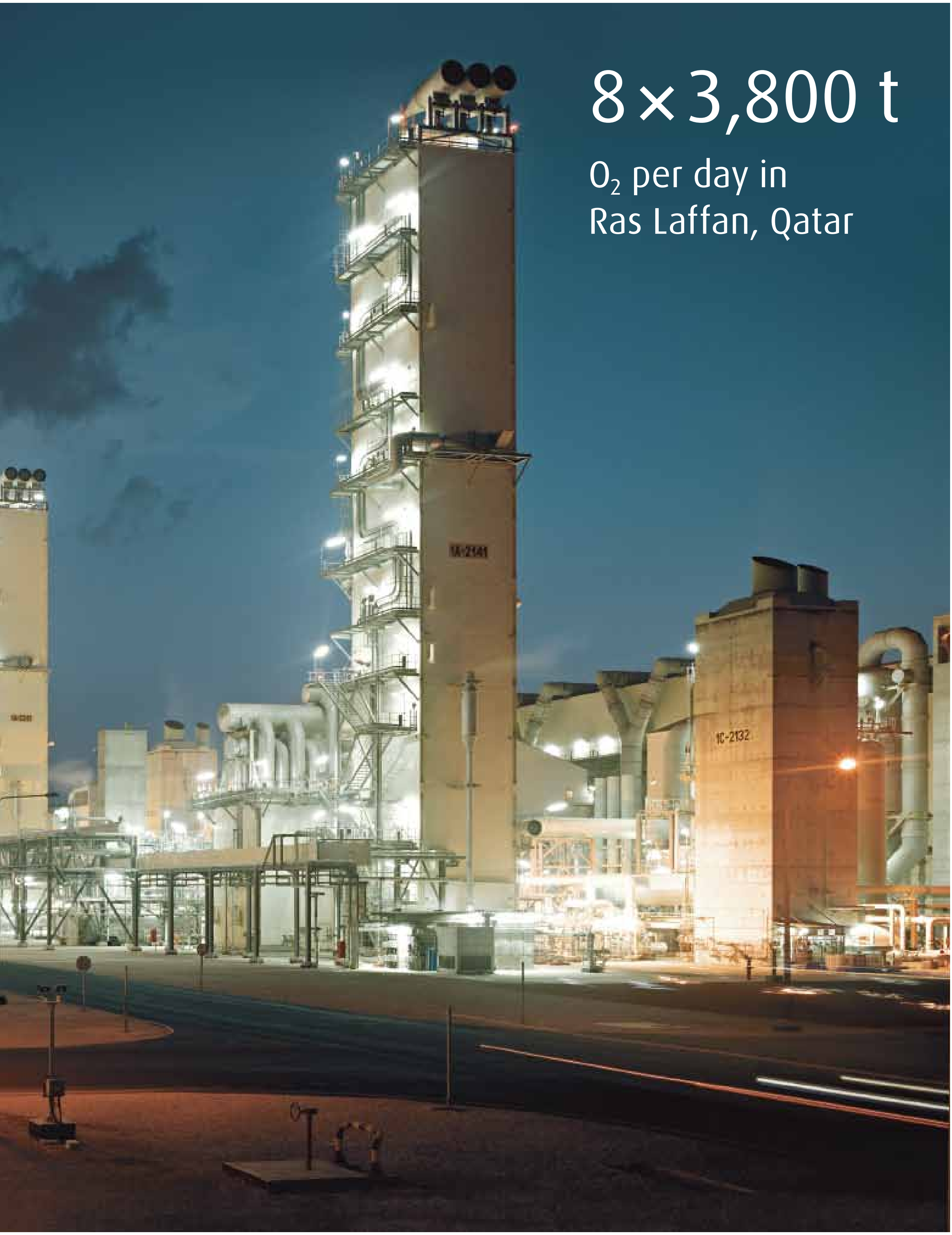
Air separation units in Cantarell, Mexico.

1997

Largest ASU for nitrogen production

2006

Largest EPC contract in the history of air separation



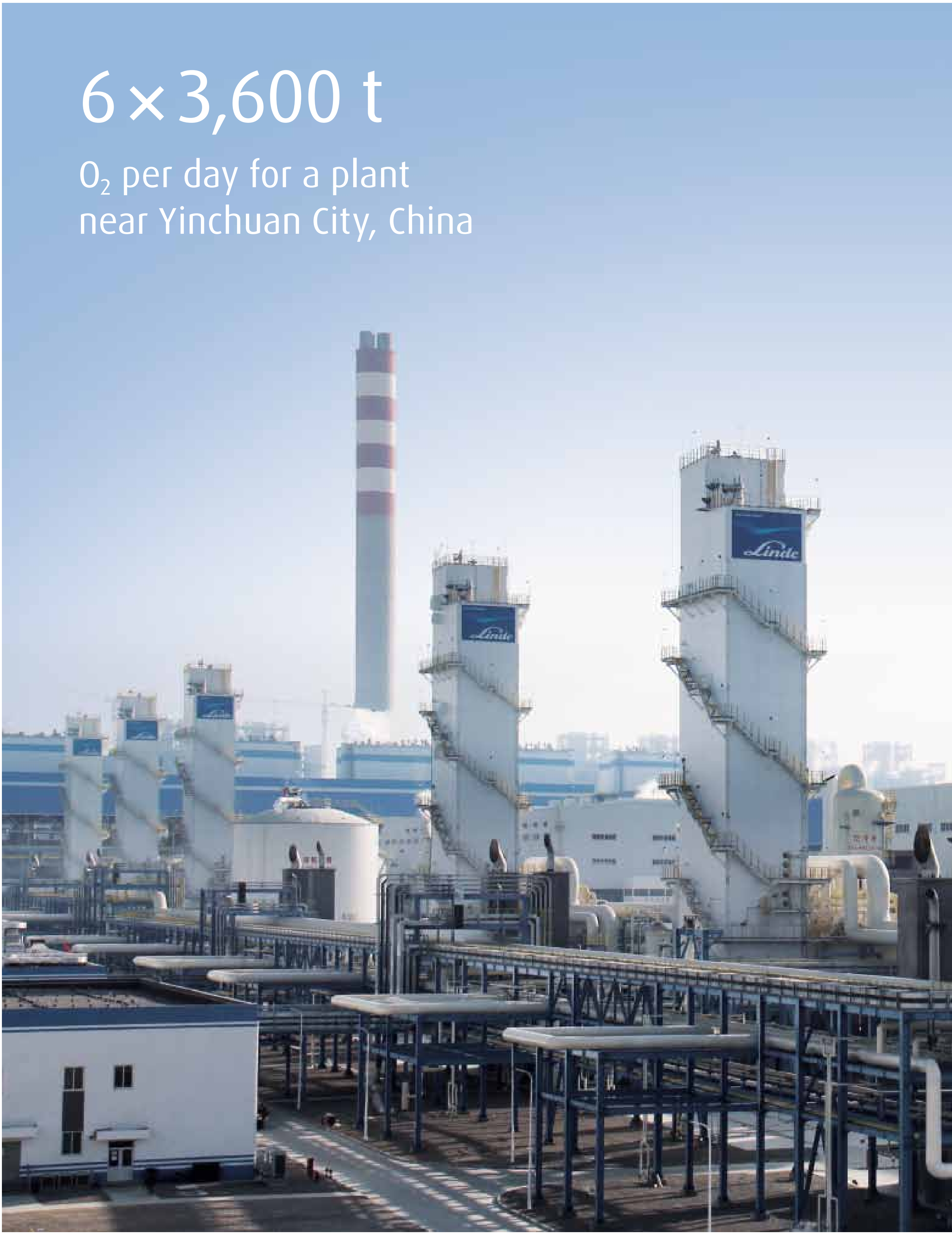
8×3,800 t

O_2 per day in Ras Laffan, Qatar

Air separation units at the Pearl GTL complex in Ras Laffan, Qatar.

6 × 3,600 t

O_2 per day for a plant near Yinchuan City, China



Air separation units near Yinchuan, China.

2016

Engineering masterpiece in China

2017

Start-up of largest ASU in the world

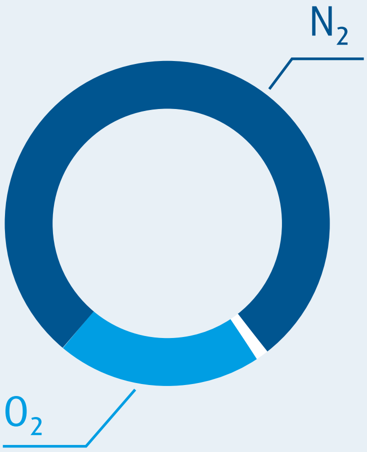
Delivery of world's largest coldbox weighing 800 tonnes for Jamnagar, India.

Linde Engineering.

Facts and figures.

Our air separation business.

Composition of air



		Vol%	Boiling point
🟦	O_2	20.95	–183.0°
🟦	N_2	78.08	–195.8°
□	Ar	0.93	–185.9°
■	Ne	0.0018	–246.1°
■	He	0.0005	–268.9°
■	Kr	0.00011	–153.2°
■	Xe	0.000009	–108.0°

Number of patents

150
new air separation patents in last 5 years

3,000+
air separation plants have been built by Linde

400
air separation units owned and operated by The Linde Group

World's largest single-train air separation unit built by Linde
5,250 tpd oxygen

1902 … World's first air separation unit for oxygen production

1990 … Linde introduced argon production by rectification

19%

TCO

(Total Cost of Ownership)

savings in past

10

YEARS

Heat exchanger

1,700 m^2/m^3

max. surface

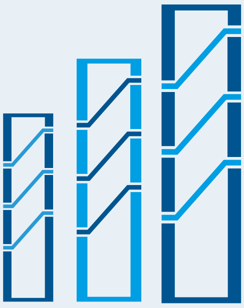
–15%

average power consumption of our ASUs over the last 10 years

Linde air separation units built in more than

90

countries



Biggest pre-fabricated coldbox:

Height 70 m

Weight 800 t

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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.

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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 and membrane 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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