International Course of Cryogenics

2nd part, CERN, Geneva, 31 August, 2010

Helium Recovery

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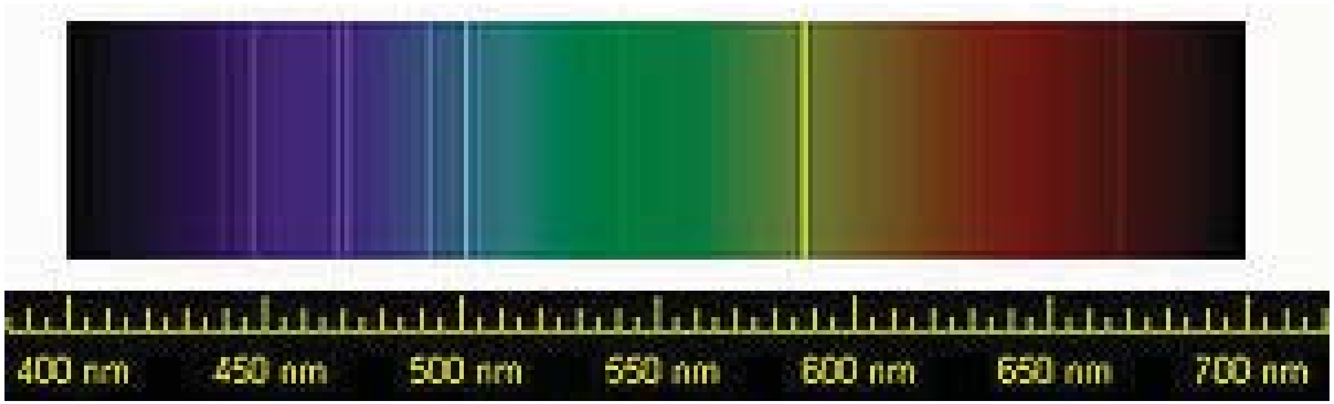
Innovation. Experience. Performance.™

Helium discovery

on the Sun

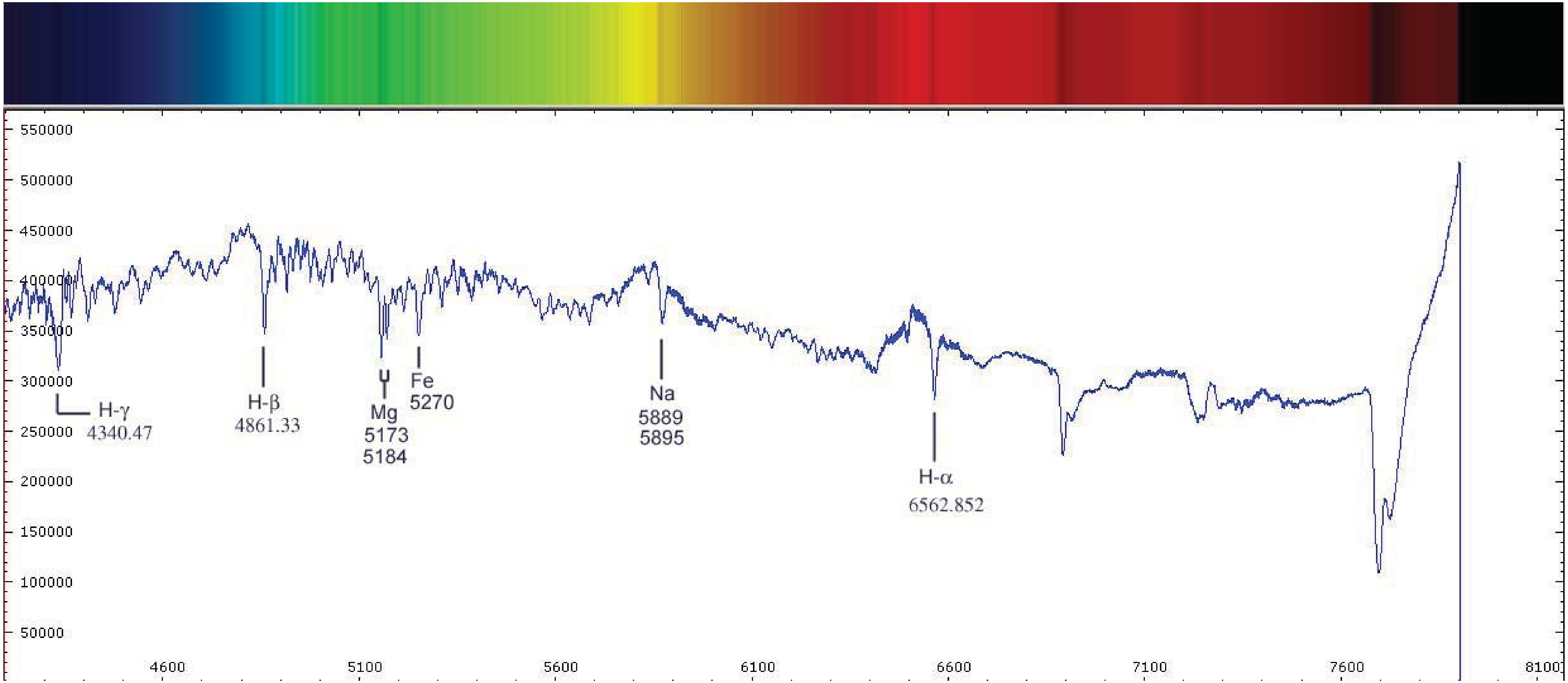
- Helium was discovered in the gaseous atmosphere surrounding the Sun by the French astronomer Pierre Janssen, who detected a bright yellow line in the spectrum of the solar chromosphere during an eclipse in 1868.



- the English astronomer Joseph Norman Lockyer concluded that that D3 line was caused by an element in the Sun that was unknown on Earth.
  Lockyer deduced the name of the new element using the greek name of the Sun, *helios.*

You may think, that it was very easy to dicover helium?

Compare to the normal spectrum of Sun:



Can you see any evidence of helium?
Someone had to come with an idea of studying the spectrum of sun chromospere selectively
and to organize measuring during a rare opportuinity of eclipse.

This tells us something on importance of intuition in science.

Helium discovery

occurance in the space

- In 1903 Ramsay and Frederick Soddy further determined that helium is a product of the spontaneous disintegration of radioactive substances.
- Helium is concentrated in stars, where it is synthesized from hydrogen by nuclear fusion.
- Helium constitutes about **23% of the mass of the universe** and is thus second in abundance to hydrogen in the cosmos.

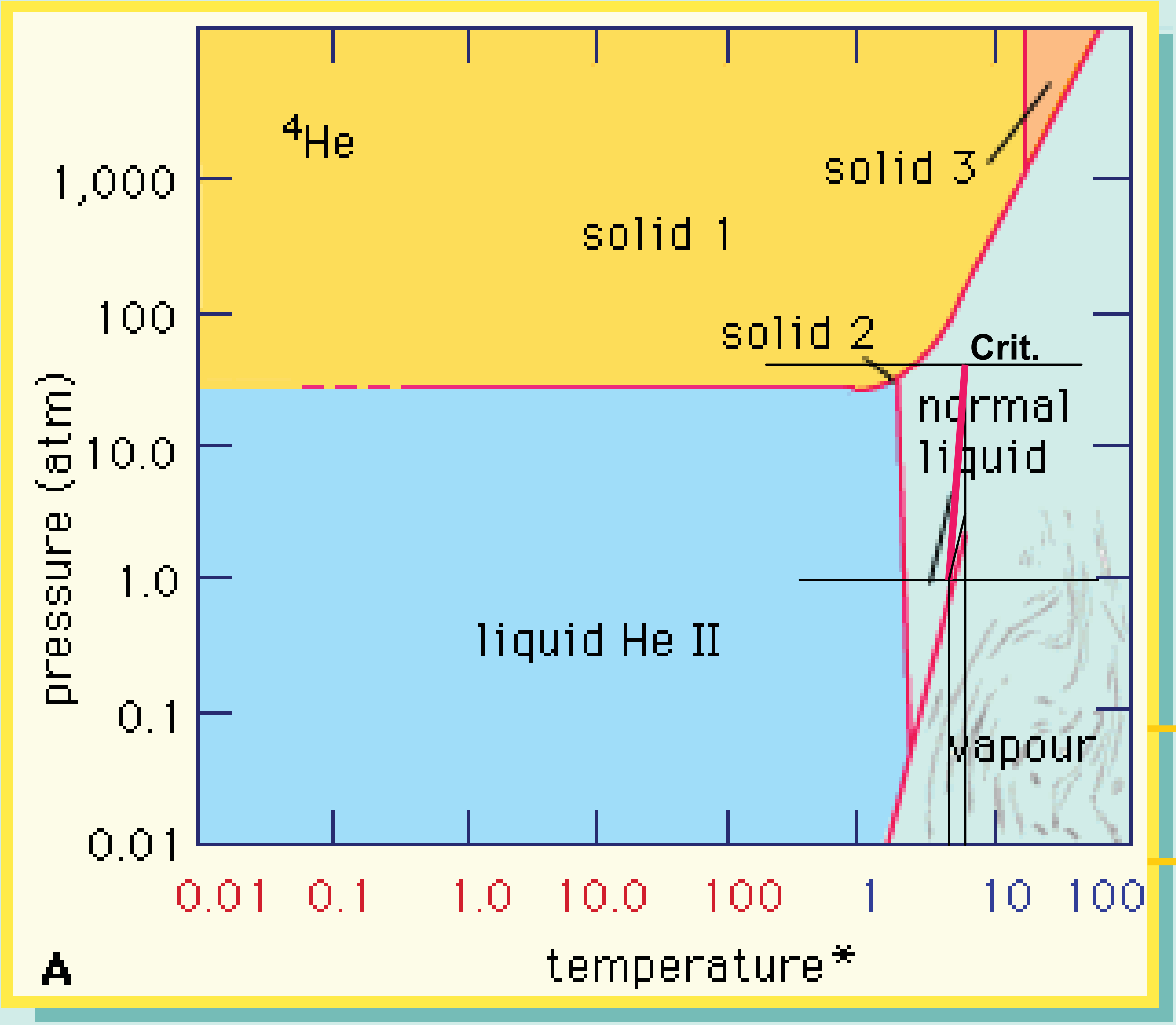
- This initiated search for **helium on the Earth....**

Helium discovery
on the Earth

- The helium that is present on Earth is not a primordial component of the Earth but has been **generated by radioactive decay**. Alpha particles, ejected from the nuclei of heavier radioactive substances, are nuclei of the isotope **helium-4**. Helium does not accumulate in large quantities in the atmosphere because Earth's gravity is not sufficient to prevent its gradual **escape into space.**

- **Consequently, the occurance of helium on the Earth is just a result of dynamic equilibrium between the generation and the escape.**
This is why helium is a really RARE GAS.

Helium isotopes ^4He and ^3He and phase diagram of ^4He



Helium-4 has two liquid forms. The **normal** liquid form is called **helium I** and exists at temperatures from its boiling point of 4.21 K (-268.9° C) down to about 2.18 K (-271° C). Below 2.18 K, helium-4 undergoes **superfluidity** (*i.e.*, its viscosity, or resistance to flow, nearly vanishes) and its **thermal conductivity** becomes more than 1,000 times greater than that of copper. This liquid form is called **helium II**.

(See the phase diagram in the left)

*[0.01-100 in milliKelvins (mK); 1-100 in Kelvins (K)]

The isotope helium-3 (0.1 ppm in He; norm. boiling point 3.2 K) has even one more liquid phase.

Helium recovery

Resources by beginning of 20th century

- Much the best practical source of helium is **thorianite**, a mineral imported from Ceylon for the manufacture of thoria. It dissolves readily in strong nitric acid, and the helium contained is thus liberated.

- The gas contains also H_2, CO_2 and N_2.
  In order to get rid of hydrogen, some oxygen is added to the helium, and the mixture exploded by an electric spark.
  All remaining impurities, including the excess of oxygen, can then be taken out of the gas
  by Sir James Dewar's ingenious method of absorption with charcoal cooled in liquid air. Helium alone refuses to be absorbed, and it can be pumped off from the charcoal in a state of absolute purity.

- If thorianite cannot be obtained, **monazite**, which is more abundant, may be utilized. A part of the helium contained in minerals can be extracted by heat or by grinding

  (J. A. Gray, *Proc. Roy. Soc.,* 1909, 82A, p. 301).

These were the only sources of helium when Kamerlingh Onnes liquefied helium first in July 1908.
For recovery one m^3 of helium 1 ton of monazite sand was needed.

Helium recovery

Resources by beginning of 20th century

Only after **air separation** developed during the same period, it offered a more economical way of recovery.

Even more important source of helium became **natural gas** (from 1917), Hamilton, Ontarion, Canada.

Finally, **waste gases of ammonia synthesis** are another important source.

Helium is an important industrial gas, today.

The resources are of strategic importance.

Helium world consumption

75 tonne/day

27 375 tonne/year

Most of it is recovered from natural gas

Cai Z. *et all, proceedings of the conference CryoPrague2006*

Helium world consumption

by region

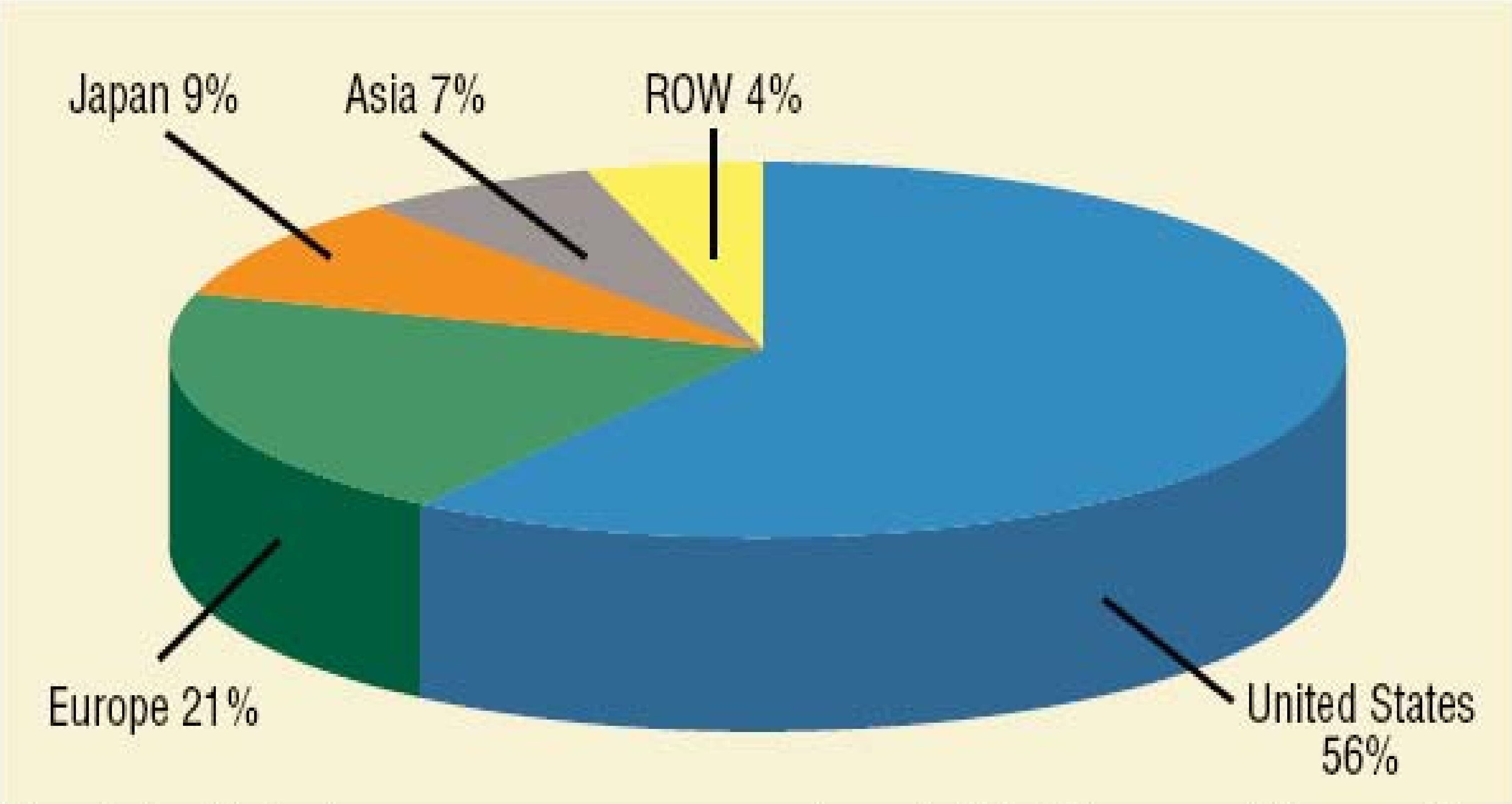


Fig 2 The U.S. alone consumes more than half of the world's supply of helium (2002)

Helium world consumption

by branch of industry

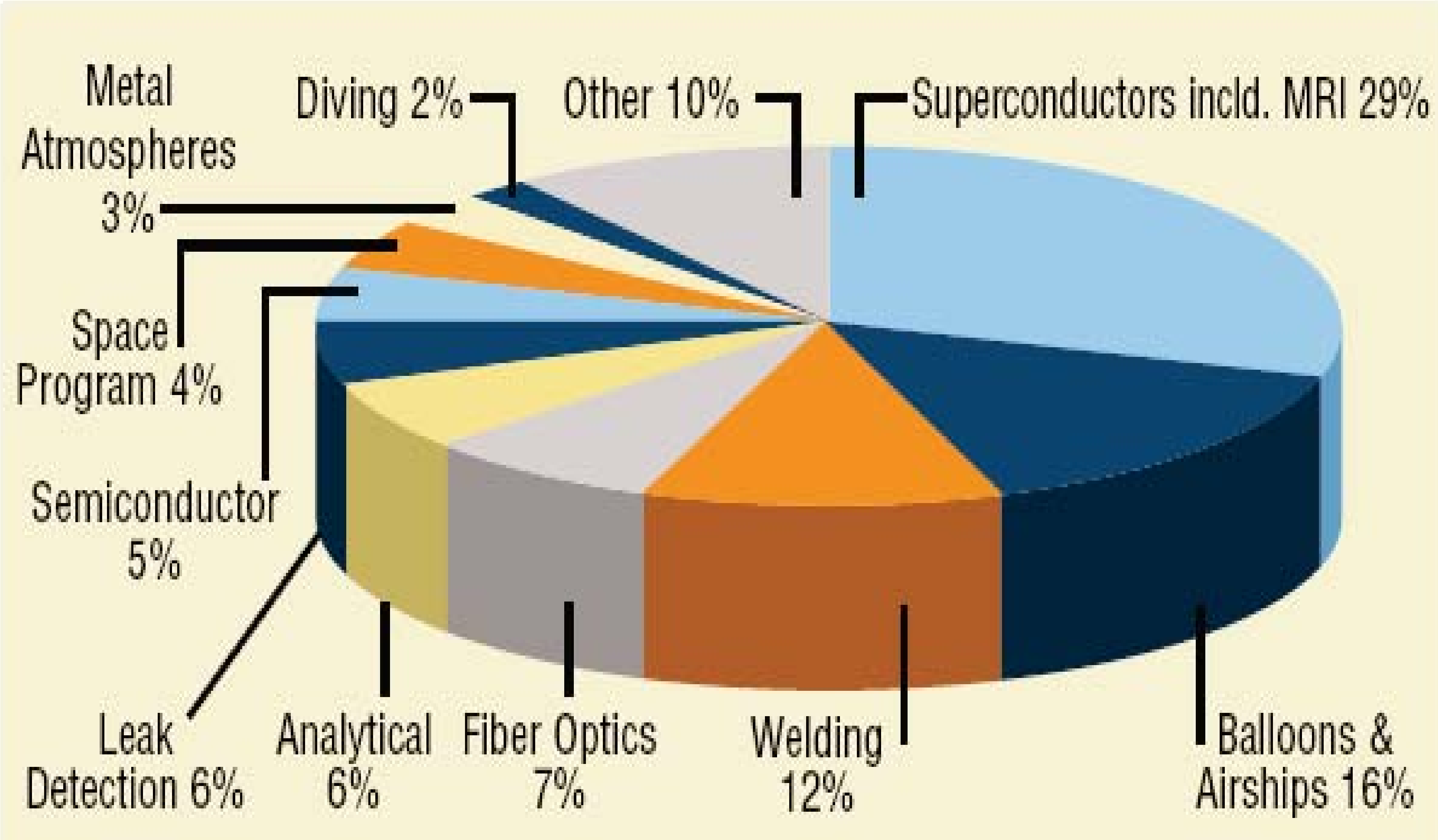


Fig 3 Helium use in various applications

Helium world consumption

by branch of industry

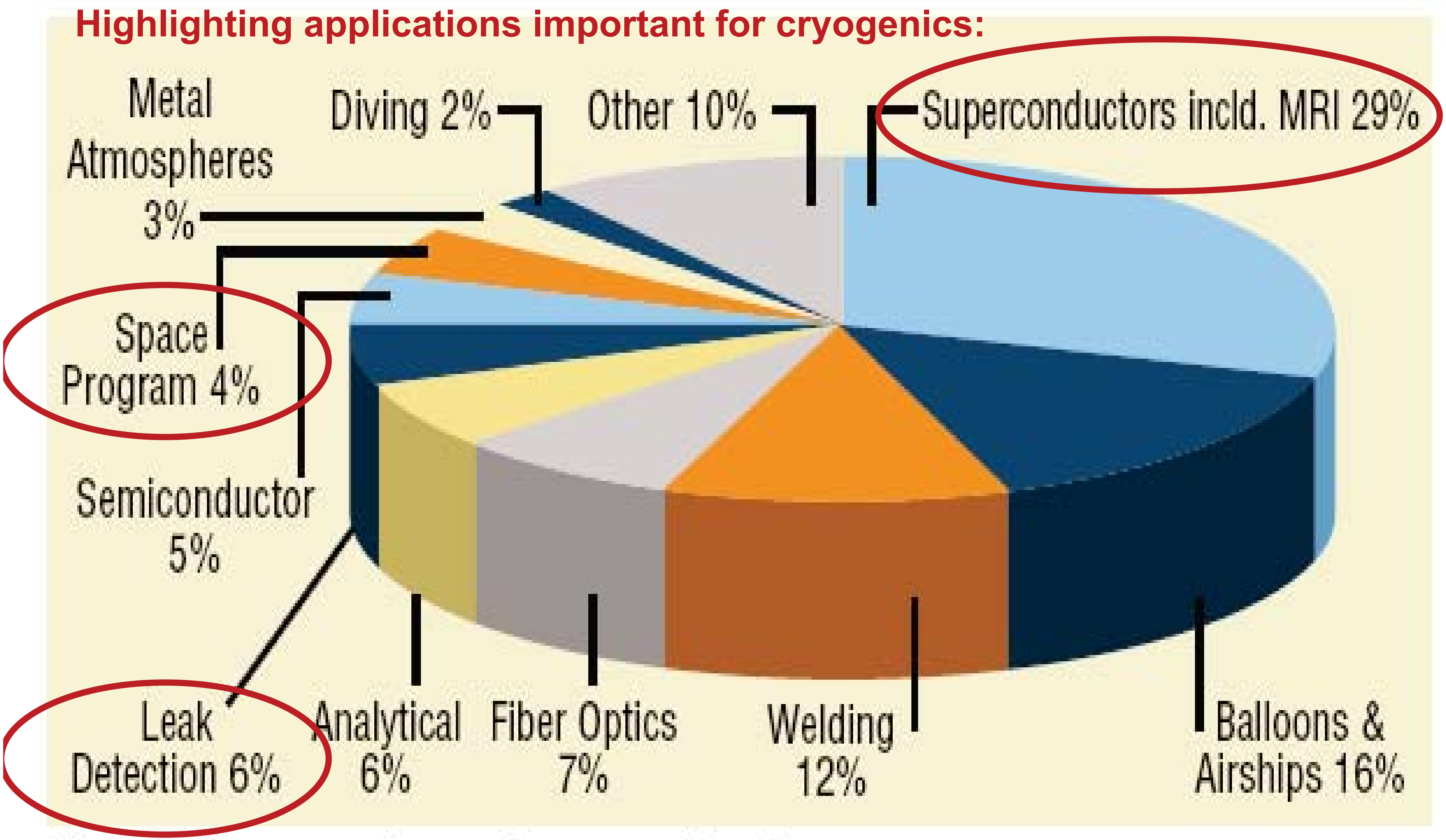


Fig 3 Helium use in various applications

Properties & Applications of Helium

Property	Application
Second lightest element (after hydrogen)	Lifting – balloons, airships
→ Smallest molecular size	Leak detection
Chemically inert (essentially no tendency to react with other elements)	Carrier gas - analytical, semiconductor Purging - semiconductor
→ Lowest boiling point; does not solidify at 0°K 1 atm. 4.2 K at atm. pressure	Liquid cooling – Superconductors Purging/pressurising LHY - rockets
Very high specific heat & thermal conductivities	Gaseous cooling – fiber optics
Highest ionisation potential	Metal arc welding – aluminium, ... Plasma arc melting – titanium, ...
Very low solubility	Diving gases
Radiologically inert (no radioactive isotopes)	Heat transfer medium in nuclear reactors
Very high sonic velocity	Metal coatings
→ Liquid becomes superfluid below 2.2K	Cooling of LT superconductors

Helium recovery

from air - air separation industry

- Air separation is an important branch of industry, as it is a source of
  - **Oxygen** (welding, oxidation processes in metallurgy, chemistry, gas industry)
  - **Nitrogen** (synthesis of ammonia, inert atmospheres in metallurgy and petrochemical processes, plasma cutting of metals)
  - **Argon** (innert for semiconductor and microprocessor production, innertization of nuclear plants, welding of alluminum)

Helium recovery

Composition of air

Component	Symbol	Volume	
Nitrogen	N_2	78.084%	99.998%
Oxygen	O_2	20.947%	
Argon	Ar	0.934%	
Carbon Dioxide	CO_2	0.033%	
Neon	Ne	18.2 parts per million	
Helium	He	5.2 parts per million (ppm)	
Krypton	Kr	1.1 parts per million	
Sulfur dioxide	SO_2	1.0 parts per million	
Methane	CH_4	2.0 parts per million	
Hydrogen	H_2	0.5 parts per million	
Nitrose oxide	N_2O	0.5 parts per million	
Xenon	Xe	0.09 parts per million	
Ozone	O_3	0.07 parts per million	
Nitrogen dioxide	NO_2	0.02 parts per million	
and some other traces			

Helium recovery

from air - air separation industry

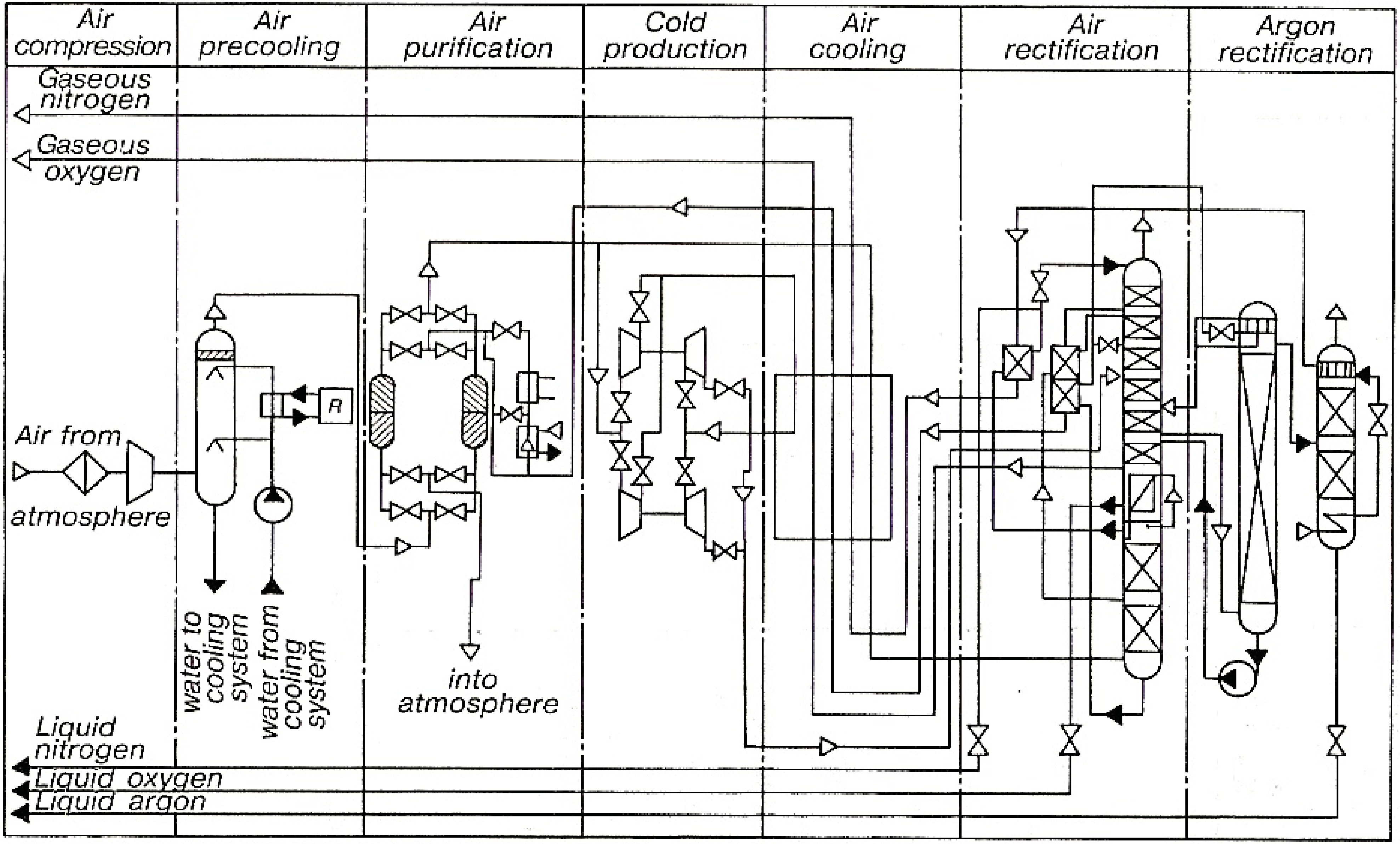


Fig. 1.4. Schematic process flowsheet of the high-pressure ASP of "AKAp" type

Helium recovery

from air - air separation industry

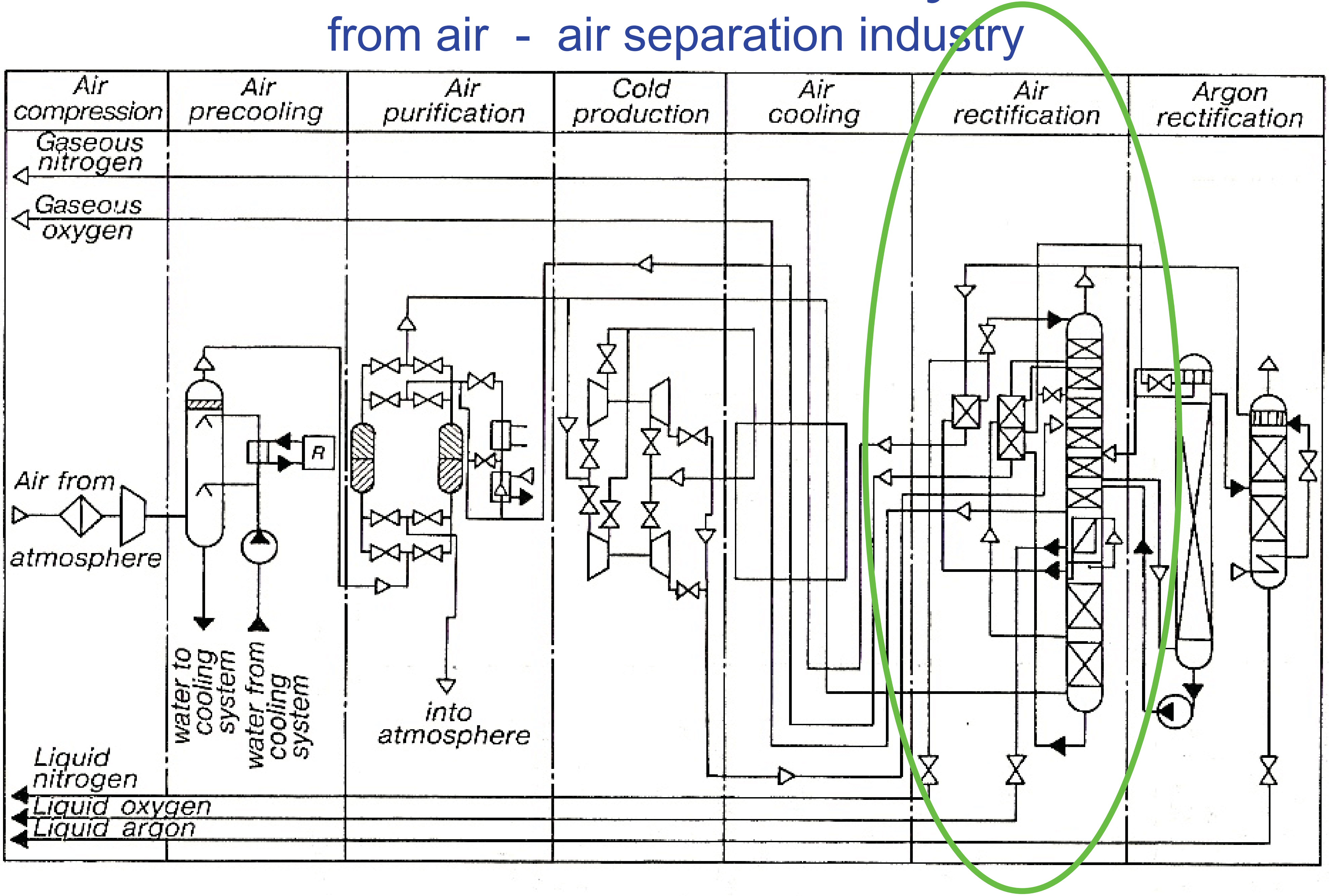
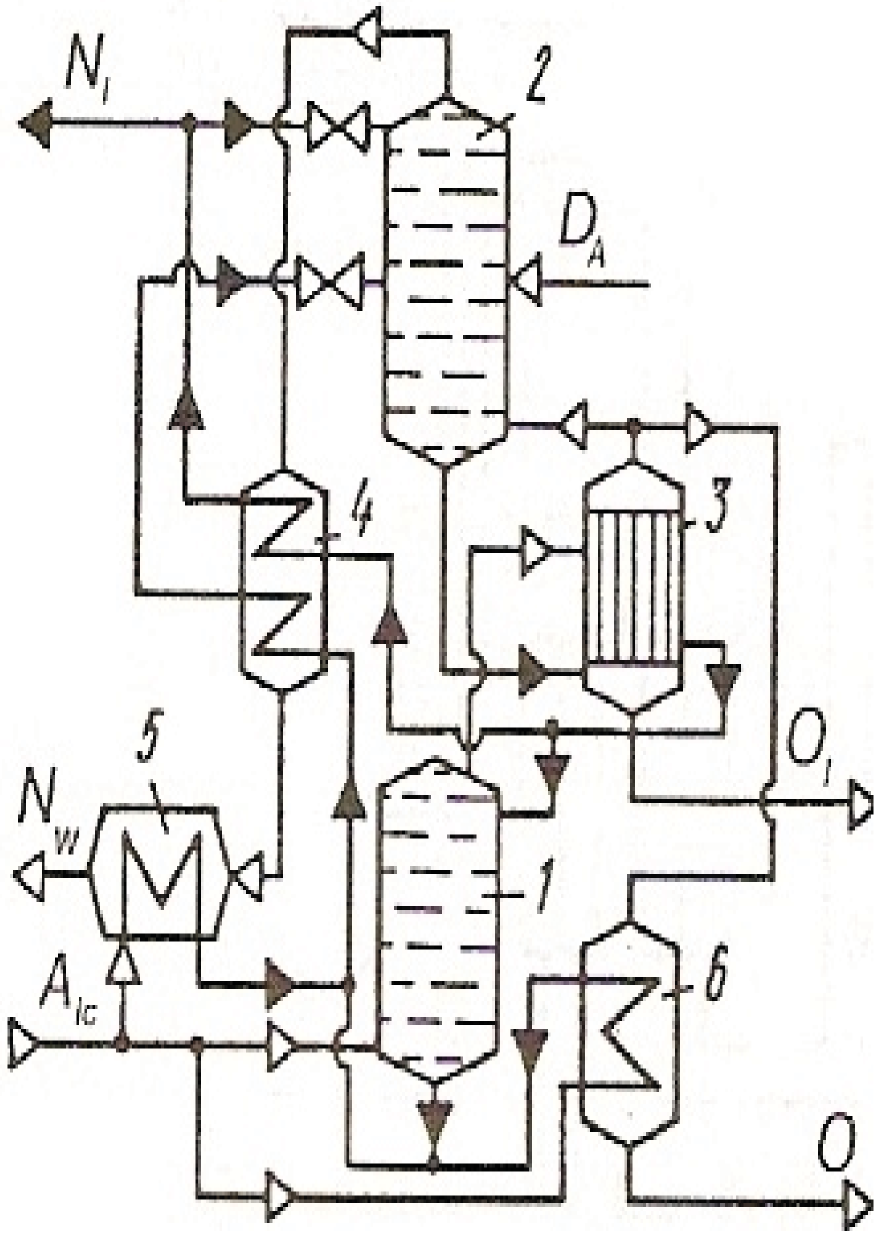


Fig. 1.4. Schematic process flowsheet of the high-pressure ASP of "AKAp" type

Helium recovery

from air - air rectification
double column system



2 – UPPER COLUMN

pressure: top: N_2 at 1.28 bar abs

bottom: O_2 at 1,45 bar

T = 93.7 K

3 – CONDENSER - VAPORIZER

O_2 in tubes T = 93.7 K

DT = 2 K

N_2 in the shell T = 95.7 K

1 – LOWER COLUMN

top: temperarture T = 95.7 K

condensation of N_2 at p = 5.70 bar

bottom: gaseous air at 5.82 bar abs

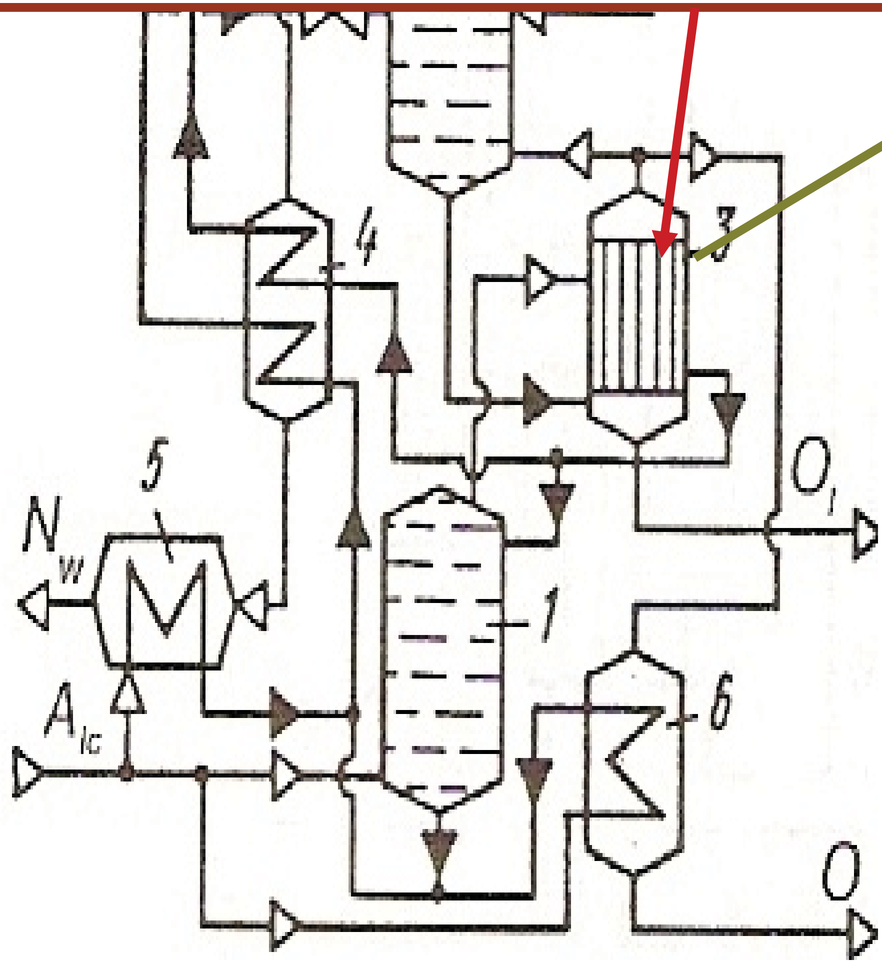
(compressor air: 6.2 barg – ENERGY)

Helium recovery

from air - air rectification
double column system

Accumulation of non-condensable gases Ne + He reduces partial pressure of nitrogen.

For achieving the same temperature, the total condensation pressure is increasing. (ENERGY!)



Ne+He mixture withdrawal

3 – CONDENSER - VAPORIZER
O2 in tubes T = 93.7 K

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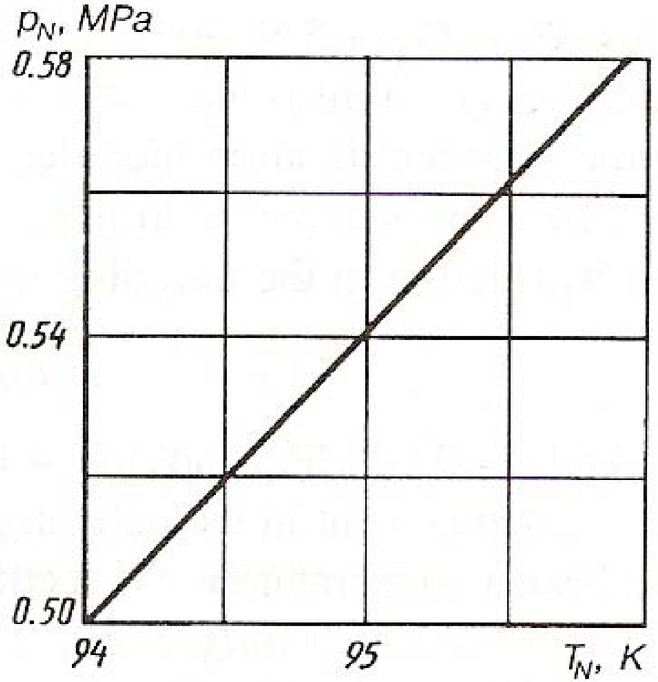
Helium recovery

from air - air rectification

' ' 'e column system



1% (Ne+He) ..... 1% pressure more

Energy consumption on the compressor

N = nRT ln(Pkomp/Patm)

dN/dPkomp = nRT(Patm/Pkomp)*1/Patm

dN = nRT/Pkomp × dPkomp

dN/N = dPkomp/ {Pkomp* [ln(Pkomp/Patm)]}

Exercise 2:

Pkomp = 6 bar, Patm = 1 bar

1% (Ne+He)

dPkomp = ...? bar

dN/N = ...? % energy on the compressor?

Ne+He mixture withdrawal

Helium recovery

from air - air rectification
double column system

1% (Ne+He) ..... 1% pressure more

Energy consumption on the compressor

N = nRT ln(Pkomp/Patm)

dN/dPkomp = nRT(Patm/Pkomp)*1/Patm

dN = nRT/Pkomp × dPkomp

dN/N = dPkomp/ {Pkomp* [ln(Pkomp/Patm)]}

Exercise 2 *(results)*:

Pkomp = 6 bar, Patm = 1 bar

1% (Ne+He)

dPkomp = 0,06 bar

dN/N = 0.56% energy on the compressor

Ne+He mixture withdrawal

Helium recovery

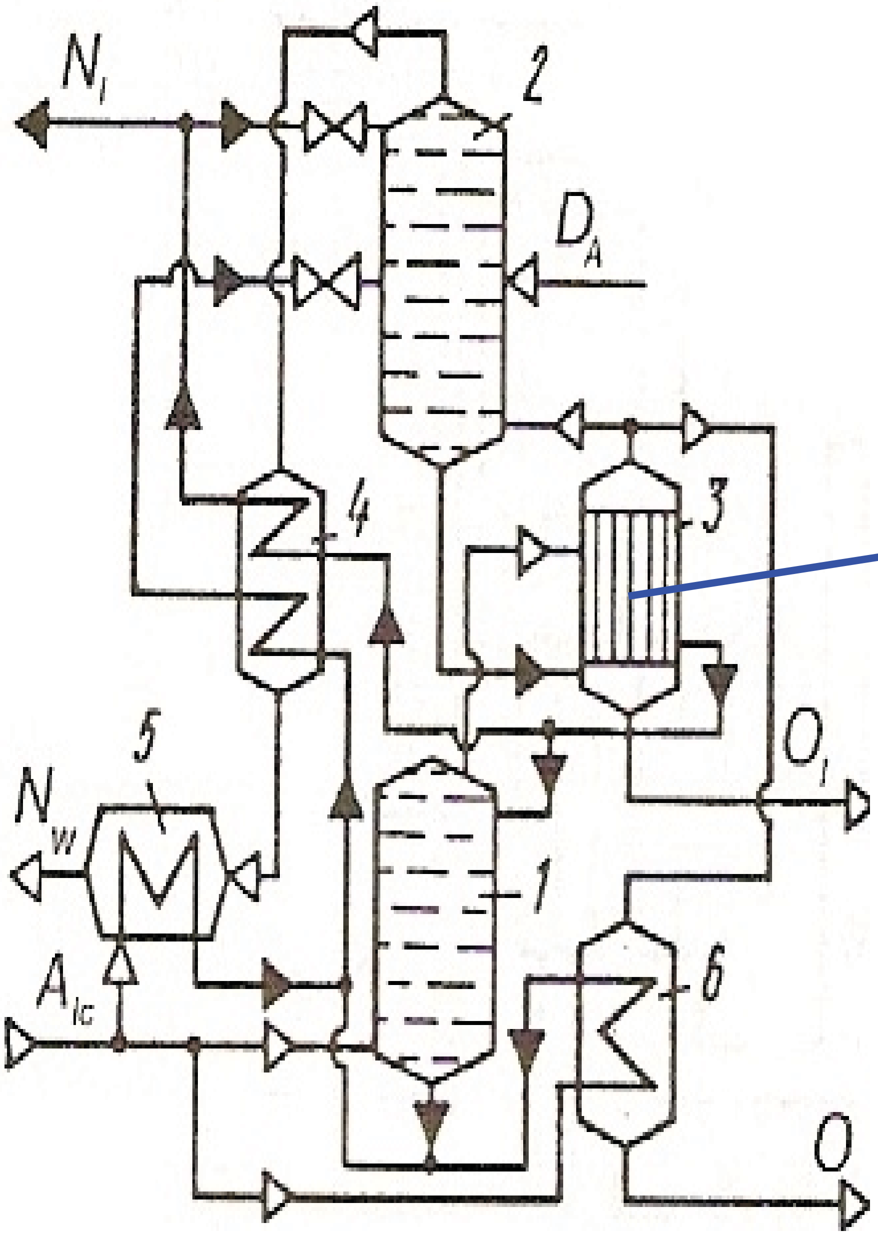
from air - air rectification
double column system

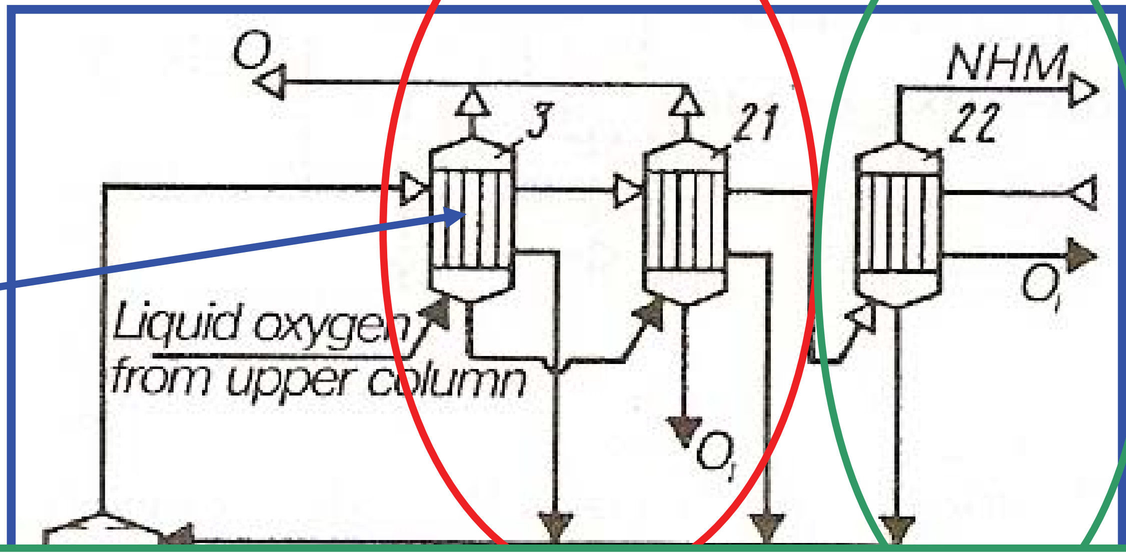
Deflegmator of Ne+He mixture

Cooled by boiling liquid nitrogen at 1,3 bar, 79.3K
DT = 0.5 K

Main condensers cascade.

Nearly no concentration (Ne+He) in the core 3





Condensing temperature 79.8 K
Concentration of neon in returning liquid phase and the withdrawn gaseous phase influence the condensation pressure.

They must be in accordance with mass balance

Helium recovery

from air - air rectification
Crude Neon Helium Mixture
(NHM)

Condensing temperature 79.8 K
Concentration of neon in returning liquid phase and the withdrawn gaseous phase influence the condensation pressure.

They must be in accordance with mass balance between large liquid return with small concentration of Ne and small vapor flow with large concentrations of inerts.

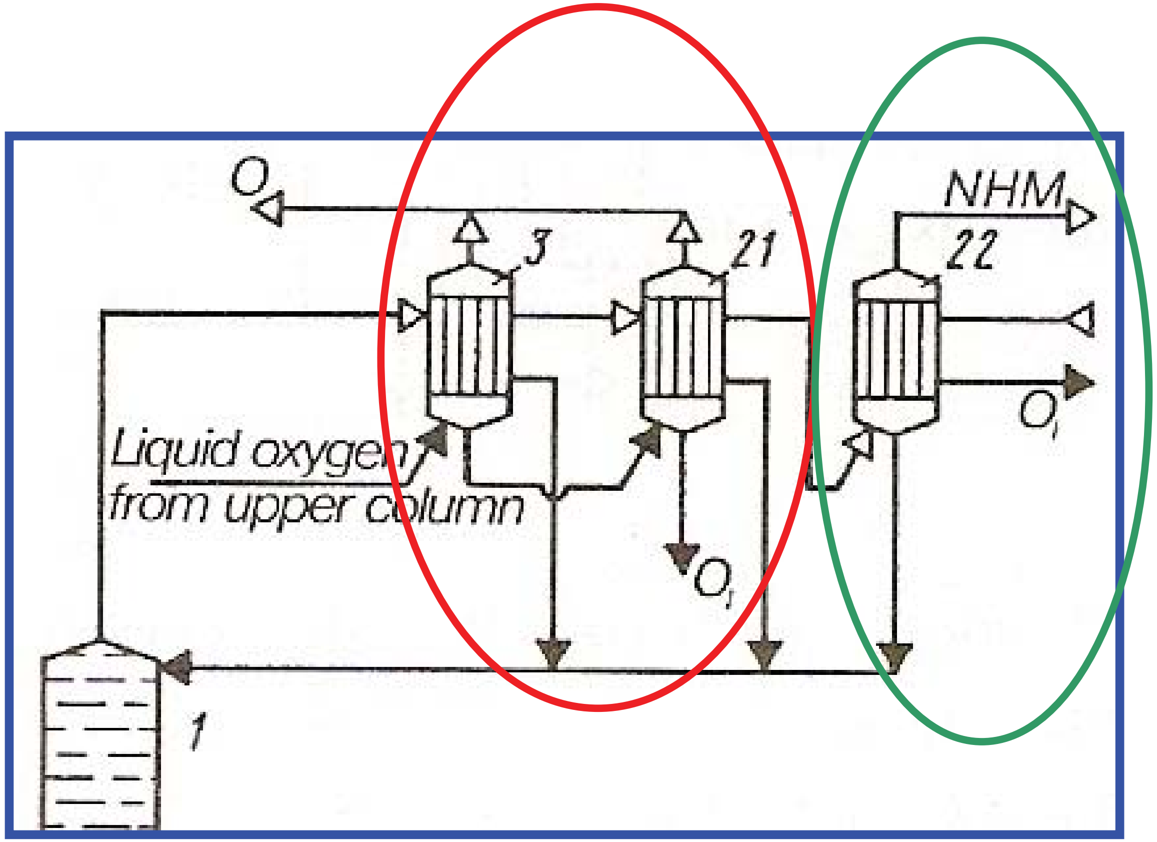
Phase Equilibrium at NHM condensation
K = y(% in vapor)/x(% in liquid)

He/N_2 at 77.3 K ... K = 800

Ne/N_2 at 77.3 K ... K = 60

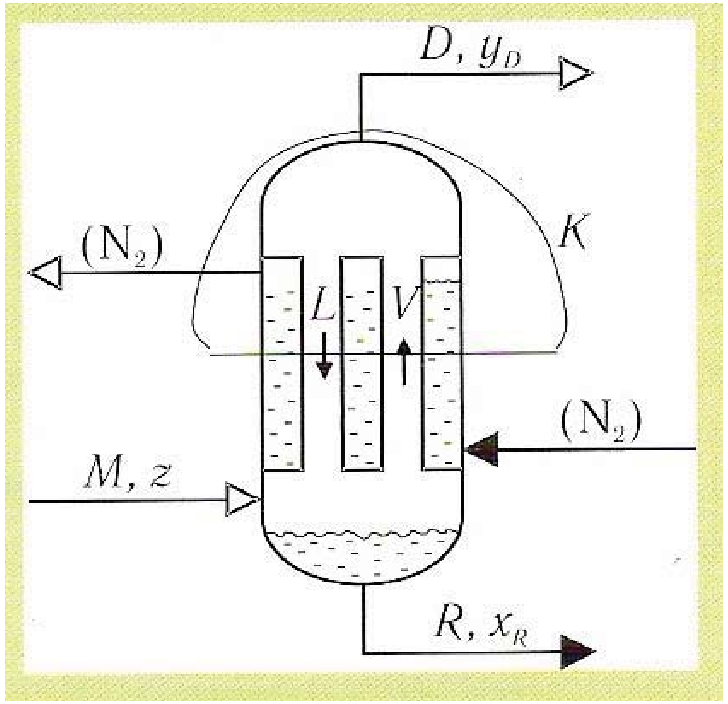
Typical composition of NHM:
40% N_2, 60% of inerts
(44% Ne, 15% He, 1% H_2)

Typical flowrate:
0,003% of inlet air of the plant



Helium recovery

from air - air rectification
Crude Neon Helium Mixture



Deflegmator for purification of the condenser vent M (z = 2% Ne+He)

to crude Neon-Helium mixture D (yd = 50% Ne+He)

Helium recovery

from air - He + Ne crude concentrate separation

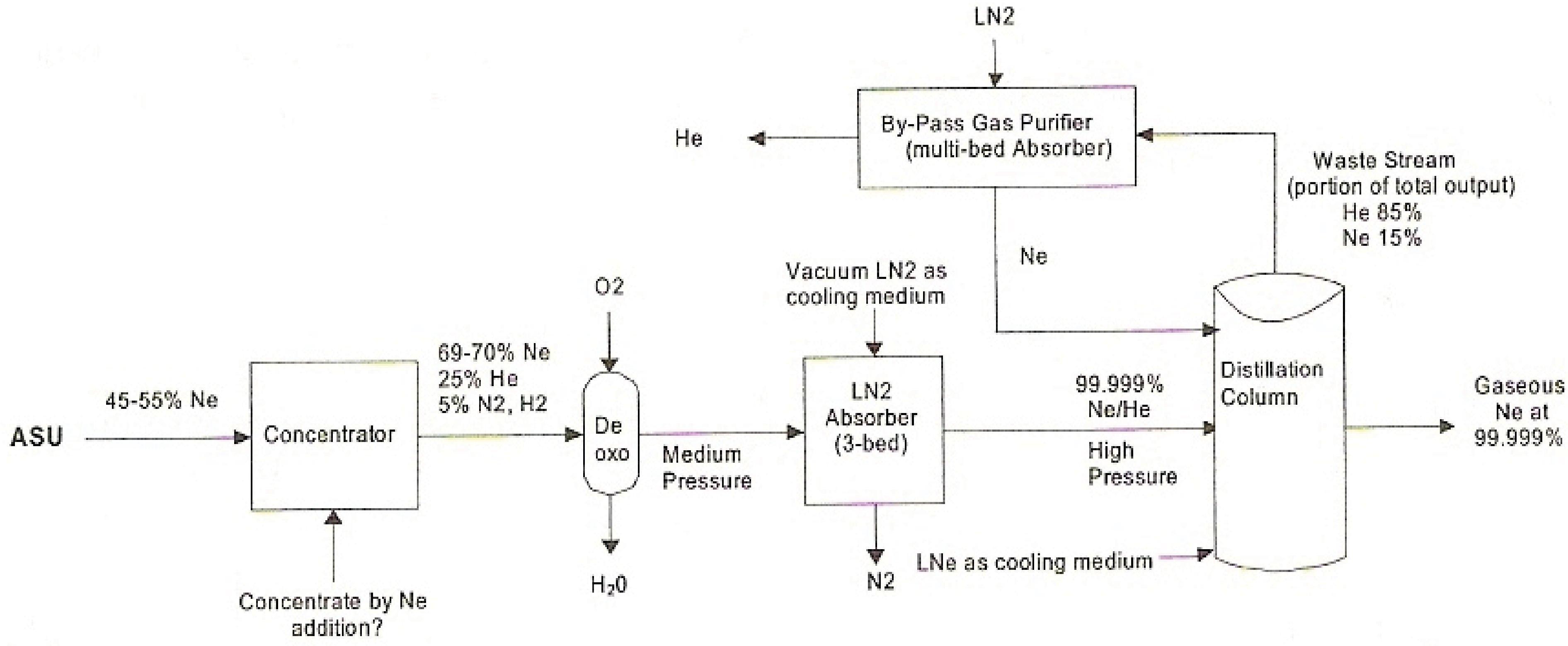
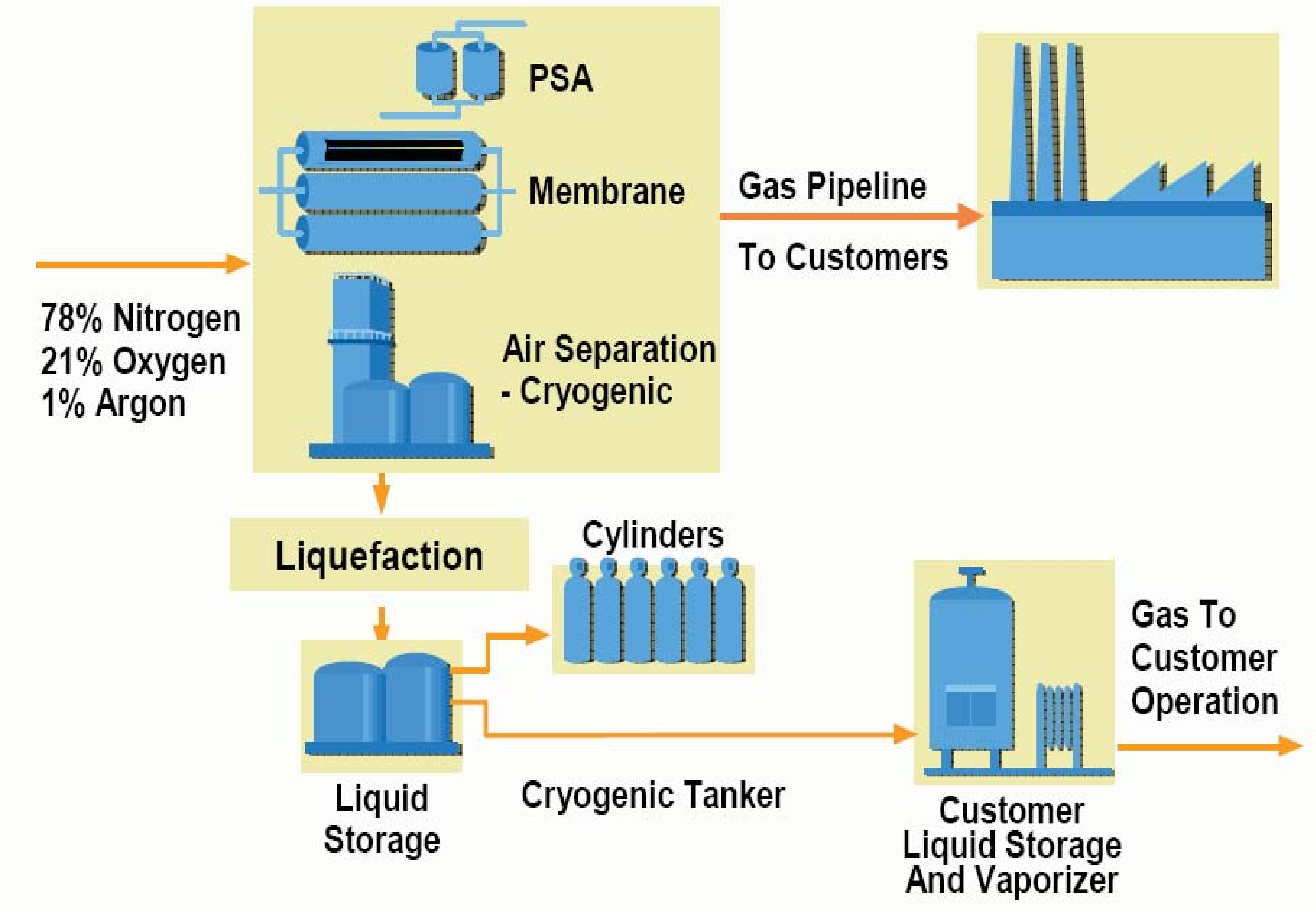


Figure 1 Neon purifier system showing de-oxo, absorber and distillation steps (courtesy BOC

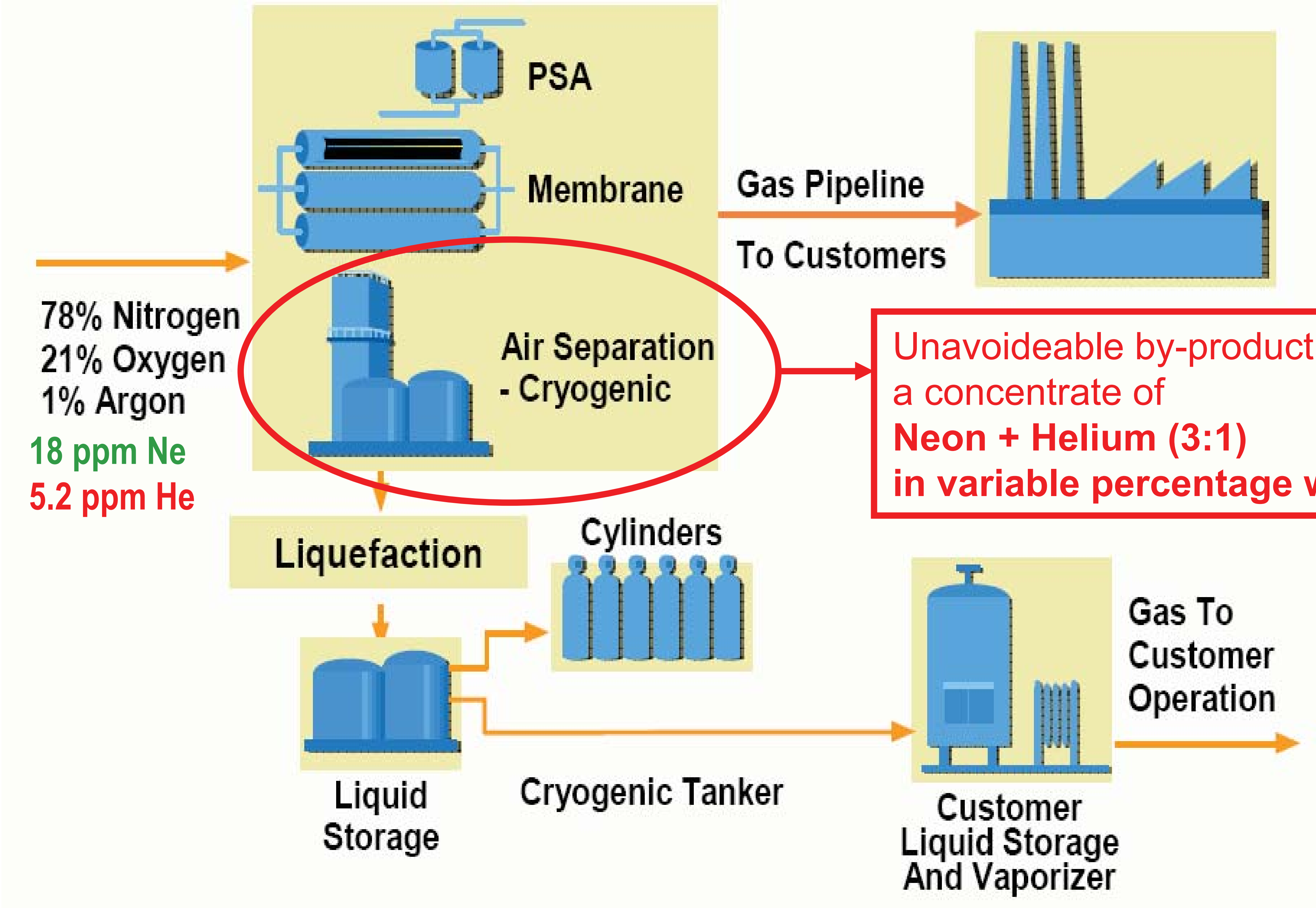
Helium recovery

from air - air separation industry



Helium recovery

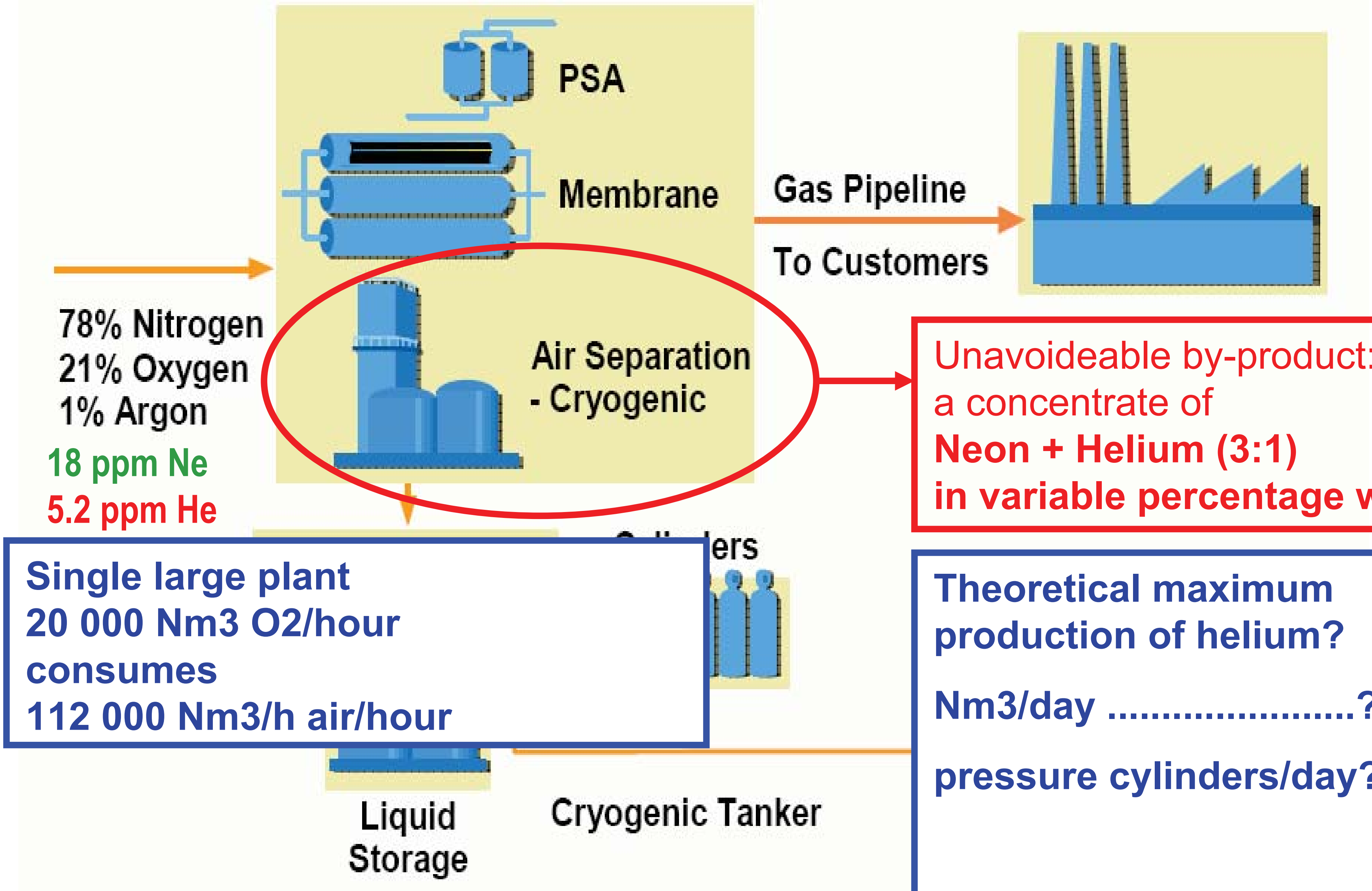
from air - air separation industry



Unavoideable by-product:
a concentrate of
Neon + Helium (3:1)
in variable percentage with N_2

Helium recovery

from air - air separation industry



Unavoideable by-product:
a concentrate of
Neon + Helium (3:1)
in variable percentage with N_2

Single large plant
20 000 Nm3 O2/hour
consumes
112 000 Nm3/h air/hour

Theoretical maximum production of helium?

Nm3/day ....?

pressure cylinders/day?

Helium recovery

from air - air separation plant

Exercise 1:

Single plant: 112 000 Nm3/h

5.2 ppm He

Molecular mass of He 4

Helium 112 000 × 5.2 × 10^{-6} = 0.58 Nm^3/h

= 14.0 Nm3/day

(in a case of 100% recovery)

Normal volume of one kilomole 22,4 m^3

Molecular mass of He 4

14 / 22.4 × 4 = 2.5 kg/day

(0.0035 of the world production)

High pressure cylinders (50 liters, 200 bar) 1.4 cylinder/day

This process is not effective any more. It is used for neon recovery only.

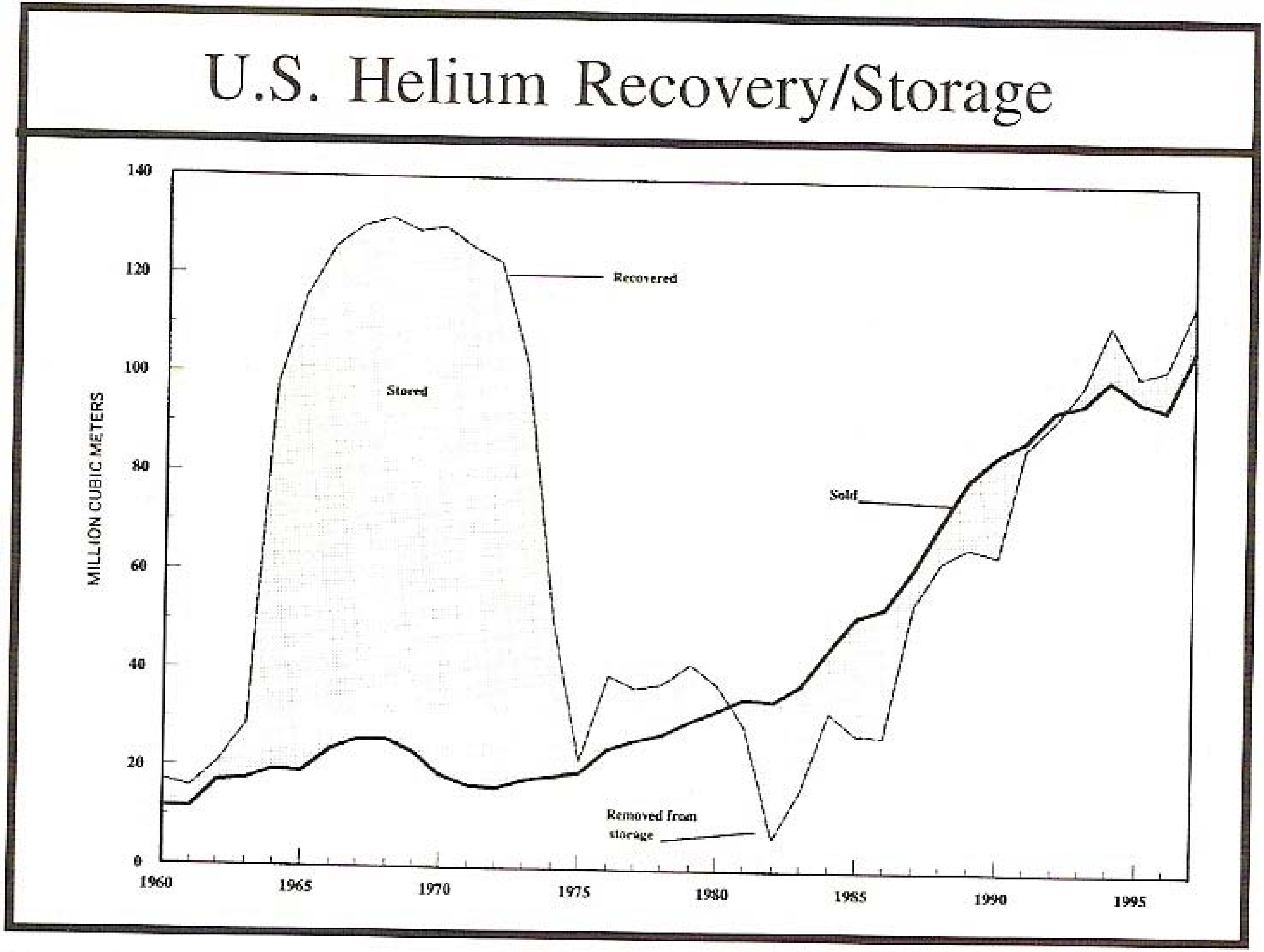
Helium from NaturaL Gas

History and content in the crude gas resources

- First found in 1905 by H.P. Cady in Dexter, Kansas, USA: 1,5% He
  His student C. Siebel analyzed helium content in many other natural gases, but he thought still in 1917, that it has „regrettably no practical application.“
- First helium recoveries:
  1917, Hamilton, Ontario, Canada, British army for airships, WW I.
  1921-1927, Fort Worth, Texas, USA
- USA: The Helium Act 1925 (Federal authority on helium production) –Lifting gas of baloons – World War II.
  Helium Act ammendment 1960 – privatization of helium recovery
  Helium Conservation Act 1960 – governmental purchase of crude helium 130 Mill. m3/year , sorage in the Cliffside gas field
  Helium Privatization Act 1996 – Sale of USA national reserves

Helium from NaturaL Gas

History and content in the crude gas resources



Helium from NaturaL Gas

History and content in the crude gas resources

- Europe: Odolanow, Poland: 0.2% He
  Production since 1975 (?),
  the most important source in Europe
  446 ton/year
- Orenburg, Russia, 0.05% He
  helium deliveries from 1990
  3200 ton/year
- Qatar North Field: 0.04% He
  3 500 ton/year of LHe from 2006
- Qatar 2
  6 500 ton/year of LHe from

Estimated energy costs of helium recovery from gases containing 0.02, 0.05, 0.35% of helium are 250, 100, 18 kWh/Nm3, respectively.

Helium from NaturaL Gas

World resources

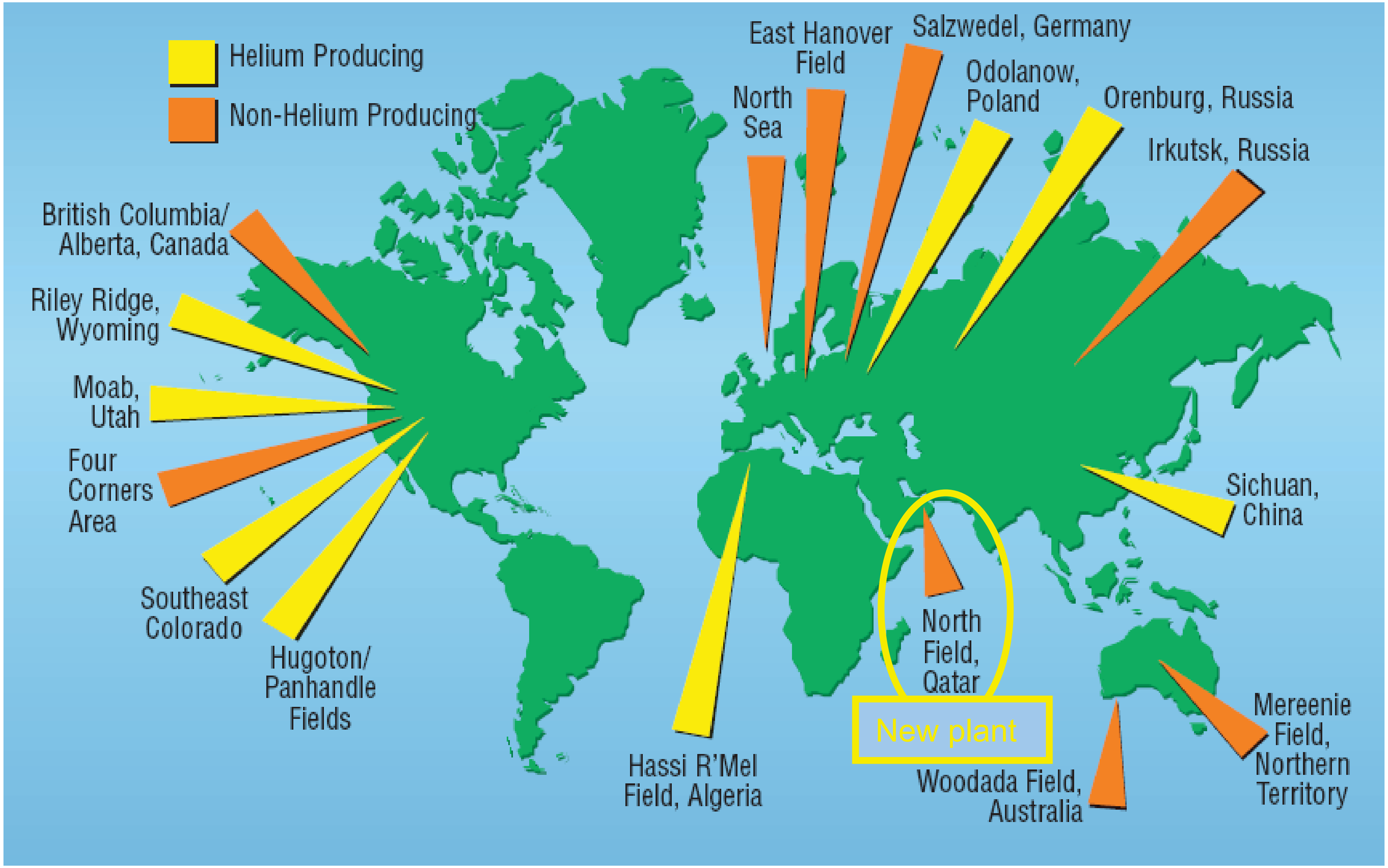


Fig 1 Helium can be extracted from only a few natural gas fields around the world. The richest field is in the state of Utah in the U.S.

Crude helium is recovered from the gas at Amoco plants, designed by Chart, in Hugaton, KS.

Crude He from an NRU

(Nitrogen rejection from the raw natural gas)

World largest Nitrogen rejection unit.

Reduction of nitrogen content in the natural gas from 15% to 3% and crude He recovery.

One train with a two-column Nitrogen rejection process operates 8600 ton of natural gas/day.

Helium from Natural Gas

Example Qatar

- Qatar is the largest exporteur of liquefied natural gas in the world.
- Helium rich mixture is recovered in the process of liquefaction of natural gas (condensation point -162°C). Helium remains as non-condensing gas and can be vented from the process condenser.

Helium from Natural Gas

Example Qatar

Table 1. Impure helium feed gas from both Qatar gas and Ras Gas sources

Feed gas		Qatar Gas	Ras Gas
He	Mol%	55.2118	41.2501
N_2	Mol%	41.4547	55.3319
CH_4	Mol%	2.3216	2.3686
H_2	Mol%	0.9963	1.0320
CO	Mol%	0.0026	0.0038
Ne	Mol%	0.0017	0.0013
Pressure	bara	2	2
Temperature	°C	ambient	ambient
Total flow	Nm^3/h	1.28	0.91

Composition of crude helium concentrate

from two Qatar natural gas base load liquefaction plants

Helium from Natural Gas

Example Qatar

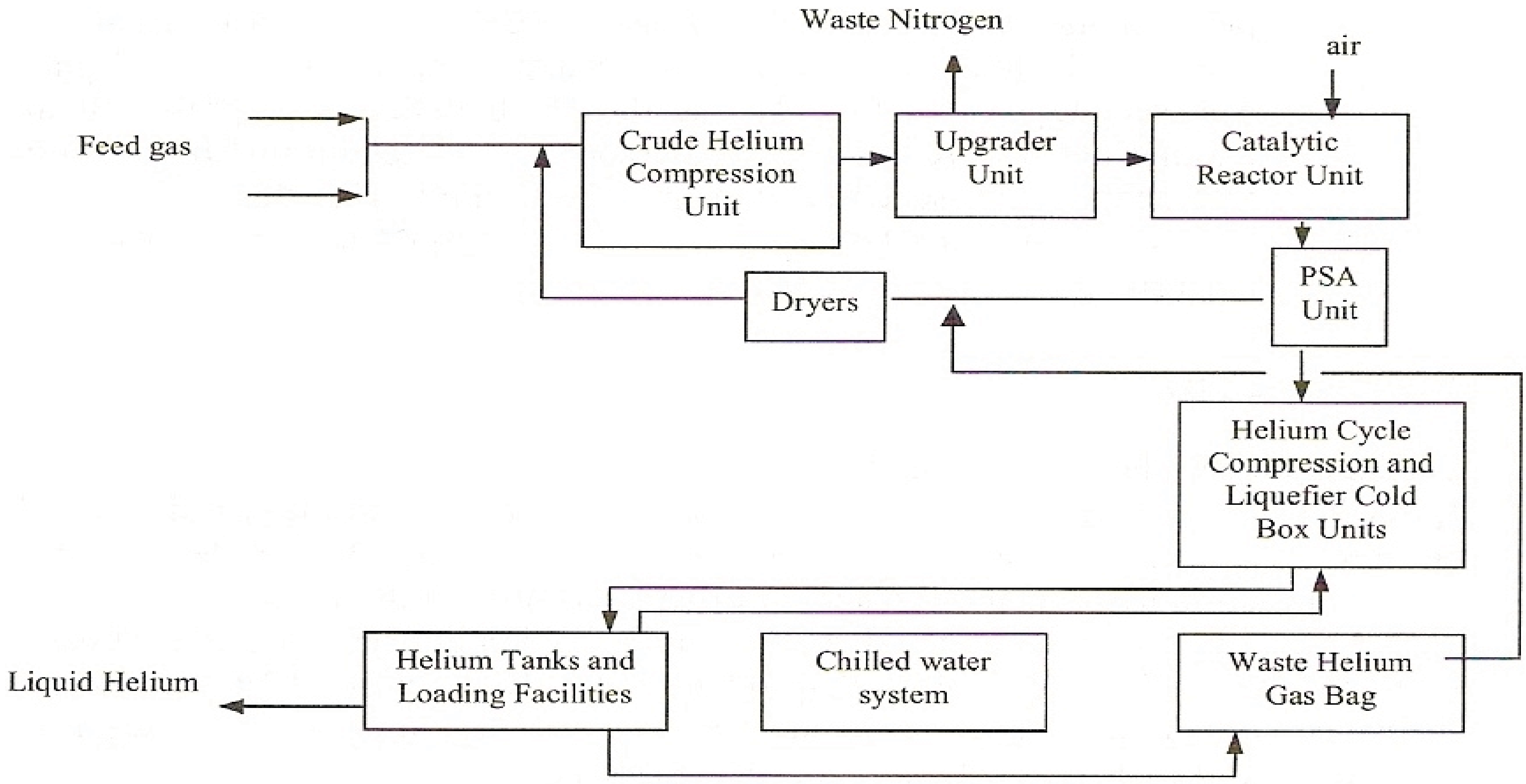


Figure 1 simplified HeRU block diagram

Block scheme of pure liquid helium recovery from the crude

Helium from Natural Gas

KRIO Odolanow

Crude gas composition:
60% CH_4, 38 %N_2, 0,3% CO_2, O,3% H_2O, 0,25% He, rest C2+

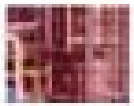
Basic process:
- Crude gas purification from condensing and freezing impurities
- Separation of nitrogen from methane ba low temperature distillation
- Compression of liquid methane in pumps
- Vaporization of methane in the main heat exchanger and delivery to pipeline

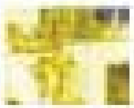
Plant capacity: 200 000 Nm^3/hopur = 3460 ton/day

Side production of 50 ton/day liquefied methane (LNG) ,

To be increased to 150 ton/day in 2009

 Low-methane gas purification

 Low temperature distillation of natural gas

 Helium purification, liquefaction and storage

446 ton/year
1.6% of world consumption

from ICEC 2010 website

Helium from Natural Gas

KRIO Odolanow **(visited by students, when the course is in Wroclaw)**

Crude gas purification:

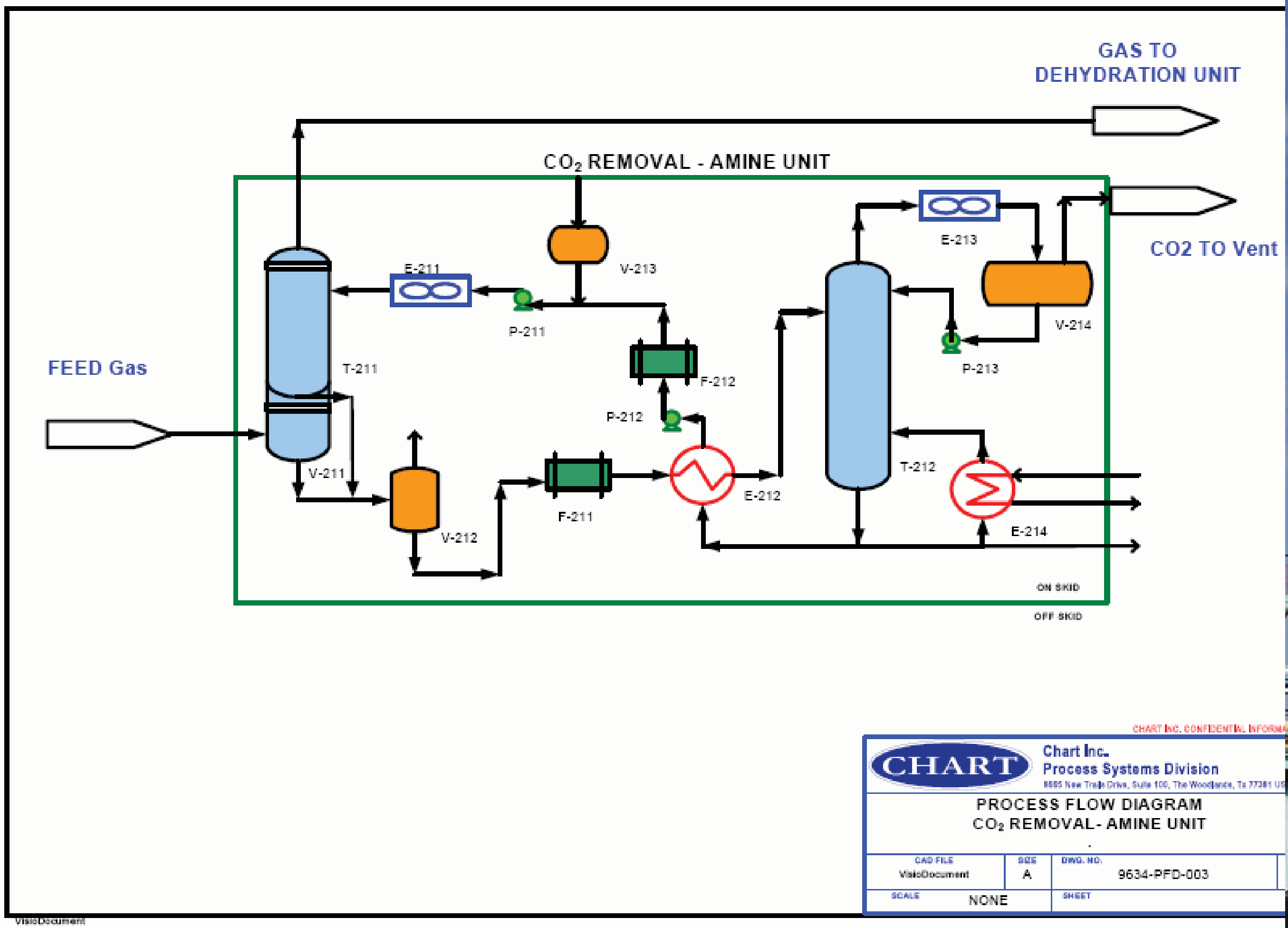
- from CO_2 with absorption on methylamine
- from CO_2 with adsorption on molesieve (synthetic zeolite)
- from C5+ hydrocarbons on charcoal (activated carbon)

Helium from Natural Gas

KRIO Odolanow

Crude gas purification:

- from CO_2 with absorption on methylamine (similar flow scheme)



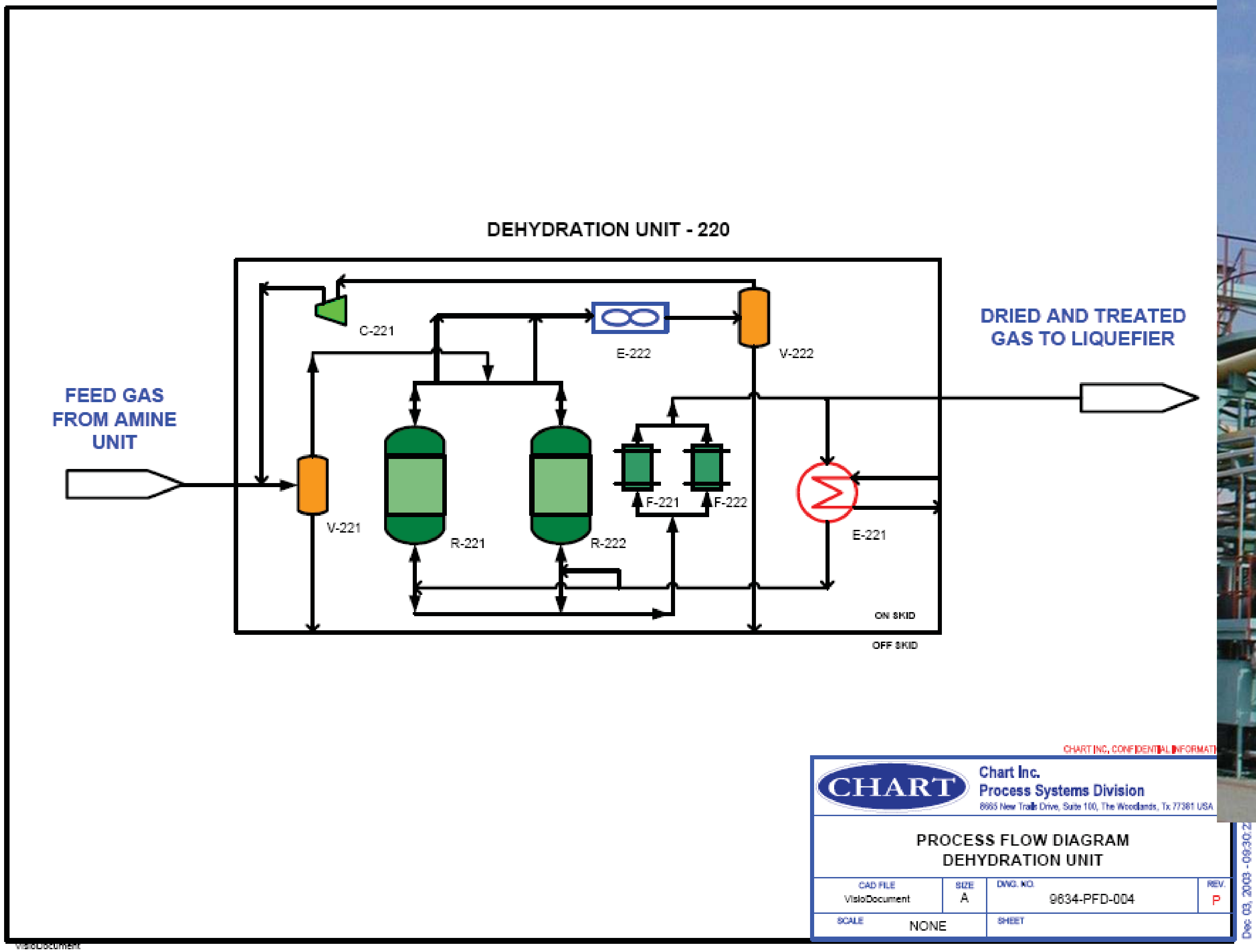
(TYPICAL AMINE UNIT)

Helium from Natural Gas

KRIO Odolanow

Crude gas purification:

- from CO_2 with adsorption on molesieve (synthetic zeolite) (similar flow scheme)

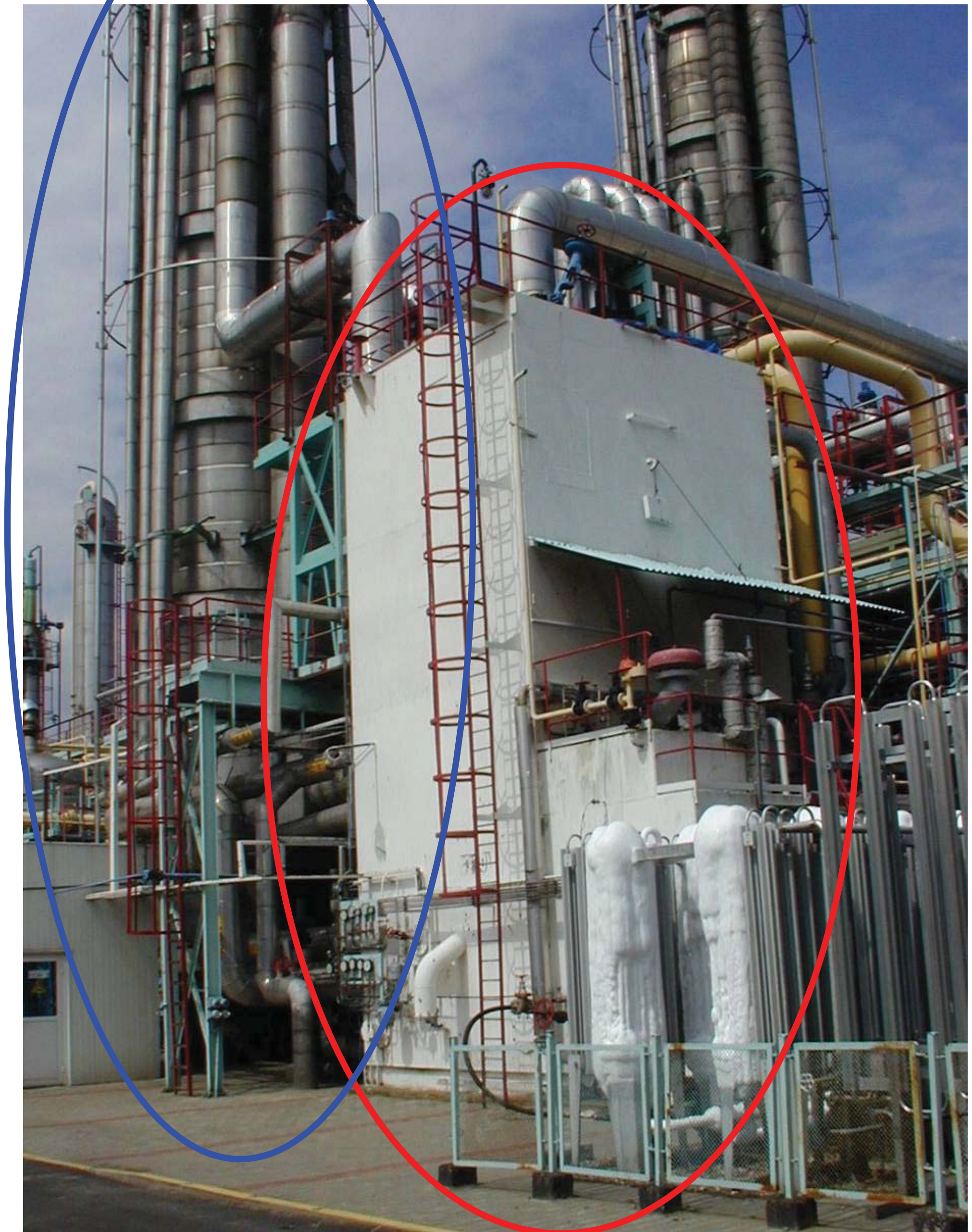


(TYPICAL DEHYDRATION UNIT)

Helium from Natural Gas

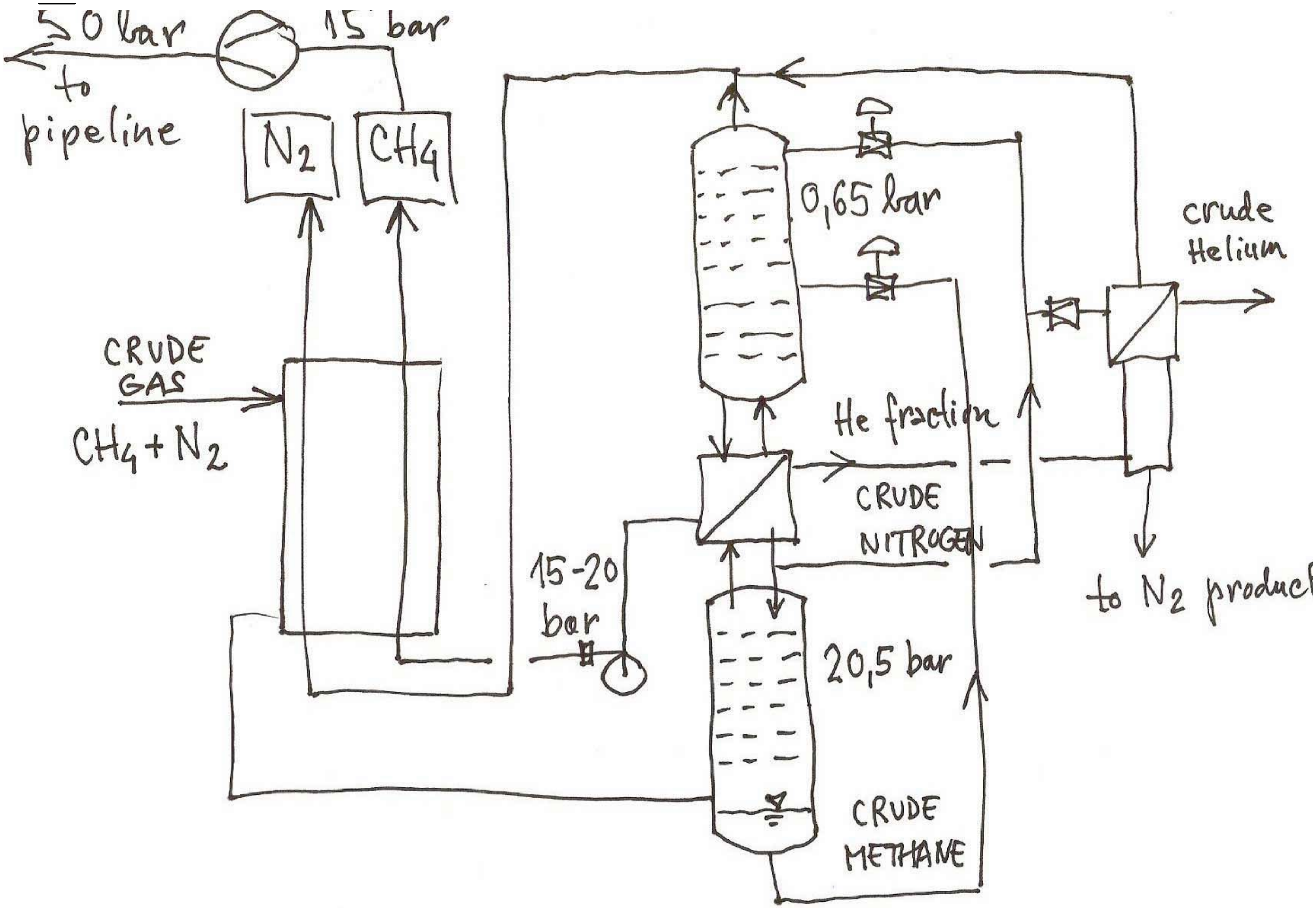
KRIO Odolanow

Cold box:
- Heat exchanger
- Distillation column



Helium from Natural Gas

KRIO Odolanow



Helium from Natural Gas
KRIO Odolanow

Helium compressor

Helium from Natural Gas

KRIO Odolanow

upper part

lower part

Helium liquefier

Helium from Natural Gas

KRIO Odolanow

Helium liquefier

upper part (closer look)

Helium from Natural Gas

KRIO Odolanow

Helium storage tank 500 m3 on the roof of the liquefier building

Helium from Natural Gas

KRIO Odolanow

Helium storage tank 500 m3 on the roof of the liquefier building

Front end of the storage tank

Helium from Natural Gas
KRIO Odolanow

Liquid helium shipping in Dewar vessels

Helium from Natural Gas

KRIO Odolanow

Compressed gas helium shipping in cylinder packs

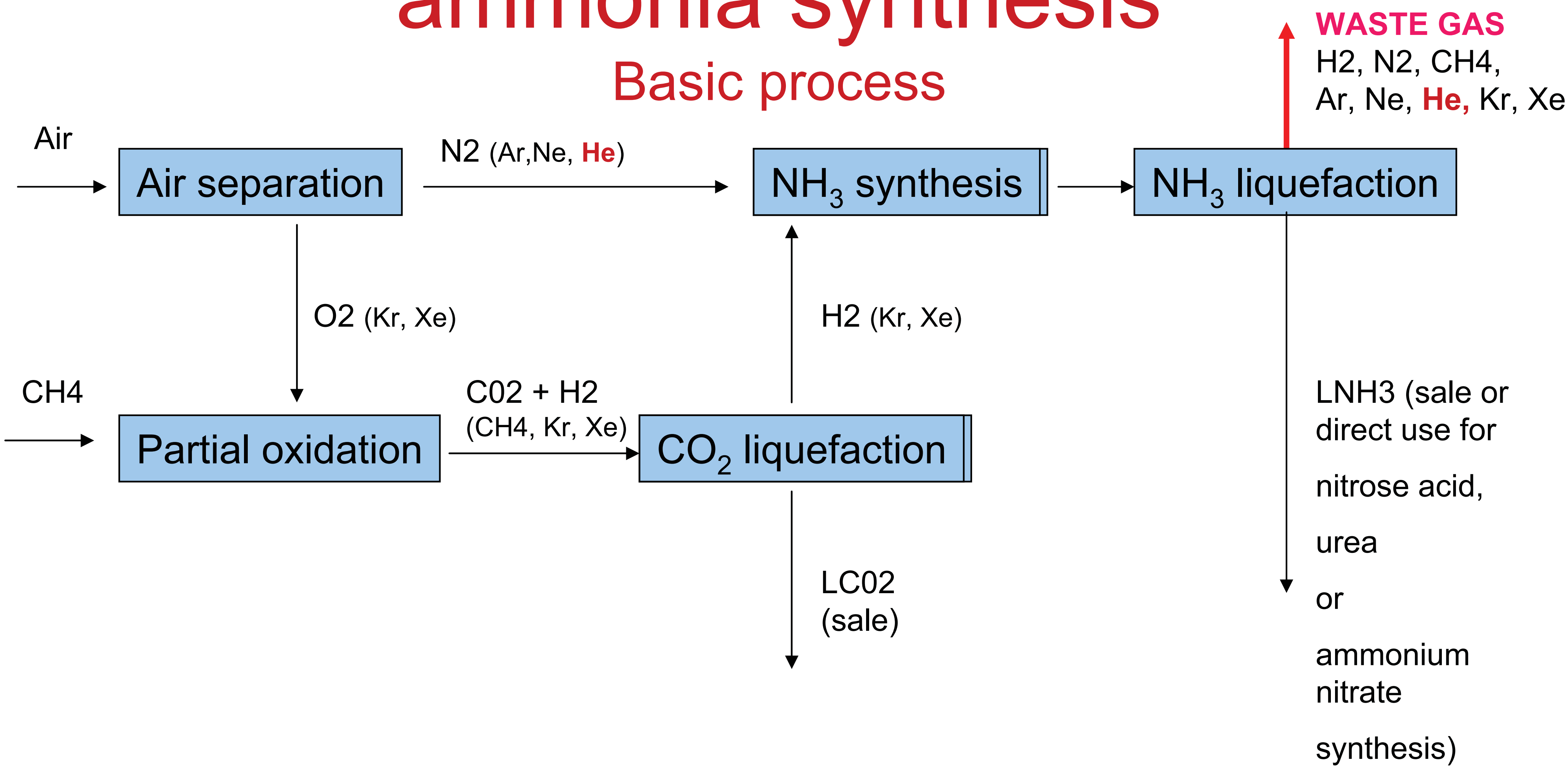
Helium from Natural Gas

KRIO Odolanow

Liquid helium shipping in road trailers

Helium from waste gases of ammonia synthesis

Basic process



Helium from waste gases of ammonia synthesis

Examples of waste gase composition

ENTERPRISE	NH_3	Xe+Kr	CH_4	Ar	N_2	Ne	H_2	He
«Azot» enterprise, Severodonetsk, Ukraine	1,7	<0,001	13,0	5,3	20,7	0,01	59	0,3
Priportovy Zavod, Odessa, Ukraine	2		8,6	5,6	19	0,01	64,4	0,4

Table 1: *Volume content of the components in the waste flows, %*

[This and further slides from: Bondarenko, Losyakov, Simonenko O., Conference Cryogenics 2008]

Helium from waste gases of ammonia synthesis

Stages of separation

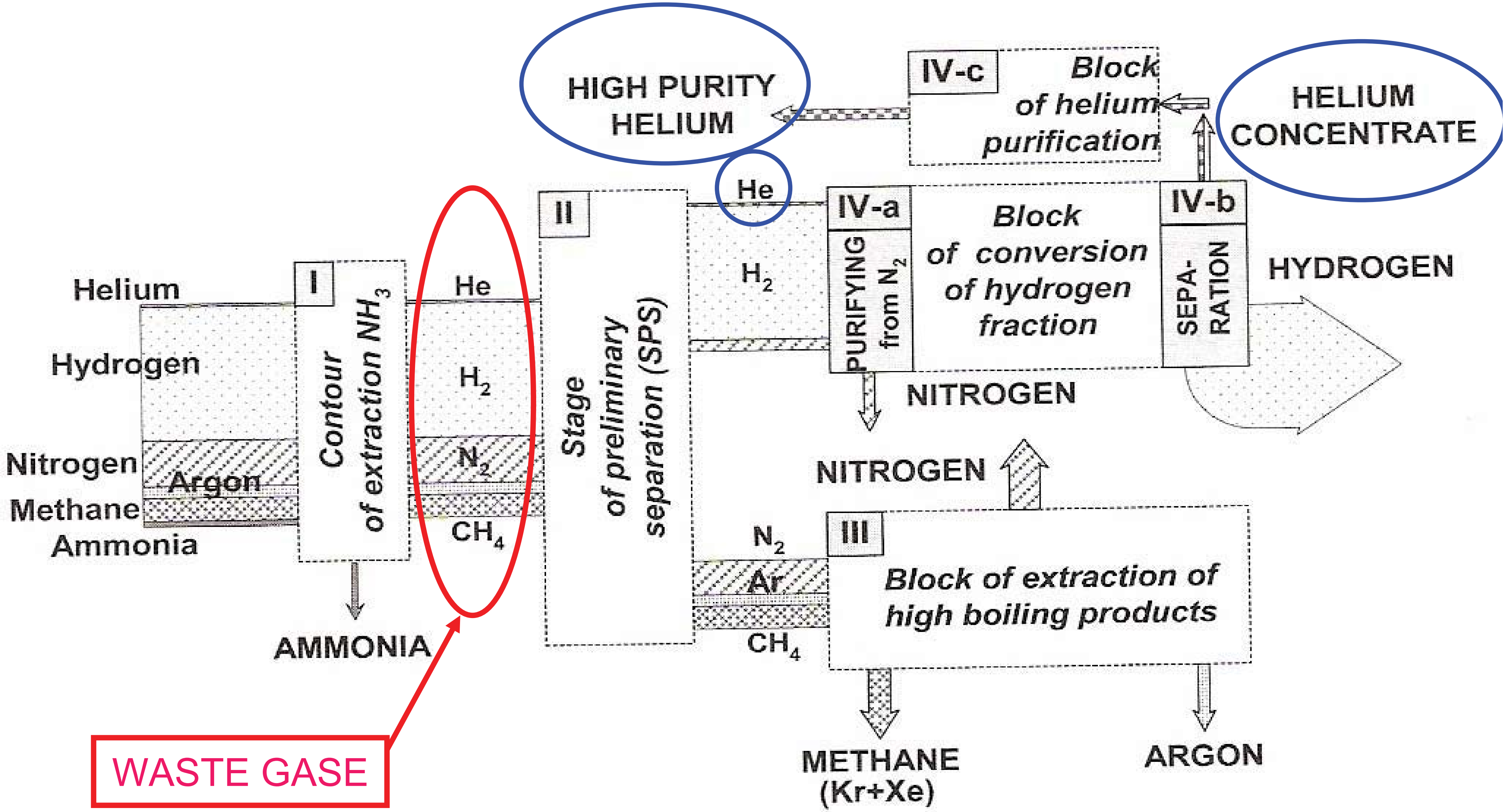


Figure 1: *The preferable sequence of complex waste flow processing*

Helium from waste gases of ammonia synthesis

Vapor-liquid equilibrium

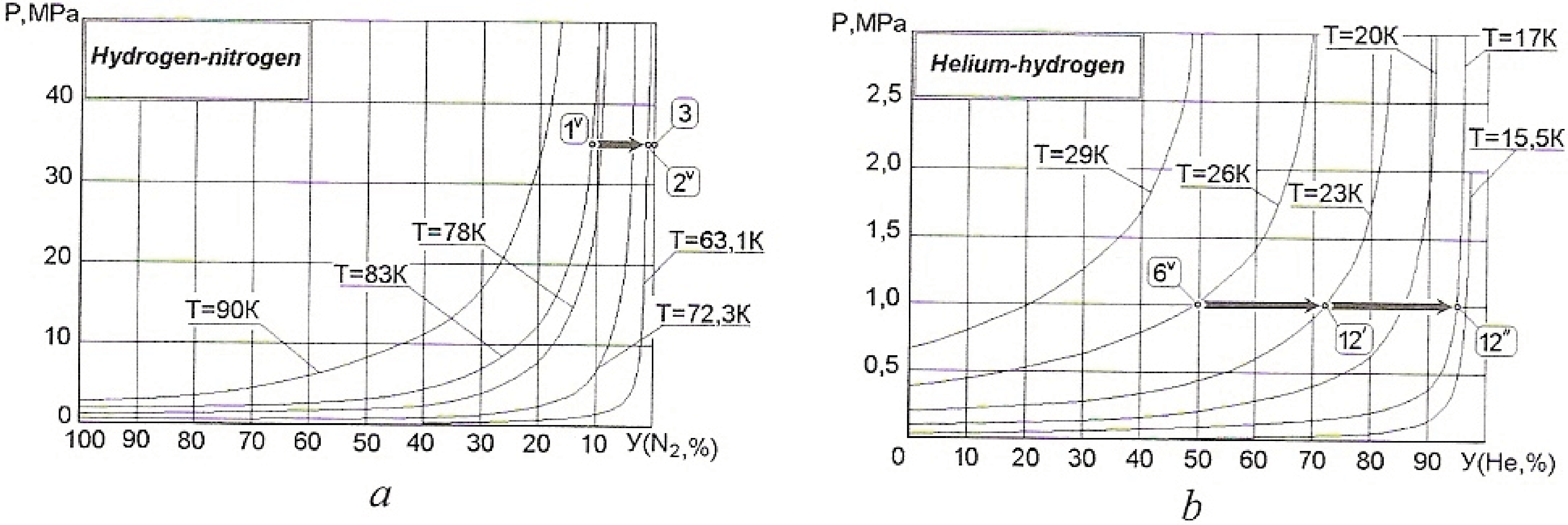
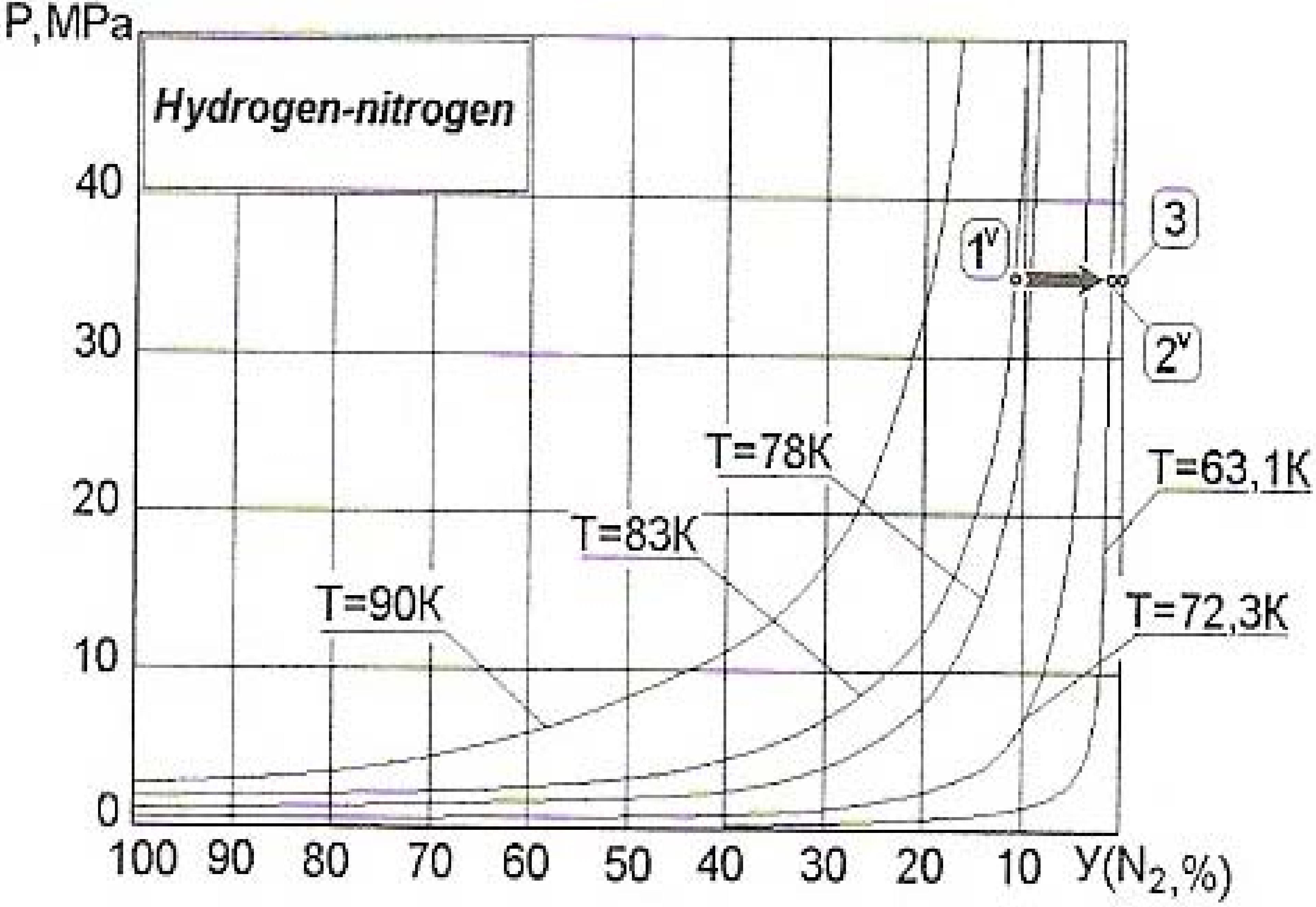
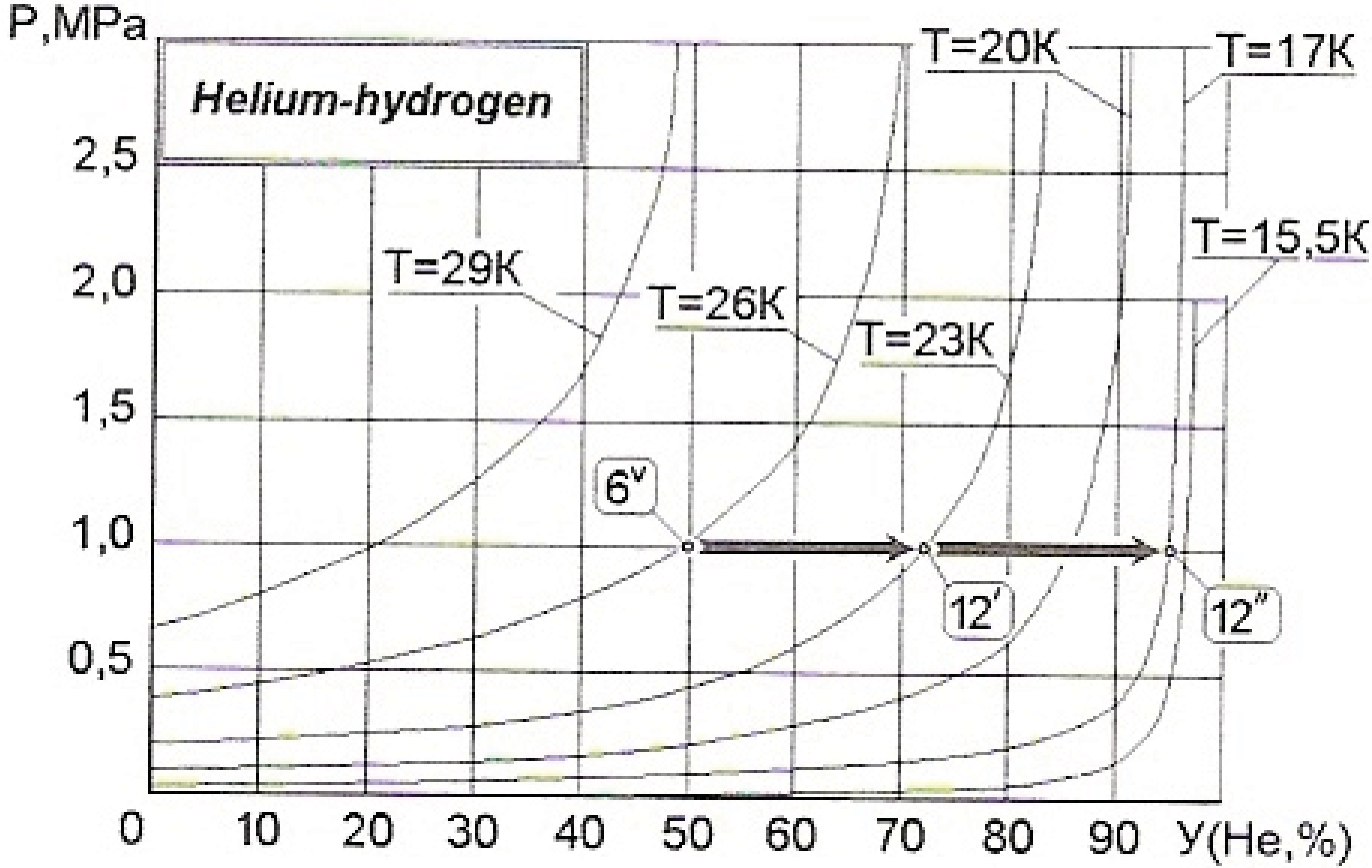


Figure 2: *Phase equilibrium isotherms of the systems H_2-N_2 (a) and He-H_2 (b) in the vapor phase.*
1^V-2^V-3 - enrichment and purification of H_2-fraction
in the additional reflux condenser RC1 and the freezer Fr (Figure 3);
6^V-12′-12″ - helium concentration process under different phase equilibrium conditions

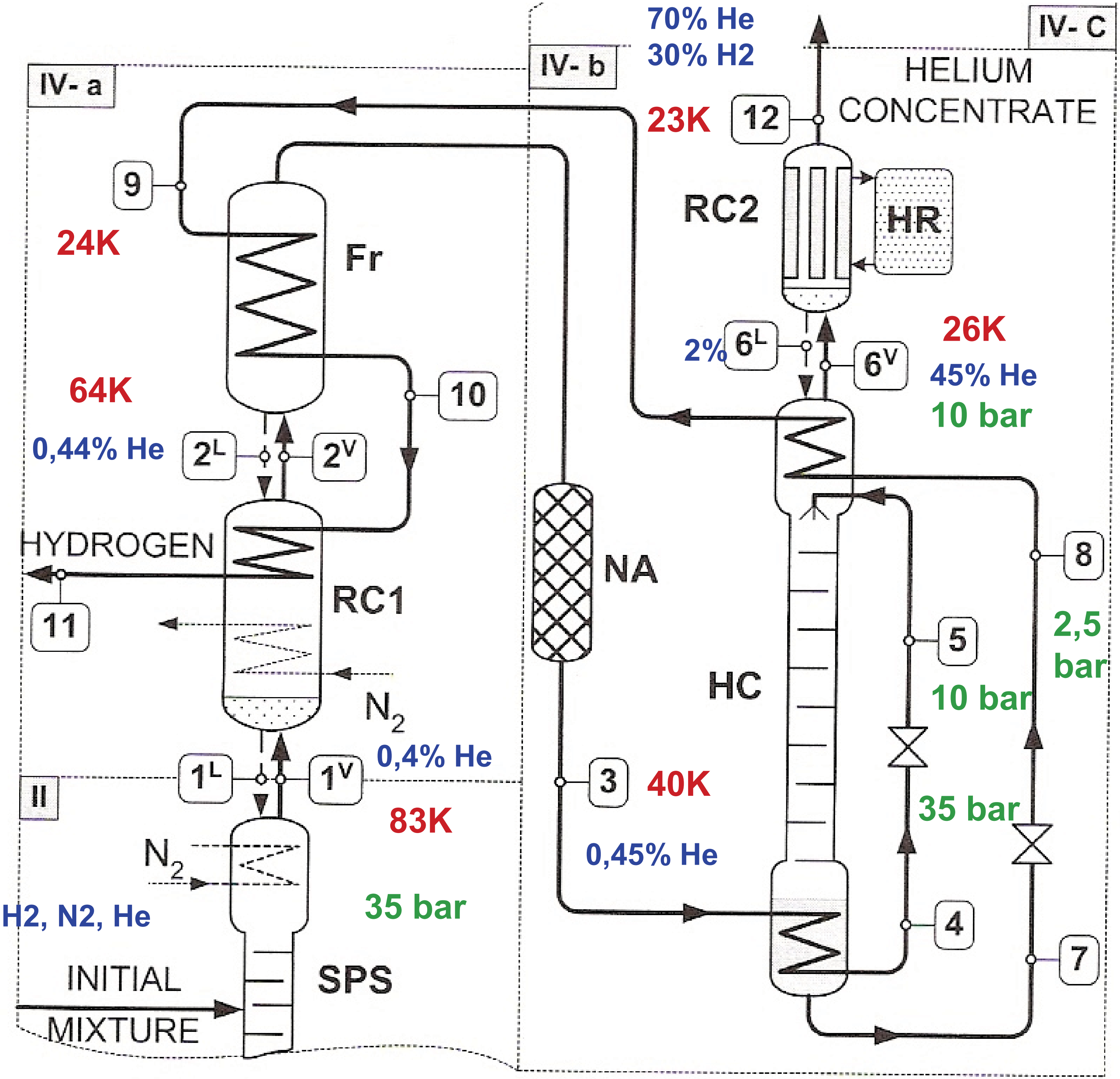

P,MPa
Hydrogen-nitrogen
40
30
20
10
0
100
90
80
70
60
50
40
30
20
10
Y(N2,%)
T=90K
T=83K
T=78K
T=72,3K
T=63,1K
1v
2v
3

a



P,MPa
Helium-hydrogen
T=20K
T=17K
T=29K
T=26K
T=23K
T=15,5K
6v
12′
12″
2,5
2,0
1,5
1,0
0,5
0
10
20
30
40
50
60
70
80
90
Y(He,%)

b



HELIUM CONCENTRATE RECOVERY

SPS- Prelim. separation

RC1- N2 reflux condenser

Fr – N2 Freezer (two of)

NA – Neon adsorber

HC – He column

RC1- He reflux condenser

HR – He refrigerator

Conclusions on He recovery

- Helium is found in some gas mixtures like natural gas or some by-products of gaseous processes in concentrations 0,005 to 2%.
- The separation methods are high-tech and energy consuming, mostly cryogenic methods
- He is an important industrial gas with unique properties, which makes it irreplaceble in many processes
- Global resources are limited and consumption is growing, which initiated administrative actions to for to prevent wasting.