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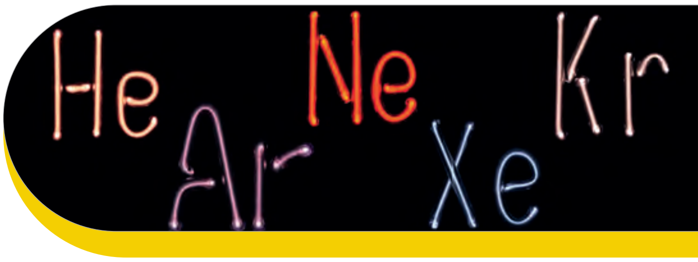

Noble gases –
supply really critical?

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The BGR (Federal Institute for Geosciences and Natural Resources) is the central geoscientific authority providing advice to the German Federal Government in all geo-relevant questions. It is subordinate to the Federal Ministry for Economic Affairs and Energy (BMWi).

DERA Rohstoffinformationen

Noble gases – supply really critical?

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Executive Summary

The chemical group of the noble gases includes the elements helium, neon, argon, krypton, xenon and radon.

All noble gases are monoatomic, colourless, odourless, non-flammable, gaseous at room temperature and chemically inert. Only xenon enters into natural compounds with halides. Helium and neon are lighter than air. Radon is radioactive.

Helium is continually formed by the radioactive decay of uranium and thorium in the Earth‘s crust and can accumulate in structural traps, similar to natural gas. More helium continuously forms than escapes into the atmosphere. Argon is formed by the radioactive decay of potassium and is highly enriched in the air (0.934% by volume). Although very common in the solar system, neon is one of the rarest non-radioactive elements on Earth. It is found in Earth‘s atmosphere about as abundantly as platinum in the crust. Krypton and xenon are much rarer both in space and on Earth.

Helium is produced almost exclusively from the liquefaction (LNG) and denitrification of natural gas. The purification of carbon dioxide natural gas and production in air separation units (ASU) play only a minor role. Argon, neon, krypton and xenon are obtained exclusively in air separation units, including argon on an exceptionally large scale in more than 950 facilities worldwide. Almost all applications require high purity, so the noble gases must be purified before use. Around 20 neon, krypton and xenon purification plants exist worldwide, located, with few exceptions, in China, Russia, Ukraine and the USA. In Germany, Linde AG and Air Liquide Deutschland GmbH each operate a crude krypton/crude xenon purification plant, while Linde AG also operates a crude neon purification plant.

Helium is used in large quantities in health technology (MRI), but also as a carrier/balloon gas, in the aerospace industry, for metal hardening, in the semiconductor industry, in analytics (gas chromatography, etc.), in gas-shielded arc welding, in metal coating, for leak detection, in technical diving, in the production of screens and optical fibres, in laser technology, in National Research Centres for cooling superconducting magnets, but also in numerous other applications, such as for filling gas storage systems for use in airbags.

In 2017, a total of 49 helium-producing facilities were in operation in Algeria, Australia, China, Germany, India, Canada, Qatar, Poland, Russia, Ukraine and the USA. With a total available capacity of approximately 252 Mm^3, approximately 165 Mm^3 of pure helium were produced, of which 55.3% originated in the USA and around one third in turn came from the Cliffside helium storage facility in Texas. 23.2% of helium production came from Qatar, 10.6% from Algeria and 2–4% each from Canada, Poland, Australia and Russia. The remaining producing countries are of no importance. For many decades, between 1917 and 1994, the USA was practically the only western helium producer. Since 1995, with the commencement of helium production in Algeria and increasing helium extraction from the Cliffside storage facility, US influence on the global helium market has begun to wane. Originating in the USA, therefore, the opinion began to spread among the professional public that global helium supplies were at risk. In 2017, the EU also classified helium as a critical commodity. However, a number of very large helium projects are underway in several countries, and in Russia in particular, and global helium potential is far from exhausted. In the medium and long term, therefore, a global helium supply shortage need not be anticipated – with the exception of short-term geopolitical shortages, such as during the 2017 *Qatar Crisis*.

Three quarters of the neon used worldwide is required in laser technology. Filling fluorescent tubes with neon for advertising purposes, however, has little relevance. Only in a few countries, such as China, Germany, France, the Netherlands, Russia, Ukraine and the USA, is crude neon produced in large air separation units or purification plants. In 2017, around 720 million litres (= 720,000 m^3) of crude neon, corresponding to approximately 360 million litres of pure neon, are said to have been produced worldwide. This supply is said to exceed demand. However, because the world neon market is very small and non-transparent, it is not possible to review and thus evaluate the few data published on neon‘s supply and demand.

Argon is used in very large quantities in the production and refinement of steel and as a shielding gas in welding, and in smaller quantities as a gas in laser technology, as a filling gas in insulating window production, in analytics and in numerous other applications. In general, argon is a suitable substitute for helium in many applications. Because of its abundance in the atmosphere, its widespread use and the numerous bulk buyers (steel smelters, metalworking companies), argon is not regarded by the international gas companies as a typical noble gas but, similar to oxygen and nitrogen, as a normal industrial gas. At least 950 air separation units were estimated to produce more than 9 bn. m^3 of argon globally in 2017. Despite rising demand, argon is a ubiquitous commodity and shortages are always regional and short-term only.

Krypton has only two major uses, for filling thermally insulating windows and for increasing the luminosity of lighting elements. For technical reasons, krypton is always produced together with xenon and is around ten times as common in air. In 2017, over 100 air separation units in numerous countries produced crude krypton/crude xenon, but crude krypton/crude xenon could only be purified to form pure krypton/pure xenon at around 20 locations. In 2017, global supply is said to have been around 130 million litres (= 130,000 m^3) of krypton; however, demand was only approximately 111 million litres. The supply situation for krypton has been non-critical for many years and the forecast for the coming years remains that way.

In contrast to krypton, xenon is around ten times less common, but its fields of application are far wider and continuously increasing. Currently, the majority of the xenon produced globally, estimated at 12.2 million litres (= 12,200 m^3) in 2017, is used to fill extremely bright bulbs (xenon spotlights), for lasers in the semiconductor industry, in basic research, as an anaesthetic and as a propellant for satellites and interstellar probes. The global xenon supply situation has been repeatedly critical in past decades, leading to large price fluctuations. Xenon is by far the most expensive noble gas and is currently one hundred times more expensive than krypton and neon, over a thousand times more expensive than helium and twenty thousand times more expensive than argon. Renewed doubling of the xenon price is predicted over the coming few years, because the foreseeable demand, assuming implementation of previously announced satellite plans, would significantly exceed the supply of xenon available on the world market. In Germany, research aimed at replacing xenon with iodine as a satellite propulsion agent, at least in the long term, is currently underway.

Acknowledgements and Feedback

The German Federal Institute for Geosciences and Natural Resources (*Bundesanstalt für Geowissenschaften und Rohstoffe* – BGR) would like to thank all companies producing and using noble gases for providing information for this study on the production, consumption and use of noble gases within their companies, in personal conversations and telephone calls. Experts from numerous companies have been friendly enough to revise the sections and subsections relating to their activities. In addition, industry associations provided statistical information, and both businesses and individuals provided the numerous photographs illustrating this study.

However, errors in the description of the sometimes very non-transparent noble gas market cannot be ruled out. Informed readers are therefore asked to notify the authors of any errors in this study.

Many thanks!

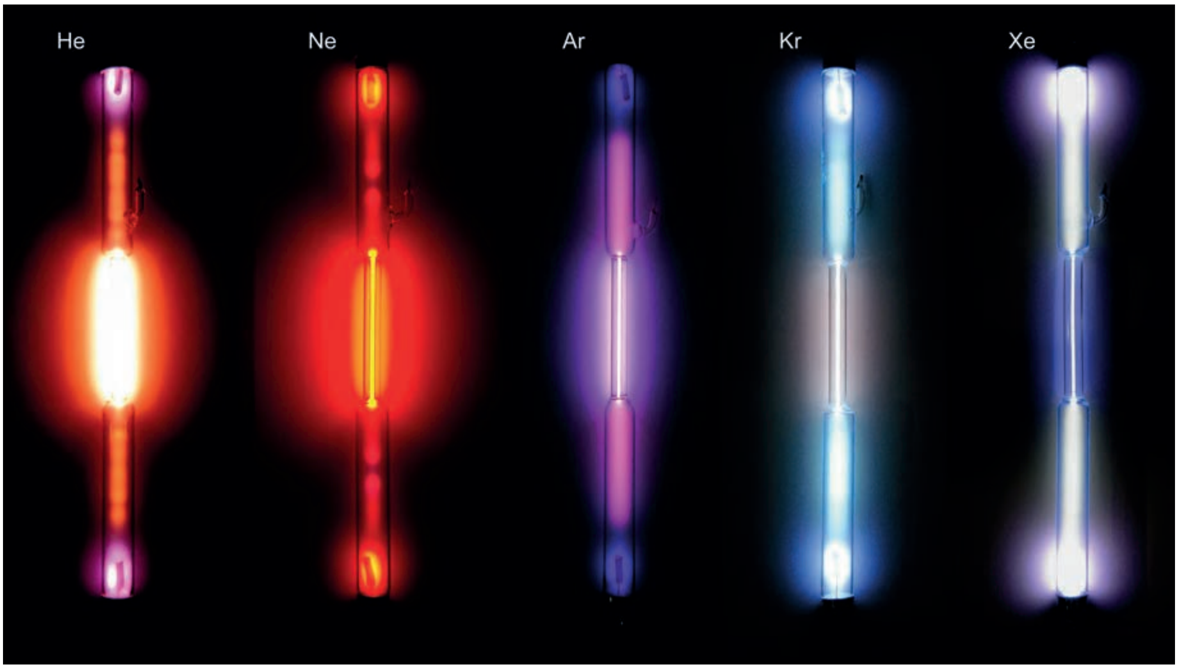


Fig. 1: The noble gases helium (He), neon (Ne), argon (Ar), krypton (Kr) and xenon (Xe) in gas discharge tubes. All noble gases glow if they are electrically excited, explaining some important applications. Photo: Heinrich Pniok (www.pse-mendelejew.de), licensed to FAL (http://artlibre.org/licence/lal/de).

„As with all rare gas shortages that I have experienced over the last 40 years,
what goes up must come down."

Richard Betzendahl, Betzendahl Gas Consultants LLC,
on the global neon market in September 2015.

1 Introduction

One of the tasks of the Federal Institute for Geosciences and Natural Resources (BGR), a federal authority subordinate to the German Federal Ministry for Economic Affairs and Energy (BMWi), together with the German Mineral Resources Agency (*Deutsche Rohstoffagentur* – DERA), is to advise the Federal Government and German companies on the availability of, and possible price and supply risks to, the supply of mineral resources.

Within this remit, BGR and DERA have previously advised German companies by hosting numerous industrial workshops or publishing studies, among other topics on rare earths, zirconium, antimony, tungsten, tin, zinc, platinum group metals, bismuth, lithium, tantalum and cobalt, as well as on quartz resources, salts, feldspar, kaolin, fluorspar and barite in Germany.

Outside the scope of these studies, only little up-to-date information is available on some of the above-mentioned resources, nor are any synoptic, recent and, more importantly, German-language publications available.

Although the United States Geological Survey (USGS) Minerals Yearbook has included a section on the *strategic resource* helium since 1933 – with an interruption during World War II – the global data situation with regard to helium, and especially the other noble gases (with the exception of radon), is otherwise very poor. In addition, the section on helium in the USGS Minerals Yearbook focusses strongly on the USA as a result of the historical development of global helium production, which was dominated entirely by the USA for decades.

While preparing this study, an attempt was therefore made to utilise independent, i.e. non-US, publications dealing with helium and the other noble gases for the evaluation, which turned out to be practically impossible. Eventually, however, two independent helium and argon studies by a commercial supplier were found, allowing a comparative discussion.

Representing technical journals, the magazine GASWORLD and its online archive were analysed; however, it turned out that the expert analyses on the supply and demand of helium published there are also entirely based on the data in the USGS Minerals Yearbook. Happily, however, there is at least one independent expert for neon, krypton and xenon, in the shape of the US consultant BETZENDAHL GAS CONSULTANTS, LCC, who monitors the global noble gas market.

With the background information, extracted from the sources discussed above, additional data available on the Internet and information provided by German market participants, it was eventually possible to compile an up-to-date overview of the noble gas resource market. However, compared to the volumes of data available, for example, on base metals or precious metals, numerous questions remain open.

With regard to the global use of noble gases, no reliable data are available, but there are good estimates, even on the rarer noble gases neon, krypton and xenon. With regard to helium, the economically most important noble gas, it is assumed, in simplification, that global demand roughly corresponds to supply in most years. This assumption must be viewed critically.

International gas companies do not publish any production figures. The volumes of neon, argon, krypton and xenon produced globally are therefore not known, although estimates are available. The helium production figures published by USGS may not be complete for the USA and flawed for the rest of the world. With regard to Russia and Poland, it was possible to research the correct production data and, with regard to the other producing nations outside the USA, some fairly reliable trade data, from which local helium production can be readily deduced.

The data situation with regard to future helium projects, on the other hand, is excellent. However, only the future will show whether these projects will be implemented as planned.

In summary, reliable conclusions on the future development of supply/demand of noble gases on the global market cannot be arrived at, unlike for most other mineral resources. Nevertheless, this up-to-date overview should assist German industry in better understanding the resource-related correlations between the noble gases – generally indispensable industrial gases – and thus in deciding either for or against possible (increased) future use of noble gases.

2 Noble gases

The group of noble gases forms the (former) main group VIII or (more recently) the 18th group in the periodic table of the elements. The name *noble gas* is derived from the fact that these elements of the 18th group of the periodic table, analogous to the precious metals, are very slow to react (inert) and are also rare – at least on Earth.

The following chemical elements are noble gases:

1. **Helium** (element symbol He, 1st period, atomic number 2), from the classical Greek ἥλιος hélios (*sun*), because it was first demonstrated in the sun‘s chromosphere in 1868.
2. **Neon** (element symbol Ne, 2nd period, atomic number 10), from the Greek νέος neos (*new*), because it was discovered as a new gas in crude argon in 1898.
3. **Argon** (element symbol Ar, 3rd period, atomic number 18), from the Greek αργό argó (*inert*), because it was discovered as a new, inert gas in air in 1895.
4. **Krypton** (element symbol Kr, 4th period, atomic number 36), from the classical Greek κρυπτός kryptós (*hidden*), because it was only demonstrated in 1896 by means of its spectral lines after almost complete evaporation of crude argon.
5. **Xenon** (element symbol Xe, 5th period, atomic number 54), from the classical Greek ξένος xénos (foreign), because it was fractionated in 1898 as a previously unknown element from crude krypton.
6. **Radon** (element symbol Rn, 6th period, atomic number 86), from the Latin *radius* (ray or beam), due to its radioactivity, and emanation, discovered in 1900 while studying the element radium and its decay products

and possibly

7. **Oganesson** (element symbol Og, 7th period, atomic number 118), artificially produced in 2006, recognised in 2015, named after the element‘s Russian co-discoverer Juri Z. Oganesjan. Oganesson has a half-life of 0.89 ms, may be reactive, is non-gaseous at room temperature and is therefore not a noble gas. Because this artificial element is of no economic importance, it shall not be given further consideration here.

The four noble gases neon, argon, krypton and xenon were discovered between 1894 and 1898 by the Scottish chemist Sir William Ramsay (1852–1916) (Fig. 2), first isolating helium from them in 1895, for which he received the Nobel Prize for Chemistry in 1904.

The international gas industry only regards the elements neon, krypton and xenon as noble gases. Helium is always considered separately and argon, similar to oxygen and nitrogen, is regarded as an industrial gas by the industry.

2.1 Properties

The unifying feature of all noble gases is that the energy levels of their atoms are all complete, i.e. completely filled with electrons. This means that noble gases only enter into chemical reactions under extreme conditions. Nor do noble gases form molecules with each other but are instead monatomic.

Despite this noble gas structure, those with a higher atomic mass (Table 1) are not completely unreactive and can form some compounds by way of van der Waals forces. The greatest variety of compounds is known from xenon and not from radon, because in the latter case the high radioactivity and short half-life make it difficult for compounds to

Fig. 2: Sir William Ramsay (1852–1916), Scottish chemist, who received the Nobel Prize for Chemistry in 1904 for the discovery of the noble gases, photo: Wikipedia.

form and be studied. Neon, in contrast, is regarded as the least reactive noble gas.

The only element capable of reacting directly with xenon and radon, and under certain conditions also with krypton, is fluorine. While the caustic and toxic krypton difluoride (KrF_2), formed in a forced reaction between krypton and fluorine, is thermodynamically unstable and can therefore only be synthesised at low temperatures, xenon and radon fluorides are also stable at room temperature. In 1962, the first artificially produced noble gas compound was the highly unstable xenon hexafluoroplatinate ($XePtF_6$). Xenon difluoride (XeF_2) is more stable and the only noble gas compound utilised technically in small quantities (see Section 3.2.5). Other elements do not react with noble gases; a variety of different compounds, made possible by fluoride reactions, are nevertheless known.

All noble gases are gaseous at room temperature. They are colourless, odourless and non-flammable. They only condense and solidify at extremely low temperatures, whereby the melting and boiling points are higher the greater the atomic mass. At 4224 K (−268.926 °C), the boiling point of helium (^4He) is only just above absolute zero (0 K or −273.15 °C); the heaviest noble gas, radon (^{222}Rn), on the other hand, boils at 211.9 K (−61.25 °C).

The densities of the noble gases also correlate with the atomic mass. After hydrogen, helium is the gas with the lowest density. Neon is the only other noble gas with a density lower than that of air, while argon, krypton, xenon and radon are denser. Radon (^{222}Rn), with a density of 9.73 g/cm^3 under normal conditions (1013.25 hPa and 0 °C), is one of the densest gases known. Hydrogen, helium and neon display static buoyancy due to their lower density than air and are therefore suitable as carrier gases (see Section 3.2), whereby neon, however, is not utilised for such applications because of its prohibitive cost. The buoyancy in the air under normal conditions (see above) is 1.203 kg/m^3 for hydrogen and 1.1145 kg/m^3 for helium.

Helium‘s unique feature is that it is the only element that does not solidify under, or even substantially above, atmospheric pressure. Instead, it enters a special state at 2.17 K (−270.98 °C), known as superfluidity (and is referred to as *Helium II*). In this state, the liquid loses its inner friction and can thus flow up high vessel walls (*Onnes effect*). Only at pressures above 25.316 bar does helium solidify at 0.775 K (−272.375 °C). These temperatures and pressures apply to the most common isotope, ^4He; the rarer, lighter, but equally stable isotope ^3He, on the other hand, has substantially different properties (cf. Table 1). It only becomes superfluid at temperatures below 0.0026 K (−273.1474 °C). The melting and boiling points of ^3He are also at different temperatures and pressures.

In addition to hydrogen and neon, helium is the only gas that heats up when it expands at standard temperatures. The heavy noble gases (argon, krypton, xenon) are also solid at room temperatures, but only under very high pressures. They should therefore also be present in solid form in the lower mantle due to the high pressures prevailing there.

Radon luminesces in both the solid and the liquid form, because of its radioactivity. Radon‘s decay products are also radioactive. Radon has 35 known isotopes, all of which are unstable. The most persistent isotope, ^{222}Rn, has a half-life of 3.824 days. The most volatile radon isotopes, on the other hand, have half-lives of less than a millisecond.

Table. 1: Selection of important atomic and physical noble gas parameters, compiled from Wikipedia, Yongchang et al. (1996), Ozima & Podosek (2002) and Messer Schweiz AG gas datasheets (note.: the parameters differ slightly depending on source).

	Helium	**Neon**	**Argon**	**Krypton**	**Xenon**	**Radon**
Symbol	He	Ne	Ar	Kr	Xe	Rn
Atomic number	2	10	18	36	54	86
Atomic weight	4.002602 u	20.1797 u	39.948 u	83.798 u	131.293 u	222 u
Atomic radius	28 pm (0.28 Å)	58 pm (0.58 Å)	106 pm (1.06 Å)	116 pm (1.16 Å)	140 pm (1.40 Å)	150 pm (1.50 Å)
Melting point at 1013 hPa	^{3}He @ 29,315 bar: 0.319 K (–272.831 °C) ^{4}He @ 25.316 bar: 0.775 (–272.375 °C)	27.09 K (–246.06 °C)	84.0 K (–189.2 °C)	116.2 K (–157.0 °C)	161.4 K (–111.8 °C)	ca. 202 K (ca. –71 °C)
Boiling point at 1013 hPa (1.013 bar)	^{3}He: 3.1905 K (–269.995 °C) ^{4}He: 4.224 K (–268.926 °C)	27.09 K (–246.06 °C)	87.295 K (–185.855 °C)	119.75 K (–153.36 °C)	165.03 K (–108.12 °C)	211.9 K (–61.3 °C)
Gas density at 0 °C, 1013 hPA (1.013 bar)	^{3}He: 0.13448 kg/m^3 ^{4}He: 0.17847 kg/m^3	0.8999 kg/m^3	1.7839 kg/m^3	3.7493 kg/m^3	5.8971 kg/m^3	9.73 g/cm^3
Gas density at 15 °C, 1000 hPA (1 bar)	^{4}He: 0.1673 kg/m^3	0.8420 kg/m^3	1.6689 kg/m^3	3.506 kg/m^3	5.514 kg/m^3	
Relative density to air at 0 °C, 1013 hPA (1.013 bar)	0.1381	0.6965	1.3807	2.9019	4.5643	7.5310
Liquid density	0.125 kg/l	1.2060 kg/l	1.394 kg/l	2.413 kg/l	2.939 kg/l	
Specific thermal conductivity at 25 °C, 1000 hPa (1 bar)	0.1567 W/(m*K)	0.0491 W/(m*K)	0.01792 W/(m*K)	0.00949 W/(m*K)	0.00569 W/(m*K)	0.00364 W(m*K)
Specific thermal conductivity at 25 °C	5192.6 J/(kg*K)	1030 J/(kg*K)	520.3 J/(kg*K)	2481 J/(kg*K)	1583 J/(kg*K)	

Under normal conditions (1.013 hPa, 0 °C) example: ^{4}helium):

- *5.60318 m^3 gaseous helium = 1.0 kg liquid helium = 8.0 l liquid helium*
- *1.0 m^3 gaseous helium = 0.17847 kg liquid helium = 1.42776 l liquid helium*
- *0.70040 m^3 gaseous helium = 0.125 kg liquid helium = 1.0 l liquid helium*

2.2 Occurrence and genesis

Helium, or its most common isotope ^{4}He (see Table 2), primarily forms during the radioactive decay of uranium (U) and thorium (Th) in granitic rocks, but also from U or Th bearing minerals in sedimentary rocks (e.g. the *Joachimsthal* pitchblende in Germany contains 0.11 cm^3 He/g of mineral) and migrates from the source along deep, steep faults and/or volcanic intrusions in the stratigraphic roof. Only where they are separated from overlying permeable rocks or the Earth's surface by thick, impermeable rock layers, usually saline rocks, anhydrites or oil shales, does the helium remain in the Earth's crust and accumulate. In addition, impermeable marginal rocks or structures are necessary to prevent the exceptionally small and light helium atoms from migrating (note: He atoms have a diameter of 56 pm (picometre: 10^{-12} m), CO_2 molecules, in contrast, are 232 pm, N_2 molecules 316 pm and CH_4 molecules 414 pm in diameter). Because accumulations of other natural gases require similar structural traps, helium is often found in natural gas reservoirs sealed over geological timescales by both overlying and lateral rocks. These natural gases are typically methane-rich (*natural gas*), but more often carbon dioxide or nitrogen-rich gases.

In the USA (cf. appendix: USA), where practically all gases are routinely examined for their helium freight, or are studied in research programmes, more than half of all gases contain < 0.1% He. Only 17.6% of all gases contain > 0.3% He and some gases substantially more. The major natural gas reserves, with economically interesting helium content (> 0.3%), are concentrated in the midwestern United States (Texas, Kansas, Oklahoma). The frequently highly nitrogenous gas reservoirs, with significantly higher helium content (up to 9.8%), however, are smaller and located in different states (Colorado, New Mexico, Utah, Arizona). They have only become economically interesting in recent years due to the rise in helium prices.

If helium is not held in structural traps in the Earth's crust during formation and reaches the Earth's surface, it escapes unhindered into the atmosphere from there and is then lost unhindered into space.

Assuming uniform uranium and thorium distribution, 13 x 10^{-12} cm^3 of helium per gram of rock may form in magmatic rocks (Yongchang et al. 1996). This corresponds to around 360 cm^3 of helium per cubic metre of magmatic rock every million years (cf. Table 5). In analogy, Ballentine & Lollar (2002) calculated the rock required and the geological timescale necessary to generate the estimated helium content (approx. 13.8 bn. m^3) of the largest natural gas field in the USA, the Panhandle-Hugoton Field (cf. appendix: USA). They arrived at 202,000 km^3 of crust over a period of 300 Ma or 114,500 km^3 of crust over a period of 530 Ma.

Depending on genesis, increased helium content can also be found in:

- Thermal waters with contact to deep magmatic rocks (cf. appendix: Germany and France)
- Mine air in anthracite mines (cf. appendix: Germany)
- Rift zones, both oceanic and continental (cf. appendix: Tanzania)

The considerably rarer, but also economically interesting, second helium isotope ^{3}He (see Table 2), originates from the decay of the hydrogen isotope ^{3}H (tritium), with a half-life of 12.32 years. All naturally occurring ^{3}He originates in Earth's mantle and can presumably be traced back to Earth's formation and to the segregation of the core, mantle and crust. ^{3}He will only play a very minor role in this study.

^{3}He/^{4}He isotope ratios are indicators of the origin of natural gases. The ratio in our atmosphere is influenced by crustal outgassing, solar winds and input into the atmosphere by interplanetary gases and is ^{3}He/^{4}He = 1.399 ± 0.014 x 10^{-6} (lower bound in the atmosphere) (Yongchang et al. 1996). In the mantle, in contrast, the ^{3}He/^{4}He isotope ratio is (1.1–1.4) x 10^{-5}.

Table 2: Frequencies of noble gases and hydrogen, after OZIMA & PODOSEK (2002), Wikipedia and www.periodensystem-online.de.

	Universe	**Universe** (atoms per 10^6 atoms of Si)	**Rank in the universe**	**Solar system** (atoms relativ to Si, Si = $1*10^6$)	**Earth atmosphere**1) (volume in ppm)	**Earth crust Clarke value** (weight in ppm)	**Stable isotopes** (natural abundance)
H_2	74.989 %	$2.79*10^{10}$ (^{1}H)	1.	$3.18*10^{10}$	1)	1500 – 29.000 (0.15 – 2.9 %	^{1}H: 99.9885 % ^{2}H: 0.0115 %
He	23.01 %	$2.72*10^9$ (^{4}He)	2.	$2.21*10^9$	5.24	0.008 – 0.01	^{3}He: 0.000138 % ^{4}He: 99.999862 %
Ne	1.298 g/kg	$3.20*10^6$ (^{20}Ne)	5.	$3.44*10^6$	18.18	0.005	^{20}Ne: 90.48 % ^{21}Ne: 0.27 % ^{22}Ne: 9.25 %
Ar	170.3 mg/kg	$8.50*10^4$ (^{36}Ar)	11.	$1.172*10^5$	9340 (0.934 %)	3.5 – 4	^{36}Ar: 0.3364 % ^{38}Ar: 0.0632 % ^{40}Ar: 99.6004 %
Kr	247.242 µg/kg	25.7 (^{84}Kr)	30.	46.8	1.14	$(1 – 2)*10^{-4}$	^{78}Kr: 0.347 % ^{80}Kr: 2.257 % ^{82}Kr: 11.52 % ^{83}Kr: 11.48 % ^{84}Kr: 57.00 % ^{86}Kr: 17.40 %
Xe	9.106 µg/kg	1.24 (^{132}Xe)	35.	5.38	0.087	$3*10^{-5}$	^{124}Xe: 0.095 % ^{126}Xe: 0.088 % ^{128}Xe: 1.919 % ^{129}Xe: 26.44 % ^{130}Xe: 4.077 % ^{131}Xe: 21.22 % ^{132}Xe: 26.89 % ^{134}Xe: 10.430 % ^{138}Xe: 8.857 %
Rn					$4.6*10^{-13}$	$7*10^{-12} – 4*10^{-13}$	5 natual, but instable isotopes

1) *Dry, water vapour-free air outside of active volcanoes and nuclear power stations*

In summary, helium is a mixture of ^{4}He and ^{3}He and forms as:

1) Radiogenic helium (^{4}He) by α decay in U and Th (cf. Table 4) in Earth's crust. One gram of thorium produces 24,600 atoms of ^{4}He/s, one gram of uranium, in contrast, 103,000 atoms of ^{4}He/s (Sears 2015).
2) Helium from Earth's crust (^{3}He). Current ^{3}He mantle outgassing is estimated at around 1000 mol/a, corresponding to approximately 4 atoms/cm^{2}/s. In the maars of the East Eifel region, ^{3}He outgassing of as much as 7400 atoms/cm^{2}/s has been measured (Ozima & Podosek 2002).
3) Atmospheric helium (cf. Table 3) from ^{4}He and ^{3}He crustal outgassing at around 190 g/s or 16.4 t/d (Clarke & Clare 2012).

   Annually, 1125 x 10^{30} He atoms are created in the mantle and the crust, of which only 7 x 10^{30} He atoms escape to the atmosphere, however (Sears 2015). Helium is therefore constantly accumulating in the crust.

Crustal **argon** is also derived from three different sources:

1) Radiogenic ^{40}Ar from the radioactive decay of ^{40}K in potassium-bearing rocks. ^{40}K represents only 0.0117% of natural potassium, 89.28 % of which decays to form ^{40}Ca. The remaining 10.72%, however, decays with a half-life of 1.28 billion years to form ^{40}Ar (cf. Table 2).
2) Argon from Earth's mantle, arriving in the crust through deep faults and/or along volcanic dykes. The ^{40}Ar/^{36}Ar isotope ratio in the mantle is very much higher than that of the atmosphere and is up to 10,000 in the upper mantle, and approximately 400 in the lower mantle.
3) Atmospheric argon from precipitation captured at the time of sedimentation. This argon has a characteristic ^{40}Ar/^{36}Ar isotope ratio of 295.5.

If argon does not also collect, together with other gases, in structural traps in the crust, it migrates to the surface and accumulates in the atmosphere, in contrast to helium. Here, it is currently by far the most common noble gas (cf. Table 2).

Neon is far more common in the universe as a whole than argon but is much rarer in Earth's crust and atmosphere (cf. Table 2). The ^{20}Ne isotope is formed in what is known as carbon burning during the fusion of ^{13}C and ^{12}C. The remaining two

Table 3: Composition of dry air, after Ozimar & Podosek (2002).

Gas	Molecular weight (^{12}C = 12)	Volume fraction	Total atmosphere
dry air[1]	28.9644	100 %	$3.961*10^{18}$ m^{3}
N_2	28.0134	78.084 % ± 0.004 %	$3.093*10^{18}$ m^{3}
O_2	31.9988	20.948 % ± 0.002 %	$8.298*10^{17}$ m^{3}
Ar	39.9481	0.934 % ± 0.01 %	$3.700*10^{16}$ m^{3}
CO_2	44.0099	0.0405 %[2]	$1.604*10^{15}$ m^{3}
Ne	20.1798	$(1.818 \pm 0.004)*10^{-3}$ % (= 18.18 ppm)	$7.202*10^{13}$ m^{3}
He	4.0026	$(5.24 \pm 0.05)*10^{-4}$ % (= 5.24 ppm)	$2.076*10^{13}$ m^{3}
CH_4	16.04	$1.87*10^{-4}$ %[2] (= 1.87 ppm)	$7.407*10^{12}$ m^{3}
Kr	83.7982	$(1.14 \pm 0.01)*10^{-4}$ % (= 1.14 ppm)	$4.516*10^{12}$ m^{3}
N_2O	44.013	$3.30*10^{-5}$ %[1] (= 0.33 ppm)	$1.307*10^{12}$ m^{3}
Xe	131.2936	$(8.7 \pm 0.1)*10^{-6}$ % (= 87 ppb)	$3.446*10^{11}$ m^{3}
CO	28.010	$(5 – 12)*10^{-6}$ % (= 5 – 12 ppb)	$1.98 – 4.75*10^{11}$ m^{3}
Rn	226.0254	$4.6*10^{-18}$ %	0.1822 m^{3}

± = Natural fluctuation in Earth's atmosphere

[1] The proportion of water vapour in the air fluctuates strongly from region to region and averages 1.3%

[2] Mean value in 2017

stable neon isotopes, ^{21}Ne and ^{22}Ne (see Table 2), on the other hand, form primarily within red giant stars from ^{20}Ne. On Earth, neon is one of the rarest non-radioactive elements and is about as abundant in the atmosphere as platinum is in the crust. Neon does not enter into any chemical compounds (cf. Section 1) and is also monoatomic. It has a small diameter (116 pm, see above) and is thus volatile. The neon that was present during Earth‘s formation has largely escaped into space and the current neon level will continue to decrease with time. New natural neon (^{22}Ne) is currently created on Earth in small quantities during decay of the radioactive isotope ^{22}Na, which has a half-life of 2.603 years. In addition, new ^{21}Ne or, more rarely, ^{22}Ne, are formed from the action of α radiation (from the decay of U and Th) on ^{18}O or ^{19}F. However, during the radioactive decay of U and Th only around one ^{21}Ne nuclide is produced for every million ^{4}He nuclides.

The heavy, non-radioactive noble gases **krypton** and **xenon** also predominantly originate from the beginning of Earth‘s formation but have not yet escaped the atmosphere because of their higher density and greater atomic diameters. In addition, the isotopes ^{128}Xe and ^{130}Xe are newly formed on Earth during the decay of ^{128}Te and ^{130}Te respectively, accounting for 31.74% and 34.08% of natural tellurium and which decay with a half-life of around one sextillion years. The isotope ^{82}Kr, on the other hand, is created during decay of the ^{82}Se isotope, representing 8.82% of natural selenium and which has a half-life of 97 quintillion years (cf. Table 4).

Radioactive radon (Rn) is completely different to the other noble gases in that it is continuously formed by the decay of radium (Ra).

The most persistent and, at almost 100%, most common of the 34 known radium isotopes is ^{226}Ra. It is created almost entirely as a decay product of ^{238}U. However, for 2.78 million ^{238}U atoms, there is only one ^{226}Ra atom. One tonne of natural uranium with a ^{238}U percentage of around 99.2% therefore only contains 353 mg of radium. In addition, three other radium isotopes in the ^{232}Th and ^{235}U decay series exist in nature: ^{228}Ra, ^{224}Ra and ^{223}Ra. However, they only occur in traces. For example, one tonne of the mineral thorite ($ThSiO_4$) contains only 0.36 mg ^{228}Ra (www.periodensystem-online.de).

The most common, and one of a total of three, natural radon isotope is ^{222}Rn (*radon*). It forms from the most common isotope of radium, ^{226}Ra, with a half-life of 1602 years, itself having a half-life of 3.8235 days and further decays via ^{218}Po, ^{214}Pb, ^{214}Bi, ^{214}Po, ^{210}Pb, ^{210}Bi and ^{210}Po, finally forming stable ^{206}Pb.

The radon isotope ^{220}Rn (*thoron*) is formed from the radium isotope ^{224}Ra, with a half-life of 3.6319 days, itself having a half-life of 55.6 seconds and decaying to ^{216}Po and then further via ^{212}Pb, ^{212}Bi and ^{208}Tl/^{212}Po to form stable ^{208}Pb.

The third natural radon isotope is ^{219}Rn (*actinon*). It forms from the radium isotope ^{223}Ra, with a half-life of 11.453 days, and decays further with a half-life of 3.96 seconds to form ^{215}Po, ^{211}Pb, ^{211}Bi and ^{207}Tl, and finally stable ^{207}Pb. Numerous other of the 35 known radon isotopes originate from the decay of radium isotopes. However, they do not occur naturally and very quickly decay further to form polonium or francium isotopes (Sextro 1994).

At the same time, only about 0.2 m^{3} of naturally occurring radon exists in the entire atmosphere (cf. Table 3). Even in near-surface air and in areas where radon is an emitted ground gas, it occurs at levels as low as about 1000 atoms per litre of soil air, i.e. in the ppt range. However, the gas is continuously formed by the radioactive decay of uranium and thorium, or radium, and cannot escape. For example, there is an increased risk of radioactive contamination from insufficiently ventilated underground mines, underground water tunnels, caves, wells or cellars. This, however, is mainly due to the formation of the radioactive heavy metals polonium and, subordinately, lead and bismuth, to which radon continues to decay (cf. Section 3.3).

Granites, rhyolites, pegmatites, volcanics (pumice, pyroclastics), carbonaceous black shales, coals, hydrothermal ore formation, for example of fluorspar, jointed and sheared rocks, as well as dry, permeable soils, all facilitate increased or high radon concentrations. The same applies to heavy mineral-, glauconite-, bauxite-, apatite-, phosphate- or uranium-/thorium-rich rocks and mining spoil tips.

Sedimentary deposits (primarily marine or fluvial sands and gravels) and sedimentary rocks (non-carbonate mudstones, quartzites, lime-

Table 4: Natural radionuclides, which decay to form noble gases (Ozimar & Podosek 2002).

Parent	Half life in billon years	Decay	Noble gas decay product	Number of noble gas atoms
^{238}U	4.468	α	^{4}He	8
^{235}U	0.8038	α	^{4}He	7
^{232}Th	14.01	α	^{4}He	6
^{40}K	1.251	β	^{40}Ar	0.1048
^{82}Se	$97*10^{18}$	ββ	^{82}Kr	1
^{129}I	0.0157	β	^{129}Xe	1
^{128}Te	$(0.7 – 2.9)*10^{21}$	ββ	^{128}Xe	1
^{130}Te	$(0.7 – 2.9)*10^{21}$	ββ	^{130}Xe	1
^{238}U	4.468	Nuclear fission	^{86}Kr, ^{136}Xe	
^{244}Pu	0.082	Nuclear fission	^{86}Kr, ^{136}Xe	

Table 5: Formation of noble gases since the origin of the Earth 4.5 billion years ago (Ozimar & Podosek 2002).

Noble gas isotope	from the crust	from the mantle	Remark
^{4}He	$5.6*10^{16}$ m³	$9.2*10^{16}$ m³	from decay of U
^{4}He	$2.0*10^{16}$ m³	$4.5*10^{16}$ m³	from decay of Th
^{23}Ne	$1.9*10^{9}$ m³	$3.2*10^{9}$ m³	from ^{18}O (α. n)
^{22}Ne	$3.6*10^{8}$ m³	$1.6*10^{7}$ m³	from ^{19}F (α. n)
^{38}Ar	$2.1*10^{7}$ m³	$3.5*10^{6}$ m³	from ^{35}Cl (α. p)
^{40}Ar	$5.0*10^{15}$ m³		from decay of ^{40}K
^{86}Kr	$2.9*10^{7}$ m³	$5.5*10^{7}$ m³	from fission of ^{238}U
^{136}Xe	$1.8*10^{8}$ m³	$3.3*10^{8}$ m³	from fission of ^{238}U

stones), clayey soils and moist soils emit little radon or retain radon.

Metamorphic rocks (gneisses, shales, etc.), sandstones and marls have quite different radon potentials and require a case-by-case investigation (SSK 1992, Schumann et al. 1994).

3 Production and uses

3.1 Production and processing

3.1.1 Helium

Helium (^4He) is produced:

a) In the liquefaction of natural gas to *liquefied natural gas* (LNG) in LNG facilities, currently in Algeria, Australia and Qatar. Here – put very simply – the crude gas is cleansed of all undesirable constituents, for example N_2, CO_2, H_2O, H_2S, H_2, O_2, Hg, He, Ne, Ar and the heavy hydrocarbons using a wide variety of methods such as *temperature-swing adsorption* (TSA) or cryogenic fractionating distillation (rectification). The remaining methane, almost pure at 98 % CH_4, is cooled to below its –162 °C boiling point and thus liquefied to a shippable and saleable product. Its constituents are separated from the remaining *tail gas* in succession and from each other using the principle of *pressure swing adsorption* (PSA) or cryogenic distillation, whereby below –246.06 °C, neon's boiling point, only helium remains as gas and is drawn off last. Helium purities of 99.999% He can be achieved in numerous process steps. In the majority of cases the helium is also liquefied, because it is then much easier to transport and market over long distances – in special containers (cf. Section 5.1).

b) During denitrification of natural gas, currently in the USA, Russia and Poland, for example. In order to reduce the excessive levels of non-combustible nitrogen in some natural gas reservoirs (and simultaneously, in China and India, to prioritise nitrogen and helium production as additional saleable products), nitrogen and helium are converted by pressure swing adsorption or separated at low temperatures by cryogenic fractionating distillation. In the USA, in particular, some older helium facilities initially produce crude helium with 60–80% He, which must then be purified in other facilities to produce pure helium at 99.995% He. Numerous variants and patents are associated with this process. In comparison, the membrane separation process via gas permeation has offered an alternative for some years, in which phase transformation of the gas does not take place. This membrane separation method is based on the selectivity of different membrane materials with respect to the diffusion behaviour of specific gas molecules. An up-to-date overview of current process technologies for the separation of helium from natural gases with a comprehensive bibliography is provided by Epcm (2017). In the USA and Canada, helium-rich nitrogen gases have also been produced for a number of years as a result of the sharp increase in helium prices and are being processed using similar technical methods, primarily to produce helium.

c) In the purification of natural carbon dioxide gas. Carbon dioxide is used in fracking in the USA, and gas producer Air Products and Chemicals, Inc. decided to process a highly CO_2-rich natural gas, thereby producing helium as a saleable product. In 2015, the world's first CO_2-based helium plant was inaugurated at the Doe Canyon/Colorado site (see Fig. 3)

d) From the nitrogen fraction in air separation (see Section 3.1.2), currently in Leuna in Germany, Ukraine and China, for example. Here, helium is obtained as a by-product of neon production, where it is present in the crude neon–helium fraction at up to 24%. It is obtained from here by compressing the gas mixture to 180 bar and then gradually cooling to –220 °C. During final decompression to 25 bar, the neon condenses, while the helium remains gaseous and can be separated. Because helium and neon levels in air are very low (cf. Table 3), this form of helium production is highly complex and expensive, and the volume of helium produced compared to helium production methods a) and b) is very low (1.4 m^3 He/h in a moderately sized air separation unit with a capacity of 2000 t O_2/d).

In contrast to ^4He which, at 99.999862%, dominates in natural helium by far, some of the ^3He in the atmosphere is artificial in origin. ^3H (tritium), created as a by-product of nuclear fission, decays to form ^3He with a half-life of 12.3 years. Large quantities of ^3He are therefore created in nuclear reprocessing plants, nuclear weapons factories and nuclear reactors. The US Department of Energy maintains a central tritium reserve for nuclear weapons production at its Savannah River facility in Georgia. The ^3He constantly being formed there is sold and utilised commercially after purification (cf. Section 3.2.1). If demand for ^3He continues

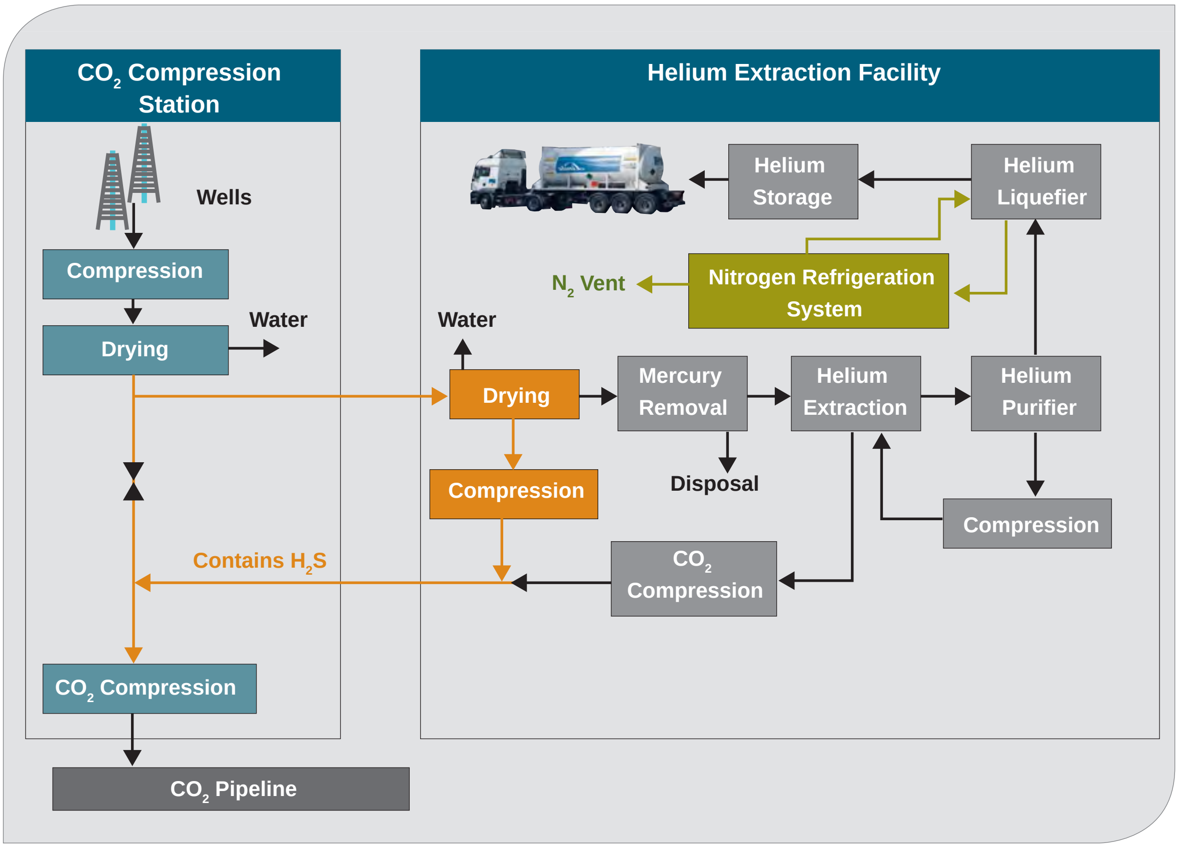


Fig. 3: Principle of CO_2 purification and separation of helium at the Doe Canyon/Colorado site, diagram: Air Products and Chemicals, Inc.

to rise sharply, it could also be obtained directly from nuclear reactors or separated from previously liquefied helium by further cooling.

3.1.2 Neon

For a long time, neon was produced exclusively in air separation using the Linde process, named after the German engineer Carl Paul Gottfried von Linde (1842–1934, founder of today‘s Linde AG) who developed it in 1895 and in which oxygen and nitrogen are produced as additional components. (Note: however, this only applies if the international demand for neon is high, because oxygen and nitrogen are always the main valuable gases, with few exceptions. In addition, separation of the noble gases neon, krypton and xenon in air separation units is only worthwhile if they have a relatively high minimum capacity of 800 t (depending on price and currently 2000 t) oxygen/d. According to Clarke & Clare (2012), the additional costs for helium/neon production in conjunction with the construction of a new air separation unit are around 1% of the total costs.

For energy reasons, the classic Linde air separation process is no longer used in newer systems and instead a two-column apparatus is used. Ambient air is compressed to approximately 6 bar and then water vapour, carbon dioxide and the majority of hydrocarbons are removed. The purified air is cooled to around –175 °C in the main heat exchanger. Cooling is carried out by means of internal heat exchanging – cold gas streams previously generated in the overall process cool the compressed air. Further cooling is achieved by relaxing a compressed air sub-flow. Here, the air is partially liquefied and can now be separated into pure oxygen and pure nitrogen in the actual air separator. The air separator consists of two separating columns, the medium pressure and the low pressure columns. The separation process exploits the different boiling points of the constituents of air: oxygen liquefies at –183 °C and nitrogen at –196 °C. Thanks to an intensive exchange of material and heat between the rising vapour and the draining liquid, pure nitrogen is obtained by continuous evaporation and condensation at the top of the low-pressure column, and almost pure oxygen at the bottom, the *sump*.

An intermediate gaseous nitrogen fraction, which also includes neon, among other things, is obtained at the top of the medium-pressure column. The nitrogen content of the continuously withdrawn nitrogen fraction is reduced by fractional distillation, until it comprises approximately 35–37% Ne, 50% N_2 and 13–15% H_2 + He. Other typical crude neon fractions contain 50–55% Ne, 30% N_2, 15–20% He and 1.5% H_2. This gas mixture can be purified further using a variety of methods: for example, it is possible to catalytically react the hydrogen with a defined volume of oxygen and to precipitate the resulting water as ice. The nitrogen can be removed by adsorption on silica gel. The resulting gas mixture comprising 70–76% Ne and 24–30% He can then be separated by compression to 180 bar and subsequently cooling, in stages, to –220 °C. Here, the neon liquefies while helium remains gaseous. In order to obtain high-purity neon, it must once again be subjected to fractional distillation in special facilities, whereby the helium, which boils at 20 K lower, can be relatively easily separated off and liquid neon, which only contains around 5–10 ppm He impurity, remains.

3.1.3 Argon

Argon, too, is primarily produced by fractional distillation from air (Linde process). To make matters worse, the boiling point of argon (–189.2 °C) lies between the boiling points of oxygen (–183 °C) and

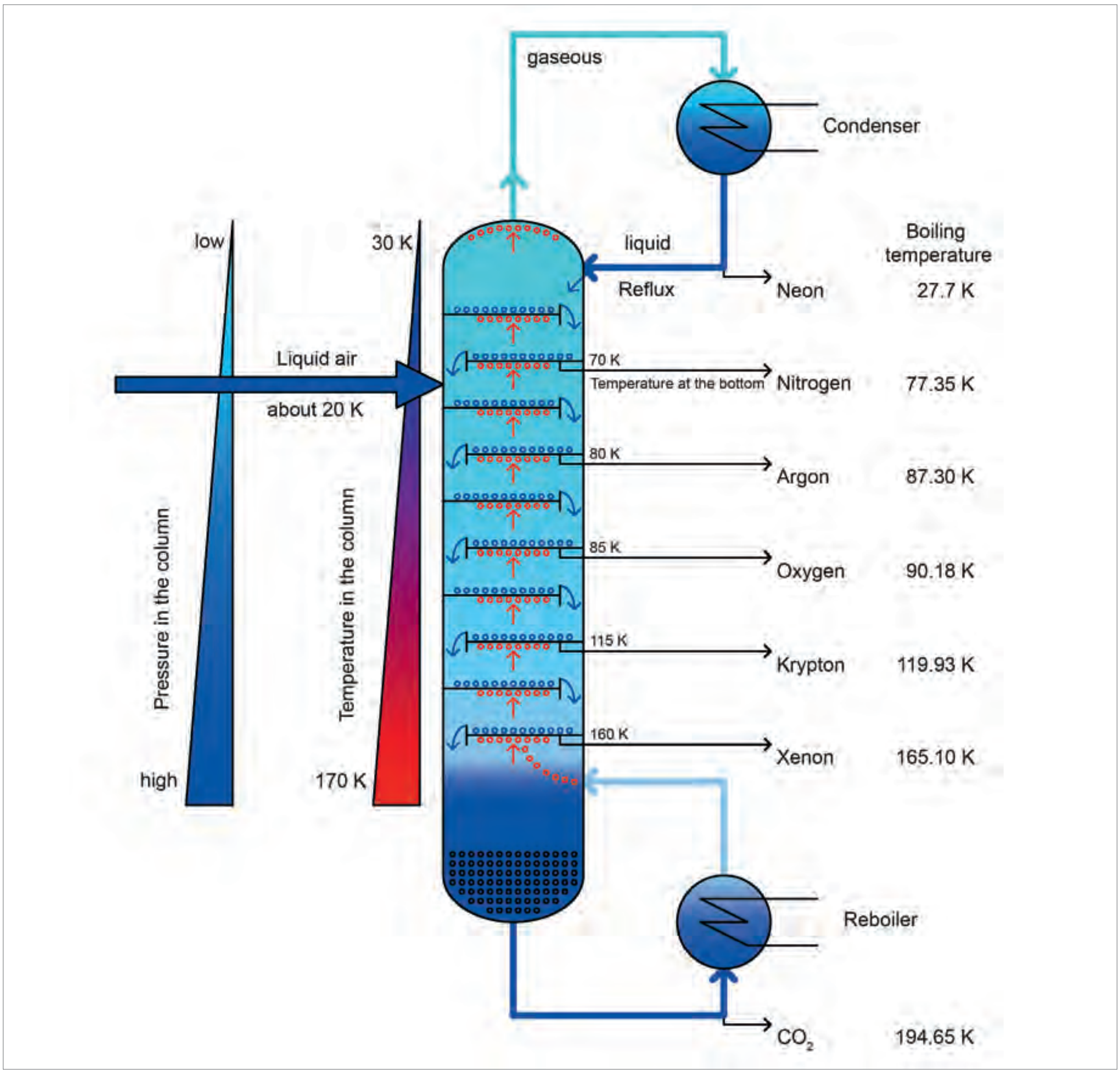


Fig. 4: Principle of fractionating distillation with the aid of a rectification column, diagram: Mordechai1/Wikipedia.

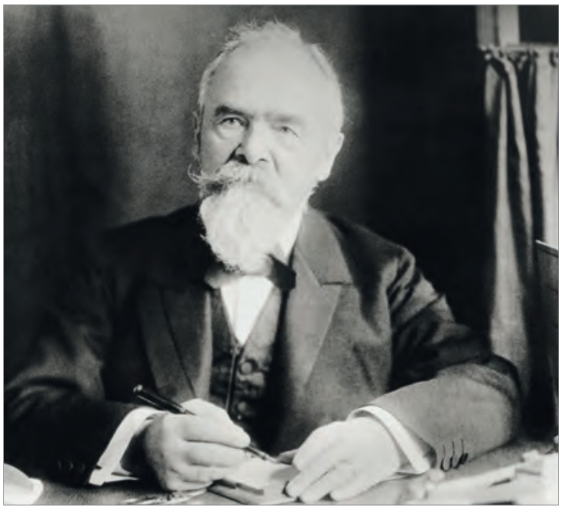


Fig. 5: Carl Paul Gottfried von Linde (1842–1934), German engineer and founder of today's Linde AG, who developed the principle of air liquefaction in 1895, photo: Wikipedia.

nitrogen (–196 °C). The argon is therefore enriched in the process to levels up to about 10% in the main rectification column but is then further processed in a separate argon column. In the argon column, crude argon at 95% Ar containing around 3–5% O_2 and 1% N_2 is first produced. Subsequently, the crude argon is purified in further stages, sometimes at other locations. The gas mixture is first heated to room temperature and compressed to 4–6 bar. In order to remove the remaining oxygen, hydrogen is then injected, which reacts with the oxygen on precious metal catalysts to form water. Once this water has been removed, in another special argon column, the argon accumulating at the bottom of the column is separated from the remaining nitrogen, ultimately leaving 99.9999% pure argon.

These days, by using different internals, it is also possible to purify the argon in the argon column to such a degree that the O_2 content already corresponds to the product specification and only the nitrogen needs to be removed. Just as in the process described above, this is done using a separate, special argon column. However, the intermediate steps with oxygen combustion by adding hydrogen can be completely dispensed with.

According to Clarke & Clare (2012), the additional costs for an argon facility in conjunction with the construction of a new air separation unit are around 15% of the total costs. As a rule, all new air separation units are equipped with an argon facility, delivering approximately 50 t Ar/d as a by-product from 1000 t O_2/d, for example. This increases revenues by 4–5% (Cockerill 2015).

Other sources for the production of argon include ammonia production using the Haber-Bosch process and syngas production, for example for methanol production. In these processes, which also all use air as a raw material, crude argon and other noble gases accumulate during the production process and can be isolated from the gas mixture. However, the resulting crude argon must then still be purified in an argon column to deliver pure argon. In North America, for example, argon is also produced in three ammonia plants (2 x in Oklahoma and 1 x in Ontario) (Suresh et al. 2016).

3.1.4 Krypton

Similar to the noble gases neon, argon and xenon, as well as helium to a lesser degree, krypton is also obtained using the Linde process in air separation units. Due to its physical properties, krypton accumulates together with xenon in the liquid oxygen in the bottom of the rectification column (*cf*. 3.1.2). Its concentration in liquid oxygen is about 500–1000 ppm. This first enrichment stage is referred to as *thin soup* in parts of the German gas industry.

Various technical processes are available to further concentrate the krypton. In a commonly used process, the krypton dissolved in the liquid oxygen is further concentrated in an additional rectification column (krypton content is then approximately 1000–2000 ppm). Because both the krypton and the hydrocarbons, which are a potential source of ignition, continue to be concentrated in the oxygen, they must be removed in the following step. To this end, the liquid oxygen is supercritically compressed, evaporated and then heated to ambient temperature. Subsequently, the hydrocarbons are burned off on a high temperature catalyst. The resulting CO_2 and H_2O molecules are removed by an adsorber station. The oxygen, now hydrocarbon-free, is cooled again and liquefied. In an additional rectification column the krypton can then be separated from the oxygen, together with the xenon. The resulting concentrate contains about 90–99% krypton/xenon, with about ten times more krypton than xenon. The remainder consists of oxygen and residual constituents, such as fluorohydrocarbons, tetrafluoromethane, sulphur hexafluoride, nitrogen oxides and carbon oxides. This highly concentrated krypton/xenon mixture is referred to as *thick soup* in parts of the German gas industry, in contrast to the *thin soup* discussed above.

Final purification of the two noble gases is again carried out in a multi-stage process in special plants. Because the volumes requiring processing in this final purification stage are only very minor, the production volume from several preliminary concentration plants is often processed together. Because this multi-stage process is extremely complex, and krypton and xenon are exceedingly rare in the air, the gases are comparatively more expensive. According to Clarke & Clare (2012), the additional costs for crude krypton/xenon production in conjunction with the construction of a new air separation unit are around 3% of the total costs.

3.1.5 Xenon

Xenon, similar to the other noble gases except helium, is primarily obtained through the Linde process (air liquefaction) in air separation units (cf. Sections 3.1.2 and 3.1.4). The krypton production process described in Section 3.1.4 also allows the simultaneous production of xenon. However, because of its concentration in the ambient intake air, this is with a xenon yield lower approximately by a factor of 10 than that of krypton. Alternatively to N_2-O_2-Kr-Xe gas mixture rectification and distillation (cf. Section 3.1.4), it is also possible to absorb xenon onto specific media and subsequently liberate it, whereby krypton, in contrast, is not easily absorbed.

Xenon production is highly complex: to produce 1 m^3 Xe (5.9 kg) under normal conditions (1013 hPa, 0 °C), more than 10 Mm^3 (12,920 t) of air must be processed!

3.2 Uses

Lighting technology

One application that unites all noble gases is their use in fluorescent tubes for illuminated advertising, because the noble gases radiate characteristic colours in gas discharge tubes or lamps (cf. Fig. 1):

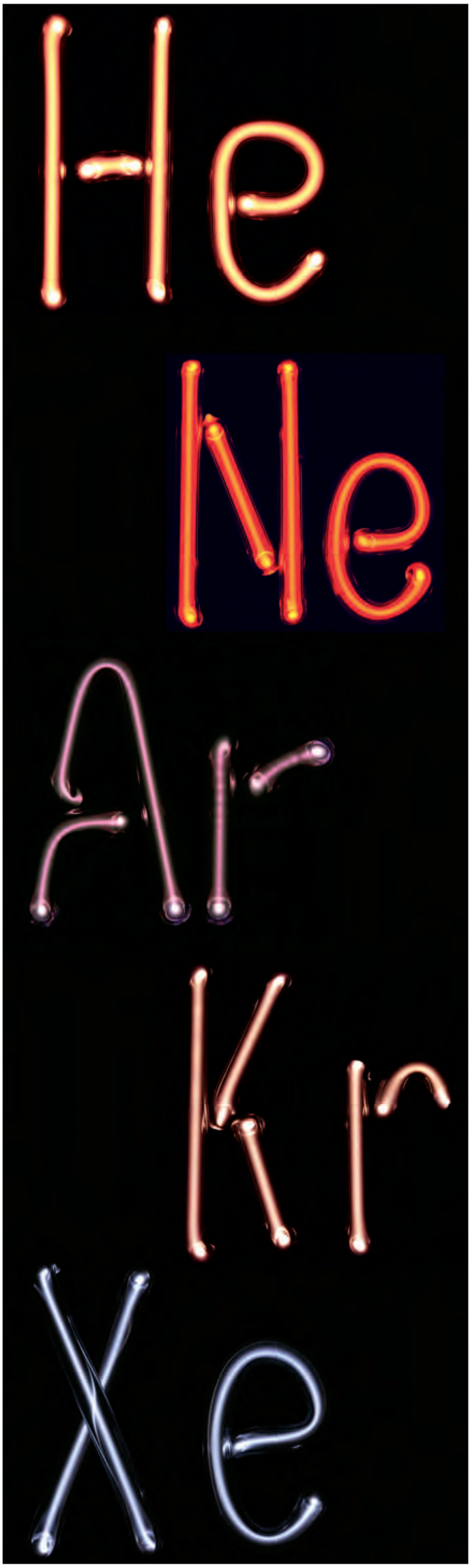
- helium: pink-white, in a yellow tube: yellow
- neon: reddish-orange, or with mercury in a yellow-green tube: green
- argon: pink-violet, or with mercury or iodine: blue
- krypton: greenish-orange, ionised: white
- xenon: blue-violet
- radon: red (no commercial use)

The generic term gas discharge lamp designates different lamp types with a principle of operation based on the excitation of noble gases or other gases such as bromine, iodine, fluorine, chlorine, nitrogen, carbon dioxide or gaseous mercury or sodium. Gas discharge lamps are subdivided according to their gas pressure into low-pressure, high-pressure and highest-pressure discharge lamps. The low-pressure gas discharge lamps include the neon lamp or tube (see below), the fluorescent lamp filled with mercury vapour and internally coated with a fluorescent material, or the metal vapour low pressure lamp (street lighting), while the krypton arc lamp (see 3.2.4) or the xenon lamp (see 3.2.5), for example, are high-pressure gas discharge lamps..

Fluorescent tubes are thin glass tubes filled with gas under low pressure, the ends of which are sealed by electrodes. If a high voltage is applied, the gas is excited and fluoresces. The colour of the fluorescent tubes depends on the type of gas or gas mixture used. The service life can be up to 20 years, depending on the gas fill. It is independent of the switching process; a property beneficial in flashing illuminated signs.

Neon tubes have an uncoated, clear or red-tinted glass tube, are filled with neon and glow red corresponding to their emission spectrum. They were invented in 1909 and have therefore been used for a long time for illuminated advertising and for lighting tall buildings.

In the neon emission spectrum, in addition to the intense lines in the red range, there are also lines in orange and yellow, while the green lines emit only weakly. A neon tube therefore usually appears bright red. To create dark red light, the glass tubes are additionally tinted red to absorb the yellow and green ranges.



3.2.1 Helium

In addition to the properties discussed in Section 2.1, helium has other properties that make this noble gas very attractive for special applications (Cai et al. 2012):

Magnetic resonance imaging (MRI)

It is estimated that 25–30% (according to Wade (2017), only 15%) of the current global demand for helium is used to cool magnetic resonance imaging equipment (MRIs) in hospitals and radiology practices (see Fig. 7). There are currently approximately 2800 MRIs in operation in Germany and around 37,000 worldwide. Medical technology, which also uses helium for other applications (see above), is therefore the largest global consumer of helium.

Magnetic resonance imaging (MRI) is an imaging technique developed in the 1970s that is mainly used in medical diagnostics to visualise the structure and function of tissues and organs in the body. The method is based on the fact that the atomic nuclei in the examined tissue are purposefully excited to a specific motion by a combination of static and high-frequency magnetic fields and then deliver a measurable signal in the form of an alternating voltage until the movement has subsided. The majority of magnetic fields are generated by superconducting NbTi electromagnetic coils, which today generally generate magnetic flux densities of 1.5–3.0 Tesla or even higher. In contrast, even sintered NdFeB permanent magnets can only produce flux densities up to a maximum of 1.3 Tesla. The electromagnets are cooled by liquid helium to temperatures around –269 °C. The electromagnets only become superconducting (NbTi from –263 °C) when they are supercooled and the current with which the magnets are initially *charged* can circulate within them without an electrical resistance and maintain an extremely homogeneous magnetic field. If the cooling fails or is deactivated by an emergency shutdown (*quenching*), the electrical resistance increases rapidly, heat develops, thereby leading to complete evaporation of

Fig. 6: Fluorescent tubes filled with noble gases, forming the respective chemical symbol of the noble gas, photos: Pslawinski/Wikipedia.

***Fig. 7:** Typical MRI in a Taiwanese hospital, photo: KasugaHuang/Wikipedia.*

the helium within minutes and thereby, in turn, to the collapse of the magnetic field. Between 1000 and 2000 litres of liquid helium are used per MRI, with older devices originally even using up to 6000 litres. Helium escapes despite multiple insulation layers (approximately 30–60 ml/h) and in the order of up to 1000 l must therefore be replaced every six to twelve months. Accordingly, the development of MRI cooling systems with significantly reduced helium demand (see Section 3.5) is ongoing, while simultaneously the use of MRI in developing countries (mainly India and Brazil) and China is steadily increasing.

Carrier gas

Thanks to its static buoyancy, helium is used as an incombustible carrier gas for filling balloons (party balloons, weather balloons) and aircraft (blimps, *Zeppelins*). In the USA, 9% of helium is used in this way.

Certainly the most well-known and by far the most important sales market for helium in the carrier gas sector is for filling party and advertising balloons. The bigger the balloon, the more helium you need to fill it. For example, 0.42 m^3 of helium is sufficient for approximately 25 standard round party balloons with a diameter of 28 cm. The gas escapes by diffusion from latex balloons within a few hours up to a maximum of two days. Foil balloons are denser and the helium remains in the balloon for several weeks. In Germany, balloon gas is available in 0.12 m^3 to 9.2 m^3 containers with 90% He.

In the USA, each of New York‘s famous Macy‘s department store parades on Thanksgiving Day requires 8300 m^3 of helium to fill the colourful giant balloons. Even the special balloon for the Red Bull Stratos Mission on 14 October 2012 was filled with around 5100 m^3 of helium. When Felix Baumgartner jumped at an altitude of 38,969 m, the balloon had expanded to a volume of about 834,000 m^3 as a result of the the lower air pressure.

Weather balloons serve to lift meteorology measuring instruments and typically have a 200 g envelope of very thin rubber and up to 3 kg load capacity. Depending on size, the fill uses 0.5–6.3 m^3 of helium – or more often hydrogen, because it is much cheaper – and the ascent rate is 5–7 m/s. Weather balloons ascend to an altitude of up to 23–40 km, whereby the envelope continues to inflate due to the ever-decreasing pressure and eventually bursts. Using a parachute, the valuable probes return to the ground from the stratosphere and can be reused. Worldwide, weather-related measurements are made in this way twice daily at around 900 observatories. It is estimated that around 4 Mm^3 of helium are used annually to collect weather data (Gubler et al. 2016).

Blimps are non-rigid airships without a rigid inner framework and are generally used for advertising purposes. They are built by The Goodyear Tire & Rubber Company, among others. Blimps commonly have envelope volumes up to 20,000 m^3.

The NT Zeppelins, known from the Lake Constance region and based in Friedrichshafen, are semi-rigid airships with an internal framework made of aluminium and carbon fibre-reinforced plastic beams, Kevlar tensioning cables and a gas-tight envelope, which is subjected to internal pressure for shaping. They provide seating for 14 passengers and two pilots. The 75 m long NT Zeppelins have an envelope volume of 8425 m^3 and usually fly at a height of 300 to 600 m, but can ascend to a height of 2600 m. The maximum speed is 125 km/h, but generally 75 km/h for tourist flights.

Each of the current six *ZLT Zeppelin Luftschifftechnik GmbH & Co. KG* NT Zeppelins is filled with around 7400 m^3 of helium under standard conditions. This corresponds to a lift of around 7.8 t at 0 °C or 8.4 t at 20 °C per airship, assuming identical air and helium temperatures. With every degree of temperature difference between the helium fill and the ambient air, buoyancy increases or decreases by 30 kg. The airship itself has an unladen mass of about 6300 kg. Of this, about 1 t is accounted for by the envelope, which is only 0.3 mm thick and consists of a multi-layer laminate. The inner layer is a gas-tight polyurethane film, followed by a tear-resistant polyester fabric. A helium-tight Tedlar film, provided with a titanium dioxide layer to increase resistance to UV radiation and ageing, also covers the polyester.

Semiconductor industry

Silicon monocrystals for subsequent use in the production of semiconductors are drawn from hot, high-purity semiconductor silicon. They are still occasionally 150 mm or 200 mm in diameter, but generally 300 mm, and now increasingly even 450 mm. Strong, superconducting magnets, supercooled by helium, are used for this purpose. Throughout the entire wafer and semiconductor manufacturing process, helium serves as a carrier gas for chemicals due to its non-reactivity as well as a cooling gas due to its good thermal conductivity. The larger the manufactured wafers, the greater the requirement for helium for cooling. Germanium monocrystals for producing semiconductors are grown in a protective helium atmosphere. Impurities, which must be avoided at all costs, also play a particularly important role in the actual production and processing of semiconductors, which are becoming continuously smaller and increasingly efficient. For this reason, as well as for temperature control reasons, semiconductor production takes place entirely under a controlled atmosphere of high-purity helium which, as far as possible, should not be contaminated by other gases, such as O_2 or N_2, or other elements. Helium gas is also used to fill gaps when manufacturing switching elements using semiconductors. It also serves to dissipate heat during the production process, thereby increasing throughput. Helium is also used in leak detection to demonstrate sealing in the helium system or in high-vacuum equipment (see section on leak detection). Stockman (2016) describes the individual applications of helium in semiconductor production and gives the annual helium demand per production plant (*Fab*) at > 500,000 m^3.

Metal hardening

Vacuum furnaces are used in many applications and in numerous sectors of industry. In industrial practice, low-pressure carburising in a vacuum furnace with subsequent high-pressure gas quenching has become established practice for case hardening steels. One of the benefits of carburising under low pressure is that the furnace atmosphere is kept free of oxygen, meaning that damage to the boundary layer by oxidation can be avoided. A vacuum furnace is usually an electrically heated furnace in which a pressure of 5–10 mbar is maintained throughout the process. In order to rapidly cool the carburized components from a temperature of 940–980 °C to room temperature, a gas with high thermal conductivity is required. For this purpose, gas mixtures consisting of helium (very high thermal conductivity) and nitrogen or argon (both gases with high molecular weight) are used, although helium can also be dispensed with if necessary.

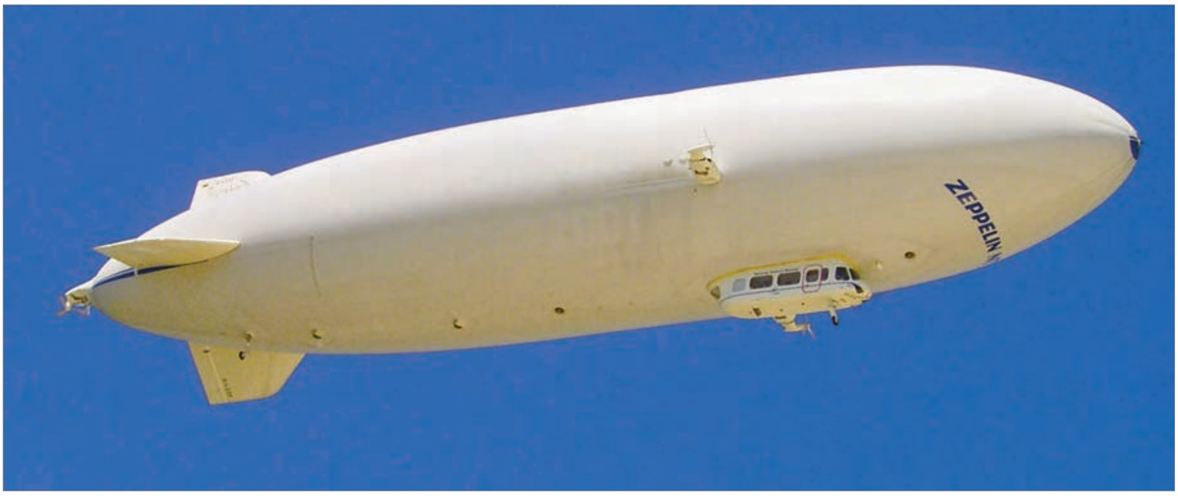


Fig. 8: Zeppelin NT over Friedrichshafen on Lake Constance, photo: Stefan-Xp/Wikipedia.

Another method of case hardening is carburising in furnaces and subsequent quenching in an oil bath. For this purpose, the carburised metal parts are cooled by helium gas, which is injected at a pressure of up to 20 bar and moved by means of two turbines. Following quenching, in contrast to oil quenching, the components do not require flushing, nor do any wastewaters that may have accrued require processing or treatment. Gas quenching is thus a relatively clean and environmentally friendly hardening process, albeit relatively expensive because of the helium demand, despite recycling.

Gas chromatography

Gas chromatography is generally used to separate mixtures in the qualitative and quantitative determination of gases. Gas chromatography is based on the fact that gas molecules of different substances travel through the gas chromatograph at different speeds due to their different physical properties (boiling point, interaction with the gas chromatograph separation column). Separation of the individual gas components is achieved in this way. The input gas mixture is driven through the separation column by a carrier gas. Between 1 and 100 ml of carrier gas are required every minute. At the outlet, the individual gas components are then qualitatively and quantitatively determined using suitable detectors (e.g. infrared spectroscope, mass spectroscope, thermal conductivity detector, flame ionisation detector). Suitable carrier gases for gas chromatography must be highly pure, oxygen-free (< 0.1 ppm O_2), dry, hydrocarbon-free and the flow rate and pressure be precisely meterable. Hydrogen, helium (greatest sensitivity in the thermal conductivity detector) or nitrogen, but also argon + 5% methane, and carbon dioxide, and in a subordinate role argon, are used. As the quality requirements in gas analysis continue to grow, the demand for high purity helium in this field is continually increasing.

Gas-shielded arc welding

Gas-shielded arc welding represents a group of welding processes, which in turn belong in the arc welding processes group. As with all arc welding methods, the heat source used for melting is a very hot electric arc that burns between the conductive workpiece and an electrode. The use of protective gases is a characteristic of inert gas welding.

Fig. 9: Tungsten inert gas welding in an inert gas atmosphere of argon or helium is suitable for welding all metals and alloys where quality is more important than welding speed, photo: US Navy/Wikipedia.

Helium has the highest ionisation potential of all shielding gases, meaning it is very difficult to ionise. The inert behaviour of helium makes it possible to weld titanium, copper, zirconium, hafnium, tantalum, magnesium or aluminium for use in aircraft construction, aerospace or shipbuilding using arc welding within a helium gas-shielded atmosphere. Very often, however, argon is used as a protective gas instead of helium, because it is less expensive and also has very good protective properties. Here, helium and argon protect the liquid metal against the influence of constituents in the air (nitrogen and oxygen) and stabilise the arc.

Gas-shielded arc welding methods include:

a) Gas-shielded metal arc welding (GSMA welding) with its two variants of metal inert gas welding (MIG welding) using inert gases (Ar, He), i.e. gases that do not react with the melt, and metal active gas welding (MAG welding) using reactive gases (CO_2, O_2, N_2, H_2), which cause desired chemical reactions, and;

b) Gas-shielded arc welding with non-consumable electrode with the variants tungsten inert gas welding (TIG welding) and tungsten plasma welding (TP welding).

In TIG welding, the arc is generated at a tungsten electrode that does not melt. Tungsten inert gas welding is highly flexible and can be used to weld almost all metals. Argon is usually used for welding for cost reasons, more rarely pure helium, but often also a mixture of both gases, with the helium content varying between 30% and 70%. In this case, the relatively expensive helium is used because of its better thermal conductivity, i.e. to increase the direct heat input into the weld pool.

In tungsten plasma welding, a further development of TIG welding, the arc is constricted by a water-cooled nozzle, thus focusing the energy of the arc on a small spot, similar to laser or electron beam welding. Because the plasma gas does not serve to protect the melt, an additional protective gas (secondary gas), usually also argon, and very rarely helium, must be supplied from a second nozzle. With the aid of the mechanically constricted electric arc, almost all electrically conductive workpieces up to a thickness of 120 mm can be cut in what is known as plasma cutting.

In the USA, about 7% of the helium used annually is used for welding.

Plasma spraying, plasma powder surfacing

Plasma spraying is an increasingly important metal coating process and is one the so-called thermal spraying processes. In a plasma cutting torch, an electric arc is ignited by a high frequency between a central, water-cooled tungsten cathode and a nozzle-shaped copper anode, likewise water-cooled. In the arc, gases such as argon, helium, nitrogen or hydrogen, or mixtures of these gases, are then introduced under high pressure. The input gases are ionised in the arc to form plasma, reaching temperatures up to 20,000 Kelvin. This hot plasma flux leaves the burner nozzle at high speed (around 1000 m/s) as a brightly glowing plasma jet. The sprayable powder (e.g. Cr, Mo or ceramic powder) is metered into the plasma gas stream with the aid of a delivery gas inside or outside the burner. The spray powder is accelerated to high speed (kinetic energy up to 450 m/s) within the plasma jet, melted there and delivered to the workpiece surface in a protective gas atmosphere (usually argon) (delivery capacity 4–8 kg/h). When they impinge on the pretreated surface, the liquid or doughy powder particles form into flat lamellae and immediately solidify. The high-energy plasma stream and the high impact velocity of the powder particles on the workpiece surface result in dense, firmly adhering and high-quality spray coatings, which are built up in lamellae. Plasma spraying is widely used in aerospace applications (application of thermal barrier coatings on turbine blades or run-in surfaces), in medical technology (implants) as well as in the chemicals, printing, paper, mechanical engineering, wind energy and household appliance industries (*Deutsche Edelstahlwerke GmbH*, undated).

In plasma-transferred arc welding (PTA), the workpiece surface is melted. Here, the arc is formed between a permanent electrode and the workpiece. The coating powder (usually alloys based on Ni, Co or Fe, but also carbides) is delivered to the burner by means of a carrier gas, heated in the plasma gas jet (for example argon, helium or an argon-helium mixture) and applied to the workpiece surface (kinetic energy up to 50 m/s). Here, it melts completely in a shielding gas atmosphere (e.g. argon or argon-hydrogen mixture) in the weld pool on the substrate. The PTA process is used to coat a variety of base materials, for example made from low alloy steel, stainless steel, cast iron, bronze or nickel-based superalloys. Workpieces for mechanical engineering, agriculture (chopper knives, counter cutting), and the mining (cutter bits, excavator teeth) and automotive industries (valves) are coated in this way.

Purging and pressurising

Because the boiling point of helium (–268.93 °C) is lower than that of hydrogen (–252.87 °C), helium is used to purge and pre-cool vessels and pipes to be subsequently filled with liquid hydrogen. This purging removes any gases, such as nitrogen or argon, that would otherwise immediately freeze in contact with liquid hydrogen, thereby clogging pipes and valves. Thanks to its low solubility in fuels, its low boiling point and its chemical inertness, helium is also the only gas that is utilised for pressurising in conjunction with special fuels and in the refuelling and launch preparation of intercontinental missiles and space rockets. See Cai et al. (2012) for technical details. Around 370,000 m^3 of helium are required for each Saturn V booster rocket launch and 210,000 m^3 of helium for each Space Shuttle launch. In the USA, around 7% of helium is used for purging and pressurising. The main public buyer here is primarily NASA, who currently use 2–2.4 Mm^3 helium annually (corresponding to 4–5% of US helium demand), according to Baker (2018). Use by the US military, on the other hand, is extremely low (Gubler et al. 2016).

Leak detection

The helium atom has the smallest diameter of all elements, very easily diffusing even through the smallest openings. It is also relatively easily detectable by special gas measuring instruments (*sniffers*) and is therefore used to detect subsurface gas movement, in permeability testing of pumps, seals, pipes, gearboxes, compressors, pacemakers and many other things, as well as for safety inspections in nuclear reactors. In the USA, about 4% of helium is used for leak detection. In many industrial manufacturing fields, high-purity vacuum conditions are necessary and must be very closely monitored. For example, following servicing on a semiconductor production facility – referred to as a *Fab* – a leak test is carried out by pressure rise measurement. Alternatively, a vacuum measurement can be carried out. Only when the leak tightness of the system has also been demonstrated using these integral tests is the process cleared for use. If the pressure increase is greater or the vacuum smaller than a defined threshold value, the system is locked. Helium leak detection is then started in order to localise and repair the leak. Technical details of the vacuum method and leak detection using helium can be taken from Umrath (2016).

Technical diving

Helium is the least soluble of all gases in water (and therefore blood), thereby establishing itself in technical diving as $He\text{-}O_2\text{-}N_2$ mixtures (*trimix*) in the place of pure N_2/O_2 mixtures. Trimix mixtures are named after the proportions of oxygen and helium. For example, a mixture with the designation Tx21/35 contains 21% O_2 and 35% He. The remaining 44% is N_2. Alternatively, a pure He/O_2 mixture (*heliox*) can be used for deep-sea diving. In the USA, about 2% of helium is used for diving air mixtures. The advantage of using helium is that the anaesthetic potential of this noble gas is virtually always zero due to its low solubility, regardless of the ambient pressure. This means that no nitrogen narcosis occurs (rapture of the deep), which becomes a problem when diving with compressed air when the ambient pressure (below approx. 40 m diving depth) exceeds a certain value. Only at an ambient pressure of > 15 bar (below approx. 130 m diving depth) does the so-called *HPNS* (*high pressure nervous syndrome*), referred to as *helium tremor*, occur if there is a substantial proportion of helium in the breathing gas and at high descent rates. In order to avoid this, a specific quantity of nitrogen, the anaesthetic potential of which can suppress HPNS, is again added to the breathing gas. One drawback of using helium is that it is a very particularly good conductor of heat and the diver therefore cools faster. In addition, helium changes the sound vibration of the diver‘s voice, which, however, can be counteracted by using special microphones.

High-temperature nuclear reactors

Helium gas is used as the preferred cooling agent in gas-cooled high-temperature reactors, because it is chemically inert, does not become radioactive, and has a relatively high thermal conductivity. At the same time, the main ^4He isotope is not activated by neutron irradiation. However, ^3H (tritium), which in turn is a radioactive beta emitter with a half-life of 12.32 years, is formed from the small proportion of 0.00138% ^3He in atmospheric helium. Another disadvantage of using pure helium is that it destroys the protective oxidation layers on metals. Small additions of corrosive agents in helium, such as water vapour, can indeed remedy this, but only at the expense of constant corrosion of the graphite components in the reactor by the water vapour. As a monatomic gas, helium diffuses easily through solid materials, making sealing against helium exceedingly difficult to achieve. A test reactor in Jülich, Germany, lost 1% of its cooling agent per day, 0.3% per day is anticipated for newer reactors. Yet another disadvantage of helium is that its viscosity increases with increasing temperature. This can cause hot areas to be percolated less and thus be less well cooled. As far as is known, only China currently operates a high-temperature helium-based reactor and continues to run corresponding research projects.

Production of glass fibre optics

Helium is used in two process steps in the production of optical telecommunications fibres. In one of the steps, oxygen is heated together with a glass base substance such as silicon tetrachloride or silanes in a natural gas flame, whereby so-called *glass soot* is formed. This *glass soot* is sintered on a silicon rod in a He-Cl_2 atmosphere. The chlorine binds the moisture while the helium drives out the gas bubbles. The sintered silicon rod is then heated in a drawing machine and drawn out to form a glass fibre. The glass fibre is quenched in a high velocity He-N_2 gas stream mixture, which has excellent thermal conductivities. Approximately 8% of helium is used in the production of optical fibres in the USA, but in China this figure is greater than 30%.

Display screen production

Although the electronics market for screens and smartphones is no longer growing by double digits as it was a few years ago, it is still very active, because end users, primarily in China, are constantly demanding new products such as larger LCD flat panel displays, OLED and 4K technologies, ultraflat screens, round and portable devices, screens in vehicles and much, much more. Mainly located in South Korea, Taiwan, China and Japan, the manufacturers of these devices currently (still) all use helium, due to its high thermal conductivity, to cool the glass during and after the manufacturing phase.

Gas lasers

Lasers (*Light Amplification by Stimulated Emission of Radiation*) emit monochrome light, which oscillates synchronously and is highly directional, thus creating a high-energy, concentrated beam. To generate laser light, one must excite the atoms of a suitable medium (laser medium) with energy (*pumping*). The excited atoms then release this energy in the form of photons with precisely defined energies. These light particles can stimulate other atoms to release energy. Two mirrors on both ends of the laser enhance the effect. The result is an extremely precise, high-energy light beam that, depending on modification, can be used for cutting, drilling, engraving, welding, soldering, cleaning or hardening. The prospective applications are correspondingly versatile and range from microelectronics to shipbuilding. The largest selection of lasers for cutting and welding is used by the automotive industry. In most types of laser, shielding gases are used to prevent oxidation of the processed surface. Gas lasers, in contrast to solid and dye lasers, use noble gases as laser medium on a large scale:

- **Helium-neon lasers** operate using a high-pressure helium-neon gas mixture (He:Ne ratio 5:1–20:1), with the helium being required for pumping while the neon is the laser medium. The emitted light beam is red. The He-Ne laser was developed in 1960 and has now been displaced by the more powerful diode lasers in most applications.
- **Argon-ion lasers** require a high power input. In addition to their use in research and development, they are also used in entertainment (for example in laser shows), in high-speed printing machines, photoplotters, or in holography and medicine (dermatology, ophthalmology and dental technology). However, argon ion lasers have more recently been replaced by solid-state lasers in most applications.
- **Helium-cadmium lasers** consist of a vacuum-tight welded tube filled with helium and cadmium metal vapour. The emitted light beam is red. Applications are in basic research, materials sciences and medical technology.
- **Carbon dioxide lasers** use a mixture of CO_2, N_2 and He as the laser medium. Here, helium is used for stabilisation and heat dissipation. Minimum purities of 99.995% CO_2, 99.996% He and 99.999% N_2 are required for the resonator gas, because lower purities would contaminate the laser optics, the so-called resonator. Carbon dioxide lasers are particularly suitable for cutting, engraving and perforating thin, organic (plastics, textiles, wood) to thicker, inorganic materials (sheet metal, ceramic, glass). The emitted light beam is in the infrared range.
- **Excimer lasers** are based on the chemical excitation of noble gases (argon, krypton, xenon) and halides (fluorine, chlorine, bromine) in a buffer gas (helium, neon) with the short-term formation of metastable noble gas halides. The stored energy is emitted in the form of electromagnetic radiation, whereby an ultraviolet laser beam is produced. The mixing ratio of the gases determines the wavelength. The most commonly used gas mixtures with their wavelengths are Ar + F + Ne (193 nm) and Kr + F + Ne (248 nm), with neon as the buffer gas making up about 96–97.5% by volume of the gas fraction (Khan 2017). The

very short wavelength enables the fabrication of structures in the nm width range and thus forms the basis for the production of all modern microelectronic components. Excimer lasers are also used for directly processing virtually all materials (ceramic, metal, plastic, etc.) for the production of sub-micron scale structures. Excimer lasers are also indispensable for cutting human tissue (dermatology, ophthalmology, plastic surgery). The gas requirement of an industrial KrF excimer laser is between 10,000 l/a and 50,000 l/a, while ArF excimer lasers require 60,000–200,000 l/a.

National Research Centres

Its superfluidity at temperatures below –270.98 °C makes liquid helium suitable as a coolant in particle accelerators, such as the German electron synchrotron DESY in Hamburg (demand according to Illichmann 2018: 1 t/a), the superconducting S-DALINAC electron linear accelerator in Darmstadt, the ELBE electron accelerator in Dresden-Rossendorf (demand according to Illichmann 2018: 12.5 t/a) or, most well-known, the LHC Large Hadron Storage Ring at the European Nuclear Research Centre CERN in Geneva. Assembled in 2008, the LHC is the largest cryogenic refrigerator (cryostat) ever built. In the LHC, the 9000 large magnets (total mass 36,000 t), which generate magnetic flux densities of up to 8.6 Tesla, are cooled to their operating temperature of 1.9 K (–271.25 °C) in two steps. In the first step, they are pre-cooled to 80 K (–193.2 °C) by 10,080 t of liquid nitrogen and then brought to their final temperature in the second step by means of 100 t of liquid helium. To keep the magnets at their operating temperature, they are constantly surrounded by about 60 t of liquid helium in the supra-fluid state. In this state, helium displays particularly good thermal conductivity. A total of 140 t of helium are held at the LHC for cooling purposes. Special vehicles arrive regularly to compensate for helium losses. They amount to around 60 t annually.

Quite variable, but probably quite remarkable total volumes of helium are also required in other physics research institutes and university physics institutes world-wide. Estimates suggest that 6% of helium

Fig. 10: View into a section of the tunnel of the LHC large hadron storage ring, the functioning of which depends on constant supercooling of the magnets by means of liquid helium, photo: Maximilien Brice, CERN.

used globally is needed by research institutes. The 17 laboratories of the US Department of Energy (DOE) alone consume around 2.4 million litres or 300 t of liquid helium per year (Gubler et al. 2016). For the *Physikalisch-Technische Bundesanstalt* in Braunschweig, Germany, Illichmann (2018) reports an annual requirement of 38,800 litres, for the Leibniz Institute for Solid State and Materials Research in Dresden, 80,000 l/a, for the Helmholtz Centre in Berlin, 6000 litres per year, for the DFG Research Centre in Karlsruhe, 170.000 l/a and for the Max Planck Institute for Metals Research in Stuttgart, 251,500 l/a. The helium is used in basic research to investigate Josephson effects in the Kelvin to milli-Kelvin range, scattering of elementary particles, quantum liquids including the development of quantum computers, in the study of intelligent materials and to optimise magnetic alloys.

Miscellaneous

Heliox therapy is recommended by doctors for the treatment of asthma, respiratory distress in premature babies and bronchial diseases. Heliox is a gas mixture generally comprising 20% O_2 and 80% He. While the oxygen is needed by the human body, helium, because of its small atomic size, has a much lower flow resistance than the other constituents of the air and thus makes breathing easier (Berganza & Zhang 2013).

In **magnetoencephalography** (MEG), the very weak magnetic fields (10^{-15} Tesla) in the brain are measured by a helmet-like object with sensors attached to the outside of the head. The magnetic coils in the sensors are cooled by liquid helium to a temperature near 0 K, allowing them to develop their superconducting properties. Around 400 litres of liquid helium per month are needed to supercool the superconducting coils.

In medicine, a method for **removing cancerous tumours** and necrotic tissue was developed, wherein the organic tissue is frozen with liquid argon or helium and can then be removed relatively painlessly.

Helium was once used in the United States to fill **car and aircraft tyres**, because it was so abundant. Today, Formula One technicians use pit stops to change tyres in seconds, using helium-driven **impact screwdrivers**.

In the gas reservoirs of **side and curtain airbags**, a gas, usually helium or a helium-argon mixture, is stored under high pressure (600 bar). When the airbag is deployed, an explosive device destroys a membrane, the gas flows into the airbag and expands it within milliseconds. Because no heat is generated and thus possible burns avoided only when using noble gases for expansion, they have a market share of about 80% of the global airbag market. Gubler et al. (2016) estimate the annual global demand for helium for airbag filling at 2–3 Mm^3. In addition, all airbag inflators will be leak tested prior to installation using helium leak detectors, regardless of whether they operate with pyrotechnics (solid propellant) or compressed inert gas.

In 1986, a **high-intensity magnetic separator** based on superconducting magnets was launched in the USA for the first time. It was able to produce a magnetic flux density of 2 Tesla and was used to separate ferrous minerals from kaolin in Georgia. Its function required liquid helium cooling, which was passed through a 1000 litre tank in a closed circuit. Ultimately, this first high-intensity magnetic separator turned out to be uneconomical due to the relatively frequent switching, because 2 litres of helium were used each time it was switched on and off. Meanwhile, improved devices with even higher flux densities have been developed and are in use globally in kaolin processing plants (Watson 1994).

Amberger Kaolinwerke Eduard Kick GmbH & Co. KG (AKW) in Hirschau/Upper Palatinate, Germany, have used such a high-intensity magnetic separator, which is cooled by liquid helium, since 1993. In 2000, a second magnetic separator of this type was put into operation (Fig. 11). Using the two facilities, the degree of whiteness in kaolin is increased by separating magnetisable, generally iron-rich minerals. This is a very important parameter for paper industry applications. Field strengths of up to 5 Tesla can be defined for the two high-intensity magnetic separators, thus increasing whiteness by 2–4 percentage points. At the same time, the utilisation factor of the finite deposits is increased, because the cut-off in terms of the degree of whiteness can be lowered. Helium losses can be limited by mechanically cooling the shielding, meaning that, in the case of AKW, helium only needs to be replenished annually, i.e. approximately 2000 l/a liquid helium is used (Dr. Stefan Huber/AKW, personal communication).

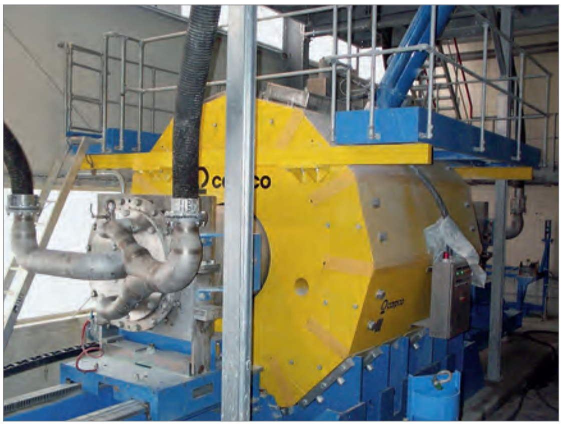


Fig. 11: High-field magnetic separator, super-cooled using liquid helium for separating ferrous minerals from kaolin, photo: Amberger Kaolinwerke Eduard Kick GmbH & Co. KG (with kind permission).

Superconducting energy storage systems are required if extremely high current levels need to be fed into a grid over very short periods of time. This is the case when operating particle accelerators and in voltage fluctuations in public power grids, where stored energy is retrieved in the form of current pulses with frequencies of 0.1–1 Hertz. To date, it has only been possible to use superconducting energy storage systems with liquid helium cooling for this purpose (Glowacki 2012).

Infrared sensors in satellites, known as astronomical telescopes, are used to monitor the weather, atmospheric pollution, sea temperatures, plant growth or ice conditions on Earth, and must therefore be cooled to temperatures of around 80 K (–193 °C) to achieve the required sensitivity. Even special infrared devices on Earth, intended to perform measurements over extremely large distances, must be highly cooled. Astronomical telescopes, used to measure the infrared wavelengths from distant galaxies, must be cooled even lower, to just above absolute zero. For this purpose, the satellites are launched carrying double-walled, and thus even better insulated, containers, filled with up to 2300 litres of liquid helium, depending on their size. The sensors on the satellite then only operate until the last drop of helium has evaporated and escaped.

In the technical **Kroll process** used in the production of titanium or zirconium metals, titanium tetrachloride (from the titanium dioxide manufacturing process for white pigment production) or zirconium tetrachloride (from zirconium) serve as the parent materials. These two metal chlorides are reduced with magnesium at temperatures of approximately 800–900 °C under an inert gas atmosphere of helium or argon to form titanium or zirconium metal.

When packaging food, helium in the form of **food additive** E 939 serves as a packaging gas. It displaces the oxygen and thus slows down discolouration and aromatic degradation, as well as food spoiling.

Supersonic wind tunnels are used to test aircraft components or aircraft in original size for suitability under controlled and reproducible laboratory conditions. Here, Mach numbers of 1.2–5 (1400–6000 km/h) are simulated. The propellant and working gases may be either air or nitrogen. In many cases, lighter gases such as hydrogen or helium are used as propellant, because they have a higher acoustic velocity and therefore higher impact Mach numbers, i.e. pressure waves in the Mach range can be achieved.

All **analytical devices**, e.g. for X-ray fluorescence analysis (XRF), should be regularly calibrated. Here, the measurements are made in a vacuum or in a helium atmosphere in order to avoid obtaining incorrect measurements. In addition, helium is used as an inert carrier gas in numerous analyses.

For several years, **hard disk drives** have been filled with helium to increase their capacity. Helium has one-seventh of the density of air and therefore allows a greater hard disk stack density as a result of lower friction and vibration. At the same time, helium conducts the generated heat better and the computer therefore requires less energy for cooling.

The Central Japan Railway Company announced that it would be operating a new line between the cities of Tokyo and Nagoya by 2027, using the Shinkansen bullet train. For the first time, the line will be built as a **maglev route** (magnetic levitation) and the magnets will be made superconducting using liquid helium.

Nuclear magnetic resonance spectroscopy is a high-resolution analytical method for non-destructive detection of a sample‘s constituents, for determining structures at the molecular level and for investigating interactions between molecules. To carry out the measurement, the sample is placed in a magnetic field, which is usually generated by means of superconducting electromagnets cooled using liquid helium and nitrogen. Less than 1 l/d (Gubler et al. 2016) of helium is used for operations.

A **helium-ion microscope** is an imaging method based on a helium ion beam sampling the object being investigated. The method is similar to that of a scanning electron microscope but offers a higher resolution in the tenth-nm range. In terms of the modus operandi, helium ions are generated in a supercooled apparatus under high vacuum in the strong electric field around a pointed tungsten needle. The helium ion beam is focused, directed and aimed at the material being investigated. The intensities of the beam passing through the sample, the beam reflected by the sample and the number of secondary electrons generated are measured.

Nuclear fusion research currently concentrates on reactor concepts based on magnetic confinement technology. The underlying concept is to introduce just a few grams of a deuterium-tritium gas mixture into an airless container several thousand cubic metres in size and to heat it to 100–150 million degrees Celsius. All gas impurities in the high vacuum (10^{-7} mbar) in this container would need to be removed beforehand, similar to the principle of purging (see above), by large refrigeration pumps based on liquid helium. At the high temperatures discussed, electrons and atomic nuclei are separated and form an electrically conductive plasma. Superconducting electromagnets are arranged around the plasma chamber, generating a magnetic field of up to 10 Tesla. This magnetic field confines the plasma within the chamber to prevent it touching the walls. Upon contact with the wall, the plasma would immediately cool and the reaction would collapse. The electromagnets required to build the magnetic field would need to be supercooled by liquid helium to generate the required superconductivity. Replacement estimates for the helium lost by diffusion processes range from only 80–800 litres per week. As a *best-case* variant, Clarke & Cai (2012) calculated a requirement of 620,000 m^3 (= 880,000 litres of liquid helium) for the initial filling and first year of operation of a typical nuclear fusion reactor with one gigawatt effective power and 55,000 m^3 (= 79,000 litres of liquid helium) in each subsequent year.

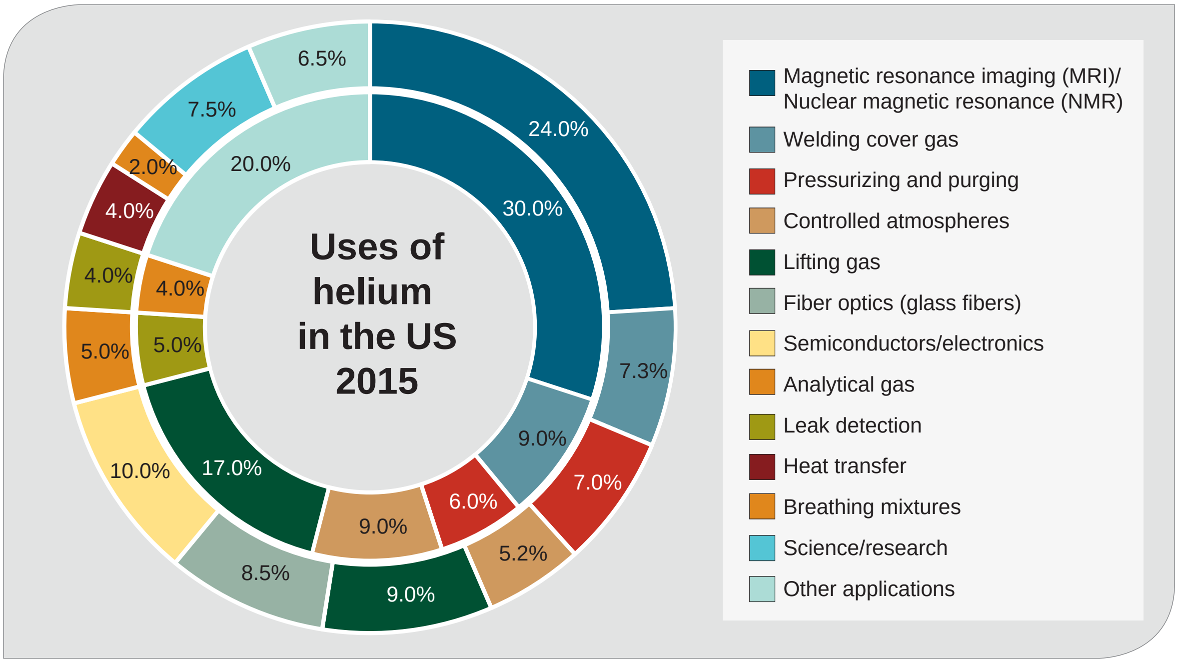


Fig. 12: Use of helium by sector in the USA in 2015, inner circle according to USGS, based on enquiries with helium producers, outer circle according to Gubler et al. (2016), based on interviews with industry and government members, and including gas dealers.

^{3}Helium

In contrast to ^{4}He, which has been discussed so far, ^{3}He is only used in a few applications, but there it is indispensable. On one hand, this includes **cryogenic research**, because using ^{3}He temperatures in the milli-Kelvin range, i.e. a few thousandths of Kelvin above absolute zero at –273.15 °C, can be

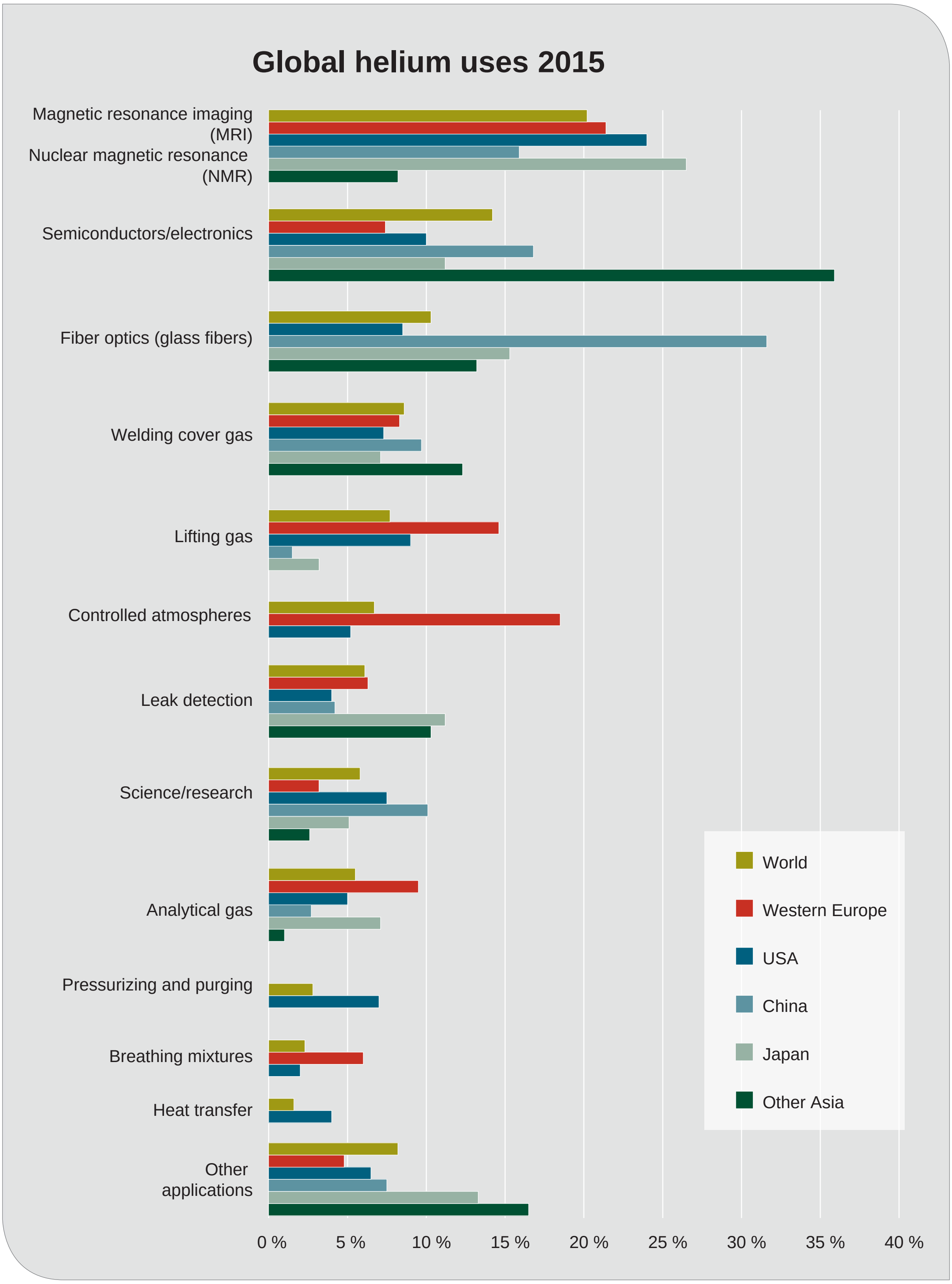


Fig. 13: Comparison of global helium use by sectors in 2015, after Gubler et al. (2016).

generated. On the other hand, it incorporates the operation of **neutron detectors** to detect neutrons and gamma radiation. The great surge in security at airports and other public facilities in the USA as a result of the September 11, 2001, terrorist attacks, has led to an explosion in the global demand for ^{3}He, with the US Department of Homeland Security now switching to ^{10}B and ^{6}Li-based solid-state neutron detectors (Osterath 2015). ^{3}He is used in neutron detectors in **crude oil exploration** to determine rock parameters during drilling. In addition, the use of ^{3}He as a **contrasting agent in lung examinations** in MRI has also been under investigation for several years. ^{3}He can be used to measure the size of individual air spaces in the lungs, the distribution of breathing air during inhalation, the regional oxygen partial pressure, blood oxygen uptake efficiency, and numerous other lung parameters.

Global helium use

The use of helium (^{4}He) in various sales fields in the USA has been published annually by USGS for decades. However, according to research by Gubler et al. (2016), these data are, at least more recently, based on four-yearly enquiries by the US Bureau of Land Management aimed at helium producers, which disregard sales via dealers representing a large market share in the USA. Gubler et al. (2016) have accordingly interviewed a larger number of market participants and have arrived at different sales market distribution figures (cf. Fig. 12). Gubler et al. (2016) also provide an overview of the distribution of helium sales markets in western Europe, China, Japan, the rest of Asia and the world, as shown in Fig. 13.

3.2.2 Neon

Because of the significantly higher price of neon compared to helium and argon, its prospective uses are limited in practice. Where possible, it is replaced by argon, which is much more abundant in the atmosphere and thus cheaper to produce.

By far the largest sales market for neon (according to Betzendahl (2015b) 80–90% market share) is the production of gas mixtures for excimer lasers (see 3.2.1), where neon is the most important constituent at > 95% by volume. Excimer lasers are used in photolithography, one of the central methods for manufacturing integrated circuits in semiconductor and microsystem technology, as well as for annealing, i.e. heating to improve the properties of polysilicon layers or wafers for semiconductors and flat screens. In addition, excimer lasers are used in medicine (cf. 3.2.1). According to Betzendahl (2015b), 70–75% of global neon demand is defined by the requirements of the semiconductor industry. Khan (2017) anticipates a growth in the demand for gas mixtures for excimer lasers used in the semiconductor industry of 6% per annum for the period 2016–2023.

The demand for neon for the production of **helium-neon lasers**, in contrast, has declined massively. For example, these lasers used to be found in cash register bar code scanners or laser print-

Fig. 14: Illuminated advertising using neon lights at a restaurant in Lustenau/Austria, photo: Reinhard Müller/Wikipedia.

Fig. 15: Stainless steel is usually welded using the tungsten inert gas method in an inert gas atmosphere of argon or, more rarely, helium, photo: Linde AG (with kind permission).

ers, but they have now been almost completely replaced by diode lasers.

The most well-known, but by no means largest, application field (according to Betzendahl (2015b) and Spiritus & Betzendahl (2018), only 1% market share) for neon is in **lighting technology** (see 3.2), because it emits a scarlet light in fluorescent tubes. In mercury-based fluorescent tubes filled with argon, the addition of around 25% neon increases the voltage across the arc, resulting in higher light output. To what extent the booming LED market will also influence the use of fluorescent tubes for advertising purposes is not currently apparent.

In the aerospace industry, liquid neon serves as a substitute for liquid helium as a cooling agent for extremely sensitive **infrared sensors**. Neon has an atomic diameter around twice as large as that of helium, meaning it diffuses more slowly into space and therefore allows satellites to operate longer (cf. 3.2.1).

In refrigeration technology, some **refrigerants** also use neon on a small scale as a substitute for helium. Although it is significantly more expensive than liquid helium, its cooling capacity is 41 times higher and three times higher than liquid hydrogen. Neon is therefore predominantly used for cooling superconducting materials, where a high cooling capacity is required.

Neon is also used for **research purposes**, in particular in the nuclear physics field.

3.2.3 Argon

Argon is used globally in large quantities as a **protective gas** in certain welding processes (see 3.2.1). Where materials do not tolerate oxygen or nitrogen for metallurgical reasons, e.g. aluminium, magnesium, chromium, vanadium, silicon, titanium or molybdenum, it prevents the ingress of air and thus the formation of oxides and nitrides. Argon therefore protects the hot melt against oxygen, nitrogen and humidity in the air.

In vacuum induction furnaces, in which **steel alloys** are produced, argon is used as a protective gas for the same reasons and in quantities up to 6 m^3 per tonne of alloy. The same applies to vacuum arc reaction furnaces, in which **titanium** is produced, which is the only metal to burn even in a pure nitrogen atmosphere.

In the production of **aluminium**, argon, together with N_2, Cl_2 and CO, promotes degassing and simultaneously removes the developing hydrogen and solid impurities from the molten aluminium.

When **casting** hot metal alloys, e.g. Al and Mg alloys for steering wheels, a protective atmosphere of argon prevents oxidation of the metals.

In **steel production**, argon is used in numerous process steps. Argon blasted in under high pressure serves to mix the liquid steel in order to homogenise the temperature and composition of the steel in the converter or pan, and to discharge undesirable gases such as N_2, CO or H_2, which impair the physical properties of the steels. Even solid impurities are discharged in the argon gas stream, thus producing a *clean* steel. With the argon, Ca and Mg are introduced into the steel melt, with the help of which the sulphur content of the steel is reduced. In addition, argon supports the carbon-oxygen reaction throughout the entire steel production process (Morgan 2007b).

Fig. 16: Refining of a CrMoWVNbN stainless steel alloy in an argon-oxygen decarburisation vessel, photo: Goodwin Steel Castings/Wikipedia.

The **argon-oxygen decarburisation process** developed in 1954 has great significance in the production of stainless and high-alloyed stainless steels. To this end, an argon-oxygen mixture is injected into the molten steel being treated, whereby the proportion of O_2 in the gas mix is continuously reduced from around 80% to around 20% during the approximately one-hour blasting. The partial pressure of the oxygen is lowered by adding argon as an inert gas. This promotes carbon oxidation to CO which, along with the equally undesirable N_2, is purged by the argon while, on the other hand, reducing the undesirable slagging of valuable alloying metals such as Cr and Mn. In order to recover the remaining oxidised alloy metals, the slag is reduced after decarburisation by the addition of lime and silicates. Subsequently, the melt is desulphurised using quicklime. During these two processes, the melt is blasted with pure argon to induce better mixing. At the end of the process, the only around 0.015% carbon remains in the steel. Around 2% chrome is lost. Around 25 m^3 O_2 and 20 m^3 Ar are used per tonne of steel.

Argon is also one of the most important gases in **semiconductor technology**, where it serves primarily as an inert gas in many production processes (Gasworld 2018). The silicon monocrystals for subsequent semiconductor production are grown in a protective argon gas atmosphere. During sputter deposition, an argon, helium or krypton plasma supports the reaction, or the noble gases serve as protective gases. Similarly, an argon plasma serves to activate the etching gases in the etching process. The smallest drops of liquid argon are used to clean the tiny, fragile computer chips.

In the production of ultra-thin Cu (In, Ga) Se_2-based **solar cells** (CIGS solar cells), the semiconductors are vapour-deposited onto the glass substrate with the aid of hydrogen sulphide and argon. Approximately 120 m^3 of argon is needed per run through the crystallisation furnace.

See Sections 3.2.1 and 3.2.2 for the use of argon in argon ion **lasers** and excimer lasers. The use of argon in airbag gas storage systems was also discussed in Section 3.2.1. The same applies to argon as a protective gas in **plasma spraying** and in **powder metallurgy** in general.

Laser beam melting is an additive manufacturing technique and one of the best known **3D printing** processes for the production of metallic components made of stainless steel, titanium, aluminium, cobalt, chromium and nickel alloys. Here, argon serves as an inert protective gas and is also particularly well suited for powder atomisation.

Because of its low thermal conductivity and its relatively low price, argon has long been by far the most important filling gas between **insulating glass panes**. Argon, or krypton, which is much less frequently used because of its higher price, reduces gas circulation and heat dissipation, which significantly improves the insulating properties of double or multiple glass panes.

In **technical diving**, argon is used – especially when using the helium-based *trimix* as breathing gas – to fill dry suits or to balance their weights. The low thermal conductivity of argon slows diver cooling (cf. 3.2.1).

In **fluorescent tubes** (here, together with mercury vapour), but also in electronic components, such as rectifiers and overvoltage fuses, argon is used as a filling gas.

Incandescent lamps, where still in use, are often filled with argon-nitrogen mixtures under high pressure (70 kPa) in the ratio 93% Ar to 7% N_2, because a protective gas filling reduces the risk of filament evaporation (GASWORLD 2014). Argon has a lower thermal conductivity than lighter gases, but is more economical than the heavier, and thus even less thermally conductive, noble gases krypton or xenon. One benefit of the lower thermal conductivity is the higher possible incandescent temperature and thus higher light output.

Argon is used as a carrier gas when carrying out numerous **analytical investigations**, e.g. in optical spectrometry, atomic absorption spectrometry, gas chromatography, ICP-MS or ICP-OES.

In wine production and food packaging, argon in the form of the **food additive** E 938 serves as a propellant and protective gas and prevents spoilage due to oxidation or infestation by bacteria and fungi.

When **extinguishing** metal fires, in particular, but also in electrical and EDP systems, highly compressed gaseous argon is used as an extinguishing gas. It is inert, heavier than air and floods the region to be extinguished particularly quickly and thoroughly. The oxygen in the air is displaced and the fire is suffocated.

In **Geiger counters** argon (or the considerably more expensive krypton) is used as a fill gas in the counter tubes. Argon is particularly beneficial for achieving the shortest possible pulses, because it does not form negative ions that migrate to the anode much more slowly than the electrons. Argon with several bars of overpressure or, occasionally, xenon, is used to detect gamma radiation.

In **plasma furnaces**, which are primarily used to incinerate toxic fly ash and filter dusts from combustion systems or metallurgical facilities, as well as weapons of war, a plasma with temperatures > 2000 °C is generated between plasma torches. The toxic materials are pneumatically blown through the plasma using argon as a protective gas, causing them to melt, collect partly as drops in a molten bath, and partly to evaporate.

In the USA, a **large-scale research project** to investigate neutrino particles is being planned. For this purpose, a *Deep Underground Neutrino Experiment* (DUNE) detector, whose four modules are each housed in a cooling system (cryostat) and will be supercooled by liquid argon instead of liquid helium, is to be built at the Batavia, Illinois site. A total of 69,600 tonnes of liquid argon will be needed over a four-year period.

3.2.4 Krypton

In the **manufacture of insulating glass**, krypton is used as a filling gas between flat glass panes for subsequent processing into heat-insulating and sound-absorbing **insulating glass windows** (cf. 3.2.3). The greater the degree of filling and the heavier the noble gas, i.e. argon < krypton < xenon, the higher the thermal protection and

Fig. 17: In 2010, 50 of the 6379 windows of New York's Empire State Building were removed every night, one after the other; the glass interstices were coated with a metal film, then filled with a gas mixture consisting of air, argon, and krypton, and subsequently reinstalled. This reduced heat loss through the windows by 75%, photo: UN Women/Ryan Brown.

soundproofing effect. Xenon is twice as efficient as krypton, which in turn is three times more efficient than argon, which is twice as efficient as air. Even in special sunscreens, partly metal-coated with the aid of krypton as a carrier gas, for the solar and automotive industries, and in commercial buildings, the gaps between the glass panes are filled with argon or, more rarely, with the more expensive krypton.

Krypton, in addition to the other noble gases, plays a key role in semiconductor technology in **excimer lasers** (see 3.2.1). Increasing krypton sales for use in lasers in numerous applications (medical, semiconductor, special fields) may have offset the declining market share of krypton for incandescent lamps (see below).

Halogen lamp filling for car headlights using krypton is the largest market for this noble gas within the lighting industry. Even in incandescent lamps, where still in use despite of the rapid market penetration of LED lamps, krypton is a significant filling gas. Because of the gas's low heat conduction, the tungsten filament can be operated at a higher temperature than with argon and nitrogen fills. As a result, the light output of the lamps is significantly increased and their colour temperature approaches that of sunlight. Krypton is only used, in comparison to argon, where high light output is required, due to its rarity and therefore higher price.

Geiger counters with a krypton gas filling are especially sensitive. Scintillation counter tubes, such as those used in nuclear medicine for PET examinations or in scanning electron microscopes, therefore also use krypton as the fill gas.

Because krypton has long been cheaper than xenon, in particular, and also because no supply difficulties are anticipated, krypton is a coveted research object. In cathode sputtering (*sputter deposition*), it has become established in part as both a protective and a plasma gas, even compared to argon.

3.2.5 Xenon

Xenon gas discharge lamps have a colour spectrum very similar to that of daylight or sunlight, and at the same time require relatively little energy in order to generate the necessary temperature. However, it is necessary to add a very small amount of mercury and a metal salt to compensate for the otherwise violet colour of pure xenon (cf. 3.2). High-pressure xenon lamps have long been used to illuminate large areas, for example airport aprons, quaysides and sports facilities, or are used in lighthouses. Runway marker lights, scanner and photocopier lights, cinema projectors, camera flashes and artificial lighting in greenhouses are all based on this technology. Relatively new, in contrast, is the use of xenon for **halogen lamps** in car headlights, which is becoming increasingly prevalent in high-end cars, but which is already being replaced by LED technology.

High-purity xenon is used as a **detector material** in the investigation of dark matter. According to Betzendahl (2016), at least 7–8% of global xenon production was used for this purpose in 2016. According to Spiritus & Betzendahl((2018), however, this xenon will not be consumed and will be available to the market after the end of research activities.

In space, **xenon ion drives** are used to drive interplanetary probes and, increasingly, manoeuvrable

Fig. 18: At night, 4000 watt high-pressure xenon Osram floodlights illuminate the Niagara Falls between Canada and the USA. At a voltage of 21 volts they together produce a light intensity of 8 billion candela, photo: Ruben Yie/Wikipedia.

satellites. A gas, usually xenon, much less often krypton or argon, is ionised and then accelerated in an electrical field to approximately 35 km/s for this purpose. After the passage of what is known as a neutraliser, which again supplies electrons to the beam and thus makes it electrically neutral, the particles are expelled in the form of a jet, thereby driving the probe in the desired direction. Probes or satellites carry several hundred kilograms of xenon at launch. Consumption is low and is around 0.35 ml Xe/s (Hall 2016) or 0.1–5 mg Xe/s, depending on the size of the satellite (Airbus Defence and Space, personal communication).

Similar to the other noble gases, xenon in the form of XeCl is important in certain **excimer lasers**, which play a key role in some semiconductor process steps (*annealing*) (see 3.2.1).

In **plasma etching**, another process step in the semiconductor industry, a high-frequency or electrodeless microwave discharge is ignited in a vacuum reactor, which is filled with an etching gas to a pressure of a few millibars, and thus a highly reactive, etching-active plasma generated. XeF_2 has been shown to be a suitable etching gas suitable for etching Si, Mo or Ge.

Currently, a **3D photolithography process**, which also requires significant amounts of xenon, is being put into practice in the semiconductor industry, led by Samsung (Betzendahl 2017, Spiritus & Betzendahl 2018).

Xenon isotopes play a role in certain special applications in **medicine**. High-purity xenon is also used to measure cerebral blood flow and, mixed with oxygen, to increase the contrast in computer tomography scans and determine blood flow.

Xenon has anaesthetising properties in specific concentration ranges and has been tested for several years as a (more expensive) alternative to existing **anaesthetics**, which are still associated with risks. Xenon barely interferes with circulation and quickly saturates and desaturates due to its poor solubility in blood. Patients recover quickly after anaesthesia. In addition, the noble gas is released only through the lungs, meaning that the doctors can control the depth of anaesthesia by measuring the concentration in the breathing air. In a two-hour inhalation anaesthesia, however, about 12 litres of xenon are consumed, thus contributing to high costs. In addition, xenon may affect pulmonary function due to its high density. Patients with lung diseases and children should never be treated with such pure xenon anaesthetics. However, when xenon is dissolved in a fat emulsion and introduced into the organism by infusion, the situation is different. Unlike intake of the noble gas through the lungs, the substance spreads through a much smaller region after intravenous administration and consumption is only 150 ml of xenon in a two-hour anaesthesia. Xenon as an anaesthetic, however, is only approved for use in Russia, the EU and a few other countries, but not in the USA.

In the electronics industry, xenon is used as a filling for special **radar technology** components.

The high demand for xenon for use in **plasma televisions** has fallen drastically since the entire market moved towards LCD televisions. However, a small market for smartphone screens on AMOLED (*active-matrix organic light-emitting diode)* basis, for the production of which xenon is also required, still exists.

Xenon difluoride, XF_2, is also a strong, if very expensive, oxidation agent in organic synthesis.

3.2.6 Radon

Due to its radioactivity, radon is used – in moderation – in **radon balneology**, for example in Bad Kreuznach/Germany (radon activity between 30,000 and 130,000 Bq/m^3 in the radon therapy mine, Falkenbach 2008), Bad Gastein/Austria (mean radon activity 44,000 Bq/m^3 in the radon therapy mine, Falkenbach 2008), Jáchymov (Joachimsthal)/Czech Republic (radon activity in baths between 4500–5500 Bq/l, Lazzerini & Bonotto 2015), St. Blasien-Menzenschwand/Germany (mean radon activity in baths 700 Bq/l), Karlovy Vary (Karlsbad)/Czech Republic and Ischia/Italy. The local spas advertise that radon therapy has anti-inflammatory and pain-relieving effects and also stimulates the immune system.

3.3 Toxicity

All noble gases are inert, non-flammable and non-toxic. However, they are also odourless, colourless, tasteless and non-irritating, and are therefore unnoticeable to humans in any form. As a result, there is the risk of unconscious – or even deliberate – inhalation of (excessively) large amounts of noble gases, in practice generally helium, which then leads to suffocation by oxygen deficiency, because the noble gases displace oxygen.

According to Radnedge (2012), two deaths from helium suffocation occurred in the United Kingdom in 2007, compared with 42 in 2011. In 2015 there were 65 cases. In the 16 states of the USA that maintain appropriate statistics, a total of 665 people were killed by helium in the period 2005–2012, with a strongly increasing tendency. However, suicide by gas, most commonly carbon monoxide, accounts for only 4% of all suicides in the surveyed states (Azrael et al. 2016). The majority of deaths from helium involve suicide by young people following instructions found on the Internet. According to statistical studies, inhalation of pure helium leads to unconsciousness after five breaths or an average of 35 seconds, but only if no oxygen is inhaled or is still in the lungs. Death follows within 2–40 minutes, or an average of 10 minutes. The medical diagnosis is: *hypoxemic asphyxiation due to helium inhalation*. Deaths from suffocation during cleaning work in large helium balloons were also reported from the USA.

An additional physiological property of the noble gases is the ability to dissolve in blood and other body fluids to a similar extent as they do in water. As a result, they have an anaesthetising effect, which is exploited during operations, particularly in the case of xenon (cf. Section 3.2.5).

When handling all liquid noble gases without appropriate protective equipment there is danger of freezing of the extremities.

Xenon difluoride is a white, crystalline powder which melts at 129 °C and decays explosively back to xenon and fluorine upon further heating. It is appropriately labelled in the hazardous substance identification system as fire-promoting and toxic. Its maximum (allowable) workplace concentration is specified as 2.5 mg/m^3. All other synthetic xenon compounds are unstable and release corrosive and therefore hazardous substances when they decay.

3.3.1 Radon

The world‘s second most common cause of lung cancer after smoking is radon. In Germany, there are an estimated 1900 (other sources: 3000) lung cancer deaths each year as a result of radon exposure. However, radon itself, similar the other noble gases, is inert and is inhaled and exhaled without being chemically bonded or accumulated. The main hazard is posed by the radioactive decay products of radon.

Radon is an indoor pollutant. The main source of radon in buildings is usually the geogenic subsurface (cf. Section 2.2). Release from building materials, as well as from domestic water and drinking water, usually only plays a subordinate role in indoor pollution in Germany. This can be different in other countries.

Of the three naturally occurring radon isotopes ^{219}Rn, ^{220}Rn and ^{222}Rn (cf. Section 2.2), the commonest radon isotope, ^{222}Rn, decays so slowly that it can reach the surface or enter the building envelope from its place of origin in the rock or soil in solution in groundwater or by diffusion. The average diffusion range of radon in dry soils is 1.6–1.9 m, in wet soils, however, it is only 1 cm (Schumann et al. 1994).

Radon‘s decay products are in turn unstable isotopes of the heavy metals polonium, lead and bismuth. Although they form as free ions, some of them are quickly redistributed by water vapour or gases and thus form groups consisting of several molecules. These are highly mobile and tend to attach to surfaces in a space or to airborne particulates (aerosols). The state of equilibrium in ambient air depends mainly on the rate of external air exchange, the aerosol concentration in the space and the surface-to-volume ratio of the space (SSK 1992).

Of the aerosols, about 20–30% are filtered out with each breath and deposited in various locations in the respiratory tract. In the respiratory tract, the proportion of isotopes not bound to aerosols, the ratio between radon and its daughter isotopes, the size of the aerosols, the respiratory volume and frequency, the ratio between air inhaled through the mouth and through the nose, the structure of the bronchi, the self-cleaning mechanism of the bronchi, as well as shielding by the possibly pre-damaged mucus layer, are all critical for the radioactive dose in the basal cells (Samet 1994).

The polonium isotopes ^{210}Po, ^{212}Po, ^{214}Po, ^{215}Po, ^{216}Po and ^{218}Po, all radon decay products, have the greatest radiological impact, because they are all alpha emitters. The penetration depth of alpha particles is exceedingly small. Inhaled, however, the alpha particles come in direct contact with living cells and damage them in a concentrated and small space. Critical regions in the lung are the basal cells of the bronchial epithelium, other dividable cells in the alveolar epithelium and the bronchioles. The damage is directly caused by changes in the genetic substance (DNA) of the irradiated cells. The time span between irradiation and the onset of lung cancer is almost never less than 5–10 years and can be as much as several decades, suggesting highly complex, multistep lung cancer mechanisms in humans (SSK 1992).

The average radon concentration in ambient air in Germany is about 14 Bq/m^3. Here, ground-level air is particularly radon-rich, see below, while air strata at higher elevations contain comparatively little radon.

The mean radon concentration value in flats in the former West German states is 49 Bq/m^3 in indoor air. Assuming an average probability of residence in such average flats and given a mean life expectancy of 70–80 years results in a cumulative exposure that is lower by approximately a factor of 4 than the exposure range of miners for whom a statistically significant increase in lung cancer risk was observed. This means that even living for decades in a flat polluted by radon, on average, does not lead to any detectable health risks. However, as the radon concentration in the indoor air increases, the risk of developing lung cancer also increases significantly.

WHO recommends an annual average target of 100 Bq/m^3, which should not be exceeded in the residential areas of buildings. If this target value cannot be achieved as a result of the prevalent boundary conditions, the reference value should not be higher than 300 Bq/m^3. According to the current German Radiation Protection Act (*Strahlenschutzgesetz – StrlSchG*), the reference value for the average annual ^{222}Rn activity concentration in the air in residential rooms in Germany is 300 Bq/m^3. This reference value is used as a benchmark for assessing the adequacy of measures but does not represent a limit value.

Because the geogenic subsurface is the main source of elevated radon concentrations in indoor air, the German Federal Office for Radiation Protection (*Bundesamt für Strahlenschutz – BfS*) has defined areas known as radon prevention zones in the context of precautionary radon protection measures for new buildings. They include all areas in Germany for which soil air radon concentrations greater than 20,000 Bq/m^3 are predicted. At these soil air levels, an exceedance frequency of a radon concentration of 100 Bq/m^3 of 1% is anticipated in the residential areas of residential buildings. The radon prevention zones are classified according to the level of radon activity concentration in the soil air – and therefore an increasing exceedance frequency of radon in indoor air. The following classes are defined:

- radon prevention zone I: 20,000 to 40,000 Bq/m^3
- radon prevention zone II: above 40,000 to 100,000 Bq/m^3
- radon prevention zone III: above 100,000 Bq/m^3

In Saxony, as Germany‘s only state to date and one which is particularly affected in addition to Bavaria and Thuringia, state-wide mapping of the geogenic radon potential was carried out on the basis of anticipated radon concentration values in the soil air. It relies on approx. 1000 measuring points. The Federal Office for Radiation Protection also provides a nationwide, generalised map of radon concentrations in soil air based on 2346 geologically representative survey points (Fig. 19).

According to a study by the Federal German Commission on Radiological Protection (*Strahlenschutzkommission – SSK*), radon concentrations in Germany are subject to pronounced temporal (daily, annual), regional and even local fluctuations. In general, in addition to the geogenic situation, the type of construction and the type of house (with a cellar, on a slope, cracks in the building, cable ducts, building materials, negative pressure through chimney effect inside the building) have a significant influence on the level of radon concentrations in rooms, as well as the air exchange rate, which in turn depends on the construction method and on the habits of the house residents.

The radon concentrations in houses in large cities are much lower than in rural areas. High concen-

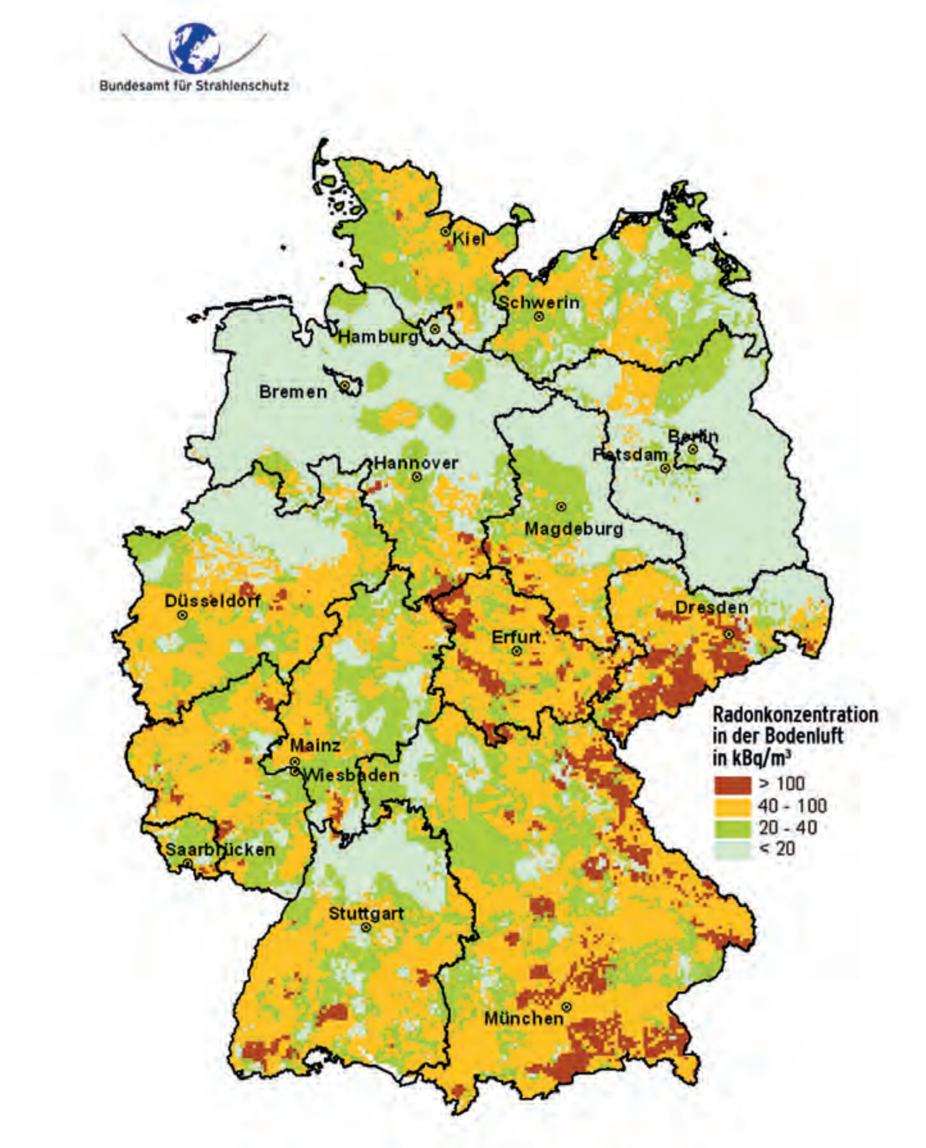


Fig. 19: Radon concentration in soil air in Germany, source: Bundesamt für Strahlenschutz.

trations of radon are more often found in detached houses, which are built with partial cellars or without cellars, as well as in older houses using natural stone or loam as wall building material (SSK 1992).

3.4 Recycling

Because of the rising prices for helium in recent years, and the already high prices for the other noble gases, recycling (or rather, reuse) in all industrial applications – where actually technically feasible – is a prominent issue.

True recycling, i.e. the use of *waste helium*, only occurs when filling or servicing MRIs. Here, the evaporating liquid helium is collected as gas, compressed and then sold as balloon gas.

The demand for helium recycling equipment noticeably increased at the end of 2012, when the global helium supply was no longer secure. Large scientific helium consumers also got together at this time and jointly acquired and developed devices for the liquefaction of gaseous helium, because liquid helium can be better recycled and transported. Gas companies often offer specific recycling programmes for customers who accumulate more than 500 litres of liquid helium annually.

Several German universities and research institutes also collect the gaseous helium they use and return it to the respective gas suppliers, partly in the gaseous state, partly liquefied, for a fee. Here, good recovery rates are between 90% and 95%. In 2010, there were a total of 34 large research facilities in Germany operating a helium recovery unit or liquefaction unit at 21 locations. The price for a complete plant such as this, with liquefaction, is said to be around €2 million (Illichmann 2018).

Since 2004, the major MRI device manufacturers, such as GE Healthcare, Philips Healthcare or Siemens Healthineers, have moved to stop releasing the escaping helium from their devices into the atmosphere, and to recycle it instead. With the development of *zero boil-off* technology in this year, the consumption of helium in MRIs dropped significantly. However, it is estimated that GE Healthcare alone requires around 6 million litres of liquid helium each year to keep its equipment exported to the USA running. In addition, 5.7 million litres of helium will be used to initially fill around 1000 MRIs annually at the production site in Florence, South Carolina. The company claims to have saved around 5% helium annually in recent years and hopes to continue this trend (Gubler et al. 2016).

NASA, too, now recovers the large volumes of helium required for pressurising and purging. Here, it is important to remove the contaminating hydrogen from the helium after use, but this is technically easily feasible (Baker 2018).

With regard to leak detection, up to 98% of the gas mixture containing helium can be reused. For this purpose, the used gas stream is collected, cleaned of oils and impurities, compressed and then used again (gasworld 2009).

As neon prices increased significantly in the first half of 2015, the only two global manufacturers of excimer lasers for the semiconductor industry, Cymer LLC/USA (3800 delivered lasers by 2016) and Gigaphoton Inc./Japan (1300 delivered devices by 2016), were asked by their customers to significantly reduce the neon requirement of the devices. Cymer LLC managed to reduce the requirement by 70% (note: it is unclear whether through technical modifications or by recycling), while Gigaphoton Inc. offered its customers a short-term and free recycling programme that was able to recycle up to 50% of the neon used (Healy 2016). It has been shown that new excimer laser software was developed at short notice in cooperation between manufacturers and customers, saving 20–25% of the previously required neon.

In the semiconductor industry, such large volumes of argon are used in some process steps that in-house and separate recycling facilities are viable with regard to this noble gas.

While there is little interest in krypton already in use, due to the global oversupply (cf. Section 5.4), xenon has been recycled for a long time, because of its rarity and high price. Since 2008, a number of gas companies have also collected the used xenon or xenon difluoride from their major customers (consumption > 10,000 litres Xe/a) in the form of polluted exhaust gases, e.g. from plasma etching processes with high Xe concentration (up to 0.5% Xe), and, after concentration and compression, transported it to special distillation plants. Here, it is completely purified and then repackaged. The recycling factor for this xenon is > 98%. The customers, e.g. semiconductor factories, then receive a credit for their next xenon order.

3.5 Substitution

At least as important as the reuse (*recycling*, see Section 3.4) of noble gases from industry and larger consumers are all developments that allow the minimisation of noble gas use, as far as possible, or their substitution in daily use by cheaper gases, possibly including other noble gases. Whenever noble gas supply shortages are reported and/or prices rise, substitution efforts naturally also increase.

The status of research on hydrogen as a substitute for helium in refrigeration systems was described by Glowacki (2012). He pointed out that liquid hydrogen (then) cost US$0.65/l, liquid helium US$4.50/l, and liquid neon US$225/l.

As a result of the high and rising costs of helium in recent years, research into a helium-free solution, or at least into lowering demand for helium for cooling in MRIs, has intensified (cf. Section 3.4). Highly leak-proof cooling systems can already reduce the need for helium during servicing. In 2016, GE Healthcare announced the development of *Freelium*, an MRI technology that will require only 20 litres of liquid helium in the initial charge instead of 2000 litres, and requires no helium at all during servicing (GE Healthcare 2016). However, technical details on *Freelium* have not yet been published. Also in 2016, Siemens announced technical advances in the development of high-temperature, rare earth-based superconductors in the place of low-temperature NbTi-based superconductors for use in MRI. These may be supercooled using liquid neon or liquid hydrogen to –220 °C instead of liquid helium to –270 °C and would no longer require power during operation (Webel 2016).

Helium can be replaced as a carrier gas by the cheaper and even more effective hydrogen. This is known to be flammable and explosive and is therefore used only in remote areas, mainly by the military, for these purposes.

For leak detection, helium can be replaced by low-concentration (explosion hazard at 4–75% H_2 in a gas!) hydrogen-gas mixtures, by helium-nitrogen gas mixtures with only 10%, or even as low as 5% He, or by carbon dioxide-argon gas mixtures. Even the gas suppliers recommend minimising the helium content in the gas mixture for leak detection to 5%, because otherwise the sensitive gas detectors could react to any helium present throughout the company (Cockerill 2013a). However, due to the small size of its atoms, helium remains the preferred gas for all the more demanding leak tests.

In technical diving, great diving depths can be achieved not only by the use of *Tri-mix* or *Heliox* gas mixtures, but also by gas mixtures such as *Hydrox*, which consists of hydrogen and oxygen, and *Hydreliox*, a gas mixture which comprises hydrogen, helium and oxygen. Using *Hydrox*, divers can already achieve in depths of 700 m.

In most welding applications, helium can be substituted by argon as a shielding gas without any significant loss of quality. For cost reasons, argon is already preferred as a protective gas in Europe, while work in the USA has almost exclusively used helium due to its easy availability. Only in the aerospace industry, where quality is of the utmost importance, does helium remain indispensable as an inert gas during welding.

Helium is already substituted by argon, where possible, in semiconductor manufacturing, as well as in the production of optical fibres. Optionally, argon-helium gas mixtures may also be used in production.

According to Khan (2017), the use of ultra-short-wave (13.5 nm) CO_2 lasers will have no impact on the use of noble gases in the semiconductor industry. In his opinion, they will not influence the rapidly growing market for excimer lasers but will instead complement them.

In the aerospace industry, liquid neon serves as a cooling agent for highly sensitive infrared sensors instead of liquid helium. Neon has an atomic diameter around twice as large as that of helium, meaning it diffuses more slowly into space and therefore allows satellites to operate longer.

Some refrigerants also use neon on a small scale as a substitute for helium. Although it is significantly more expensive than liquid helium, its cooling capacity is 41 times higher, and three times higher than liquid hydrogen.

In gas chromatography, hydrogen instead of helium has the advantage of lower viscosity, which makes analysis faster and more gases can be detected in the small capillary columns. This leads to overall higher laboratory productivity. Flame ionisation detectors (FID), thermal conductivity detectors (TCD), flame photometric detectors (FPD) and electron capture detectors (ECD) can all work on the basis of helium in addition to hydrogen.

However, according to Gubler et al. (2016), users of gas chromatographs in the USA during the helium shortage in the years 2011–2013 did not change from helium to the cheaper, but flammable or explosive hydrogen, but instead to the non-combustible argon, as a precautionary measure which, however, has a higher viscosity.

Substitution is not possible, however, in helium ionisation detectors, which use helium as the detection medium, nor in the analysis of unsaturated or aromatic hydrocarbon solutions, because hydrogen may react with these solutions and thereby alter them (Cockerill 2013b).

In screen production, it would be possible to cool the glass using argon or even nitrogen instead of helium. However, these *cooling agents* are not yet in use by the screen producers in south-east Asia and China, because of the high flow rates required.

It is not possible to substitute helium in the field of superconducting magnets, in basic research in the milli-Kelvin range, or for purging fuel tanks for filling with liquid hydrogen or oxygen. In oxygen tanks, hydrogen, as a substitute for helium, would react with the oxygen, or nitrogen as a substitute would contaminate the tank. In hydrogen tanks, all gases except helium and hydrogen would freeze and clog the plant components.

In order to reduce costs, the argon-oxygen decarburisation process sometimes uses nitrogen or simple compressed air instead of argon at the beginning of the process.

In insulating glass production, the filling gas used between the panes is usually the much cheaper argon, instead of the highly efficient krypton.

In headlamps, instead of halogen lamps with xenon filling, krypton filling can also be used.

Due to the high price and the occasionally poor availability of xenon in the past, research is being performed with the aim of using krypton as a substitute in satellite ion drives in the future. According to a personal communication with Airbus Defence & Space, however, iodine is much more similar to xenon based on its atomic mass and density and offers a much better *power-to-thrust ratio.*

3.6 Chemical requirements on noble gases

In line with the quite different areas of use, especially of helium and argon, these noble gases are required in different qualities and are offered accordingly. In general, the requirements on noble gases continue to rise in some industrial sectors, as the requirements on the quality of the end products manufactured with the help of noble gases also continuously increase. However, these increased quality requirements do not apply to all sectors. For example, helium was formerly offered and used as a 99.995% (4.5) standard, but today is routinely offered in 99.999% (5.0) quality, even though this is not always necessary. The reason for this lies in the starting material, i.e. liquid helium at 99.999% He, which can now be easily transported, but which is then generally used as gaseous helium (cf. Section 5.1). The purity requirements not only with regard to helium used for leak detection, but also for helium for rapid heat transfer or removal, for airbag filling, and especially as a carrier gas (typically 95–97.5% He), are not this stringent. However, the separate handling of balloon helium and helium 5.0 would require new or secondary storage loops even for smaller gas producers and traders, which is understandably avoided for cost reasons.

In semiconductor production, the permissible noble gas impurities are in the ppt range for many applications. Frequently, the helium supplied by the helium producers is purified even further to 99.999–99.9999% (5.0 to 6.0) purity. For *resonator gas*, in contrast, the minimum purities are lower at > 99.996% He (4.6). Even lower purities than this would contaminate the optics in the laser, the so-called resonator.

In gas chromatography, too, impurities in the ppm range only are permissible. This corresponds to a minimum purity of 99.9999% He (6.0).

The quality requirements for protection gases in welding are specified in DIN EN ISO 14175. Here, a purity of at least 99.99% (4.0) is required for inert gases (argon, helium). In Germany, the standard purity 99.996% (4.6) is used. Here, a moisture content of 40 ppm is not exceeded. In main group I (inert gases) in ISO 14175, the subgroups 1 (pure argon), 2 (pure helium) and 3 (argon-helium gas mixtures at 0.5% < He < 95%) are differentiated.

Guaranteed grades of helium, argon, neon, krypton, and xenon for various uses by leading global gas companies are listed in Tables 6–10.

Fig. 20: Today, helium is almost exclusively offered in the standard quality 5.0 (99.999% He), photo: BGR.

Table 6: Guaranteed qualities of helium for different uses or in different degrees of purity, by company data sheets.

	He (vol.-%)	H_2O (ppmv)	O_2 (ppmv)	N_2 (ppmv)	Ne (ppmv)	H_2 (ppmv)	HC (as CH_4) (ppmv)	CO + CO_2 (ppmv)	halog. HC (ppbv)
Air Liquide									
Helium N46 1)	≥ 99.996	≤ 5	≤ 5	≤ 20	≤10	–	≤ 1	–	–
Helium N50 2)	≥ 99.999	≤ 3	≤ 1	≤ 4	≤ 1	–	≤ 0.5	–	–
Helium N60 3)	≥ 99.9999	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.1	–	–
ALPHAGAZ™ 1 Helium 4)	≥ 99.999	≤ 2	≤ 2	≤ 5	–	–	≤ 0.2	–	–
ALPHAGAZ™ 2 Helium 5)	≥ 99.9999	≤ 0.5	≤ 0.1	–	–	≤ 0.1	≤ 0.1	≤ 0.2 6)	≤1
Helium Electronic Grade 1	≥ 99.999	< 0.5	< 0.5	< 0.5		< 1	< 0.2	< 1.0 13)	
Helium Electronic Grade 2	≥ 99.9995	< 1	< 1	< 5		< 0.5	< 0.2	< 1.0 13)	
Baloongas 7)	≥ 95.00	–	–	–	–	–	–	–	–
Helium 3 8) 11)	≥ 99.995	< 3	< 1	< 10	< 10 10)	–	–	< 1 9)	–
Air Products									
Helium Chromatographic Grade	99.9999	< 0.2	< 1	< 1	< 0.5 12)	–	< 0.1	–	–
Helium GC Grade	99.999	< 0.02	< 0.01	< 5	–	–	< 0.1	< 0.5	–
Helium Research Grade	99.9999	< 0.2	< 1	< 1	< 0.5 12)	–	< 0.01	< 0.1 9)	–
Helium Ultra Pure Carrier Grade	99.995	< 1.0	< 1	< 5	–	–	< 0.5	–	–
Helium UHP/Zero Grade	99.999	< 3.5	< 4	–	–	–	< 0.5	–	–
Helium High Purity Grade	99.997	< 3.5	< 5	–	–	–	–	–	–
Helium Premium	99.9992	< 2	< 1	< 5	–	–	< 0.5	–	–
Helium BIP	99.9997	< 0.02	< 0.01	< 1	–	–	< 0.1	< 0.5	–
Helium BIP ECD	99.9997	< 0.02	< 0.01	< 1	–	–	< 0.1	< 0.5	< 1
Helium BIP Plus	99.99997	< 0.02	< 0.01	< 0.1	–	< 0.1	< 0.05	< 0.05	–

Table 6 (continued).

	He (vol.-%)	H_2O (ppmv)	O_2 (ppmv)	N_2 (ppmv)	Ne (ppmv)	H_2 (ppmv)	HC (as CH_4) (ppmv)	CO + CO_2 (ppmv)	halog. HC (ppbv)
Linde									
Helium 4.6	≥ 99.996	≤ 5	≤ 5	–	–	–	–	–	–
Helium 5.0	≥ 99.999	≤ 3	≤ 2	≤ 5	–	–	≤ 0.5	–	–
Helium 6.0	≥ 99.9999	≤ 0.5	≤ 0.5	≤ 0.5	–	≤ 0.5	≤ 0.1	≤ 0.2 6)	–
Helium Pharmaceutical Grade	≥ 99.5	< 67	≤ 50	–	–	–	≤ 50	≤ 10 16)	–
Helium 5.0 Zero	≥ 99.999	≤ 3	≤ 2	≤ 5	–	–	≤ 0.2	≤ 1 13)	–
Helium 5.5 ECD	≥ 9.9995	≤ 1	≤ 1	≤ 2	–	–	≤ 0.1	≤ 1 13)	≤ 1
Helium 7.0	≥ 99.99999	≤ 0.05	≤ 0.03	–	–	≤ 0.03	≤ 0.03	≤ 0.06 17)	≤ 1
Messer									
Helium 4.6	> 99.996	< 5	< 5	< 20	–	–	< 1	–	–
Helium 5.0	> 99.999	< 3	< 1	< 4	–	–	< 0.2	–	–
Helium 5.6	> 99.9996	< 2	< 1	< 1	–	–	< 0.1	< 0.1	–
Helium ECD	> 99.9996	< 2	< 1	< 1	–	–	< 0.1	–	< 1
Helium 6.0	> 99.9999	< 0.5	< 0.5	< 0.5	–	–	< 0.1	< 0.1	–
Praxair									
Helium Research. 6.0	99.9999	≤ 0.2	≤ 0.1	≤ 0.4	12)	≤ 0.5	≤ 0.1	≤ 0.2 6)	–
Helium Chromatography. 6.0	99.9999	≤ 0.2	≤ 0.5	-	–	–	≤ 0.1	≤ 0.2 6)	–
Helium Semiconductor. 6.0	99.9999	≤ 0.2	≤ 0.2	≤ 0.5	15)	≤ 0.1	≤ 0.1	≤ 0.2 6)	–
Helium Trace Analytical. 5.5	99.9995	≤ 2	≤ 1	≤ 2	–	–	≤ 0.1	≤ 1.0 13)	≤ 0.5
Helium Semiconductor. 5.5	99.9995	≤ 0.5	≤ 0.5	≤ 2	–	–	≤ 0.5	≤ 1.0 13)	–
Helium Laser Star. 5.5	99.9995	≤ 1	≤ 1	–	–	–	≤ 0.1	–	≤ 0.05

Table 6 (continued).

	He (vol.-%)	H_2O (ppmv)	O_2 (ppmv)	N_2 (ppmv)	Ne (ppmv)	H_2 (ppmv)	HC (as CH_4) (ppmv)	CO + CO_2 (ppmv)	halog. HC (ppbv)
Praxair *(continued)*									
Helium UHP Plus. 5.5	99.9995	≤ 1	≤ 1	≤ 3	-	-	≤ 0.5	≤ 1.0 [13]	-
Helium Semiconductor. 5.0	99.999	≤ 3	≤ 2	≤ 6	-	-	≤ 1	≤ 2 [14]	-
Helium Ultra High Purity. 5.0	99.999	≤ 2	≤ 1	≤ 5	-	-	≤ 0.5	-	-
Helium Laser Star. 5.0	99.999	≤ 2	≤ 1	-	-	-	≤ 0.5	-	-
Helium Laser Star. 4.7	99.997	≤ 3	≤ 3	-	-	-	≤ 1	-	
Helium Zero. 4.8	99.998	≤ 3	≤ 4	-	-	-	≤ 0.5	-	
Helium High Purity. 4.8	99.998	≤ 5	≤ 5	-	-	-	-	-	

Note: In some cases, company data sheets with different specifications exist for the same products!

[1] Laboratory & analytics: leak test medium, welding & cutting: protective gas for TIG, MIG, plasma and laser welding, semiconductor industry: cooling, photovoltaics

[2] Laboratory & analytics: demanding applications, carrier gas for gas chromatography, leak test medium, welding & cutting: protective gas for TIG, MIG, plasma and laser welding, semiconductor industry: cooling, photovoltaics

[3] Laboratory & analytics: demanding applications, carrier, purging and zero gas, semiconductor industry

[4] Laboratory & analytics: carrier gas (GC), operating gas (MS, elementary analysis), purging (TOC, thermal analysis) and zero gas, leak test medium, semiconductor industry: cooling

[5] Laboratory & analytics: carrier gas (GC), zero gas, purging gas, recommended for ECD (electron capture detector), semiconductor industry

[6] < 0.1 ppmv each

[7] Filling and flying balloons, balloon decorations

[8] Laboratory & research, low-temperature physics, low-temperature refrigerants

[9] Only CO_2

[10] Ar

[11] Tritium: < 5 ppb Ci/l

[12] Ar < 0.5 ppmv

[13] < 0.5 ppmv each

[14] 1 ppmv each

[15] Ar < 0.1 ppmv

[16] Only CO_2

[17] 0.03 ppmv each

Table 7: Guaranteed qualities of argon for different uses or in different degrees of purity, by company data sheets.

	Ar (vol.-%)	H_2O (ppmv)	O_2 (ppmv)	N_2 (ppmv)	HC (as CH_4) (ppmv)	$CO+CO_2$ (ppmv)	H_2 (ppmv)	halog. HC (ppbv)
Air Liquide								
Argon N46 [1]	≥ 99.996	≤ 10	≤ 6	≤ 20	–	–	–	–
Argon N50 liquid [2]	≥ 99.999	≤ 0.2	< 2	< 5	< 0.2	–	–	–
Argon N50 Photovoltaic	≥ 99.999	≤ 1	≤ 2	≤ 5	≤ 0.5	–	–	–
Argon N60 [3]	≥ 99.9999	≤ 0.5	≤0.1		≤ 0.1	≤ 0.2 [4]	≤0.1	–
ALNAT 6	≥ 99.999	≤ 2	≤ 3	≤ 5	–	–	–	–
ALPHAGAZ™ 1 Argon [5]	≥ 99.999	≤ 2	≤ 2	≤ 5	≤ 0.2	≤ 0.2 [6]	–	–
ALPHAGAZ™ 2 Argon [7]	≥ 99.9999	≤ 0.5	≤ 0.1		≤ 0.1	≤ 0.2 [4]	≤0.1	–
Electronic Grade 1	≥ 99.999	< 1	< 1	< 5	< 0.2	< 0.5 [6]	<1	–
Electronic Grade 2	≥ 99.9995	< 1	< 1	< 3	< 0.2	< 0.2 [4]	<0.1	–
Electronic Grade 3	≥ 99.9999	< 0.5	< 0.2	< 0.5	< 0.1	< 0.2	<0.1	–
Air Products								
Argon liquid	99.999	< 2	< 3	< 5	< 0.5	–		–
Argon Premium	99.9992	< 2	< 1.5	< 4	< 0.1	–	–	–
Argon BIP	99.9997	< 0.02	< 0.01	< 1	< 0.1	< 0.1	–	–
Argon BIP Plus	99.99996	< 0.02	< 0.01	< 0.3	< 0.05	< 0.05	–	–

Table 7 (continued).

	Ar (vol.-%)	H_2O (ppmv)	O_2 (ppmv)	N_2 (ppmv)	HC (as CH_4) (ppmv)	$CO+CO_2$ (ppmv)	H_2 (ppmv)	halog. HC (ppbv)
Linde								
Argon 4.8	≥ 99.998	≤ 5	≤ 5	≤ 10	–	–	–	–
Argon 5.0	≥ 99.999	≤ 3	≤ 2	≤ 5	≤ 0.5	–	–	–
Argon 6.0	≥ 99.9999	≤ 0.5	≤ 0.5	≤ 0.5	≤ 0.1	≤ 0.2 [4]	≤ 0.5	–
Argon Pharmaceutical Grade	≥ 99.998	≤ 5	–	≤ 10	≤ 1	–	–	–
Argon 5.0 Zero	≥ 99.999	≤ 3	≤ 2	≤ 5	≤ 0.2	≤ 2 [9]	–	
Argon 7.0	≥ 99.99999	≤ 0.05	≤ 0.03	-	≤ 0.03	≤ 0,06 [10]	≤ 0.03	≤1
Messer								
Argon 4.8	> 99.998	< 4	< 3	< 10	< 0.2	< 0.2	–	–
Argon Spektro	> 99.998	< 2	< 2	-	< 0.2	< 0.2	–	–
Argon 5.0	> 99.999	< 3	< 2	< 5	< 0.1	< 0.1	–	–
Argon 5.7	> 99,9997	< 1	< 0.5	< 1	< 0.1	< 0.1	–	–
Argon 6.0	> 99.9999	< 0.5	< 0.5	< 0.5	< 0.1	< 0.1	–	–
Praxair								
Argon Semiconductor, 6.0	99.9999	≤ 0.2	≤ 0.2	≤ 0.5	≤ 0.1	≤ 0.2 [4]	≤ 0.1	–
Argon Research, 6.0	99.9999	≤ 1	≤ 0.2	≤ 1	≤ 0.1	≤ 0.2 [4]	–	–
Argon Chromatography, 6.0	99.9999	≤ 1	≤ 0.2	≤ 1	≤ 0.1	≤ 0.2 [4]	–	–
Argon Trace Analytical, 5.5	99.9995	≤ 0.5	≤ 0.5	≤ 2	≤ 0.5	≤ 0.2 [4]	–	–
Argon Semiconductor, 5.5	99.9995	≤ 0.5	≤ 0.5	≤ 2	≤ 0.5	≤ 1 [8]	≤ 0.5	–
Argon Carrier, 5.5	99.9995	≤ 0.5	≤ 0.5	≤ 5	≤ 0.3	≤ 2 [9]	–	–
Argon UHP Plus, 5.3	99.9993	≤ 1	≤ 1	–	≤ 0.5	≤ 2 [9]	–	–

Table 7 (continued).

	Ar (vol.-%)	H_2O (ppmv)	O_2 (ppmv)	N_2 (ppmv)	HC (as CH_4) (ppmv)	$CO+CO_2$ (ppmv)	H_2 (ppmv)	halog. HC (ppbv)
Praxair ***(continued)***								
Argon Ultra High Purity, 5.0	99.999	≤ 3	≤ 2	–	≤ 0.5	–	–	–
Argon Semiconductor, 5.0	99.999	≤ 3	≤ 2	≤6	≤1	≤ 2 [9]	–	–
Argon High Purity, 4.8	99.998	≤ 3	≤ 4	–	–	–	–	–
Argon Zero, 4.8	99.998	≤ 3	≤ 4	–	≤ 0.5	–	–	–

Note: In some cases, company data sheets with different specifications exist for the same products!

[1] *For welding & cutting: protective gas for TIG, MIG and plasma welding; plasma cutting*

[2] *Semiconductor industry: inertisation, purging, hardening, gas discharge in metallisation (sputtering), hot-melt metallurgy: inertisation, purging, laboratory & analytics: demanding applications, protective and plasma gas for ICP equipment, operating gas for spark spectrometry, welding & cutting: protective gas for TIG, MIG and plasma welding; plasma cutting*

[3] *Semiconductor & photovoltaics*

[4] *< 0.1 ppmv each*

[5] *Heat treatment of metallic materials, annealing, high-pressure quenching and inertisation, laboratory & analytics carrier gas (GC), purging and zero gas, operating gas (spark spectrometry, plasma gas for ICP, protective gas for AAS), semiconductor industry: inertisation, purging, hardening, gas discharge in metallisation (sputtering), hot-melt metallurgy: inertisation, purging*

[6] *as* CO_2

[7] *Laboratory & analytics: carrier gas (GC), purging and zero gas, operating gas (plasma gas in ICP, protective gas for AAS)*

[8] *0.5 ppmv each*

[9] *1.0 ppmv each*

[10] *0.03 ppmv each*

Table 8: Guaranteed qualities of neon for different uses or in different degrees of purity, by company data sheets.

	Ne (vol.-%)	H_2O (ppmv)	O_2 (ppmv)	N_2 (ppmv)	H_2 (ppmv)	He (ppmv)	Ar (ppmv)	Kr (ppmv)	HC (as CH_4) (ppmv)	$CO+CO_2$ (ppmv)
Air Liquide										
Neon N40 1)	≥ 99.99	< 2	< 1	< 5	–	< 100	–	–	–	–
Neon N50 1)	≥ 99.999	< 1	< 1	< 2	–	< 6	–	–	< 0.1	< 0.5
Neon Research	≥ 99,996	< 1	< 1		–		–	–	-	< 2 2)
Neon Research Plus	≥ 99.999	< 1	< 1	< 2	< 1	< 8	–	< 2	< 0.05	< 2 2)
Linde										
Neon Research	99.999	< 0.5	< 0.5	< 1	–	< 8	–	–	< 0.5	< 1 3)
Neon UHP	99.996	< 1	< 1	< 4	–	< 35	–	–	< 1	< 2 2)
Messer										
Neon 5.0	> 99.999	< 1	< 1	< 2	–	< 6	–	–	< 0.1	< 0.5
Praxair										
Neon Research, 5.0	99.999	≤ 1	≤ 1	≤ 5	–	≤ 4	≤ 1	–	≤ 0.5	–

Note: In some cases, company data sheets with different specifications exist for the same products!

1) Laboratory & research, lighting equipment

2) < 1.0 ppmv each

3) < 0.5 ppmv each

Table 9: Guaranteed qualities of krypton for different uses or in different degrees of purity, by company data sheets.

	Kr (vol.-%)	H_2O (ppmv)	O_2 (ppmv)	N_2 (ppmv)	Xe (ppmv)	Ar (ppmv)	H_2 (ppmv)	CF_4 (ppmv)	HC (ppmv)	$CO+CO_2$ (ppmv)
Air Liquide										
Krypton N40[1]	≥ 99.99	< 5	< 2	< 20	< 50	< 10	–	–	< 1	–
Krypton N48[2]	v99.998	< 1	< 0.5	< 5	< 5	< 5	-	< 1	< 0.5	–
Krypton Research Plus	≥ 99.999	< 1	< 1	< 2	< 5	< 1	< 1	< 0.5	< 0.5	< 1
Krypton Insulated Glass	≥ 99	< 10	< 1 %	< 1 %	< 1 %					
Linde										
Krypton Research	99.995	≤ 0.5	≤ 0.5	≤ 2	≤ 5	≤ 2	≤ 0.5	≤ 0.5	–	≤ 1.5
Krypton UHP	99.97	≤ 1	≤ 1	≤ 5	≤ 25	≤ 2	≤ 2	≤ 1	–	≤ 1[3]
Messer										
Krypton 4.0	> 99.99	< 5	< 2	< 20	< 50	< 10	–	–	< 1	–
Krypton 5.0	> 99.999	< 1	< 0.5	< 5	< 5	< 1	–	< 0.5	< 0.5	–
Praxair										
Krypton Research, 5.0	99.999	≤ 3	≤ 2	≤ 5	< 4	< 4	< 4	< 3	< 0.2	< 0.5[3]

Note: In some cases, company data sheets with different specifications exist for the same products!

[1] *Laboratory & research, glass industry: fill gas for insulated windows, lighting equipment, excimer lasers, surface finishing*

[2] *Laboratory & research, glass industry: fill gas for insulated windows, lighting equipment, excimer lasers*

[3] *Only CO_2*

[4] *CO 1.0 ppmv*

Table 10: Guaranteed qualities of xenon for different uses or in different degrees of purity, by company data sheet.

	Xe (vol.-%)	H_2O (ppmv)	O_2 (ppmv)	N_2 (ppmv)	Ar (ppmv)	Kr (ppmv)	H_2 (ppmv)	CF_4 (ppmv)	C_2F_6 (ppmv)	SF_6 (ppmv)	KW (ppmv)	$CO+CO_2$ (ppmv)
Air Liquide												
Xenon N40[1]	≥ 99.99	< 5	< 2	< 10	< 10	< 50	–	–	–	–	< 1	–
Xenon N48[1]	≥ 99.998	< 1	< 0.5	< 5	< 5	< 8	–	< 0.5	–	–	< 0.1	–
Xenon N48 halogenfrei[2]	≥ 99.998	< 1	< 0.5	< 5	< 5	< 8	–	< 0.1	–	<0.1	< 0.1	–
Xenon Research Plus	≥ 99.999	< 1	< 1	< 2	< 1	<5	< 1	< 0.1	< 0.1	<0.1	< 0.5	< 1
Linde												
Xenon 5.0	≥ 99.999	≤ 2	< 0.5	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	–	≤ 0.5	≤ 1
Xenon Research	99.999	≤ 0.5	≤0.5	≤ 2	≤ 1	≤ 5	≤ 2	≤ 0.5	–	–	≤ 0.5	≤ 1[4]
Xenon UHP	99.995	≤ 1	≤ 1	≤ 5	≤ 10	≤ 25	≤ 5	≤ 1	–	–	≤ 1	≤ 2[4]
Propulsion	99.9995	≤ 0.1	≤ 0.1	≤ 1	≤ 1	–	≤ 1	≤ 0.1	–	–	≤ 0.1	≤ 0.2[5]
Messer												
Xenon 4.8	> 99.998	< 1	< 0.5	< 5	< 5	< 8	–	< 1	–	–	< 0.1	–
Praxair												
Xenon Aerospace Grade, 5.5	99.9995	≤ 0.1	≤ 0.1	≤ 1	≤ 1	≤ 2	≤ 2	< 0.1	–	–	≤ 0.1	≤ 0.4[3]
Xenon Research, 5.0	99.999	≤2	≤1	≤5	–	–	–	–	–	–	≤1	≤1[4]

Note: In some cases, company data sheets with different specifications exist for the same products!

[1] Laboratory & research, semiconductor industry: electron donor in ion implantation, lighting equipment, aerospace industry

[2] Laboratory & research, semiconductor industry: electron donor in ion implantation, lighting equipment

[3] 0.2 ppmv each

[4] Only CO_2

[5] 0.1 ppmv each

3.7 Requirements on helium deposits

Based on decades of experience in the USA, it has long been regarded as a global guideline that natural gas reservoirs must contain > 0.3 vol.% He to make separation of the helium economically viable. Yakutseni (2014), in contrast, assumes a minimum content of 0.15 vol.% He for reservoirs outside the USA. This does not take into account the relatively large minimum volumes of available helium, without which the construction of a stationary and expensive processing plant would not be profitable.

If helium extraction is politically desirable from a strategic perspective, the helium content in natural gas reserves from which this noble gas would need to be separated may also be much lower. China‘s only natural gas field used for helium production has an average helium content of 0.16% by volume (see appendix: China), the Orenburgskoye natural gas condensate field, which is also used for helium production in Russia, even has as little as 0.055 vol.%.

A comparison of the helium content with the tonnage (grade-tonnage diagram) of the currently producing helium-rich natural gas reservoirs is unfortunately not possible in the context of this study, because no reliable data on both the original and the remaining natural gas and helium volumes of most natural gas resources in the USA have been published (see appendix: USA).

Above all, the production of helium from residual gases in natural gas liquefaction plants, but also the increased prices for helium, have meanwhile led to a spreading of the minimum requirements worldwide. The US company IACX Energy LLC (see appendix: USA) specialises in the construction of small, mobile helium plants at pumping stations on helium-rich natural gas reservoirs. Here, the total available helium tonnage is far less relevant than a high helium content of several percent by volume, where possible. According to their data, IACX Energy currently has seven such helium plants in operation in the USA (as of spring 2018).

For natural gases undergoing liquefaction in existing or planned LNG plants, and from which helium is separated from the residual gases, a minimum helium content of 0.05 vol.% is anticipated based on the North Dome natural gas field in Qatar.

The residual gas fed into the helium plant must have at least 3.0 vol.% He. For example, the residual gas used in the Darwin helium treatment plant (see appendix: Australia) contains 3.0 vol.% He, but the residual gas used in the Skikda helium plant in Algeria (see appendix: Algeria) has 4.6 vol.% He (D.N. Baciu, Linde AG, personal communication). In order for helium separation to pay off in the long term, of course, the LNG plants must also be supplied from the largest possible natural gas reservoirs.

The following reservoirs are or shall be exploited to produce helium (cf. appendix):

- Algeria: Hassi-R’Mel field with 2415 bn. m^3 natural gas at an average of 0.19% He
- Australia: Bayu-Undan field with 88 bn. m^3 natural gas at 0.013–0.28% He, average 0.18% He
- Qatar: North Dome field with 34,200 bn. m^3 natural gas at an average of 0.05% He
- Russia (planned): Kovyktinskoye field with 1563 bn. m^3 natural gas at 0.24–0.28% He
- Russia (planned): Srednebotuobinskoye field with 182 billion m^3 natural gas at 0.2–0.6% He
- Russia (planned): Chayandinskoye field with 1,000 bn. m^3 natural gas at 0.50–0.54% He

Fig. 21: IACX Energy helium plant on the Harley Dome natural gas field with 7.0% He average in Utah, photo: www.iacx.com.

4 Demand

4.1 Helium

The historical development of the demand for helium since the First World War is summarised in the section dealing with the USA (see appendix). Kornbluth also provides an overview of the period 1990–2015. The following description of the evolution in demand since 2000 is based on the evaluation of various papers in the gasworld journal, as well as analyses by industrial gases experts, generally American (also cf. Section 6.1):

In 2001, global demand for helium is said to have been 159 Mm^3.

Growth in demand in 2004 was 4–5%, dropping to 2–3% in 2006, and even negative in 2007. Nevertheless, there is said to have been a global scarcity of helium in the years 2006–2007; this is referred to by some US analysts as *Helium Shortage 1.0*.

Global demand for helium was estimated at around 175 Mm^3 for 2008, of which approximately 44% was in the USA, 26% in (western) Europe, 2% in the Pacific region (China, Southeast Asia) and 8% in the rest of the world, where growth in demand was highest at 7–8%/a.

Due to the global economic slowdown, demand in 2009 is expected to have dropped to an estimated 158 Mm^3 of helium. Of this, 44% was in the USA, 24% in the Pacific region, 21% in Europe and 11% in the rest of the world, where growth in demand remained above average at 4–5%/a.

Given an assumed supply of 166 Mm^3 (cf. Sections 5.1 and 6.1), the demand for helium in 2010 was once again at 171 Mm^3. This demand was at 39% for the USA, 27% for the Pacific region, 21% for Europe and 13% for the rest of the world, where growth in demand remained high at 4–5%/a. In contrast, global growth in demand of only 2–3%/a was predicted for the coming years to 2012 for the rest of the world.

If enough helium had been available in 2011, 178 Mm^3 of helium would probably have been used. The figure was actually only 172 Mm^3. 36% of this use was within the USA, 28% in the Pacific region, 22% in Europe, and 14% in the rest of the world, with the latter region once again experiencing a 4–5%/a growth in demand.

From mid-2011 into 2013, there was once again a global shortage of helium (cf. Sections 5.1 and 6.1), referred to by some US analysts as *Helium Shortage 2.0*. According to concurring analyst opinions, the reason for this was the low global helium supply and not an increased demand for the noble gas. According to Kornbluth (2015), supply was at 20%, and occasionally more, below demand. For Germany, gas companies report (anonymous, personal communication), sometimes very differently, a shortage of helium in the period 2011–2013, i.e. similar to the USA, but also for 2013 only. According to estimates by Gubler et al. (2016), approximately 15–20% of global helium demand was irreversibly lost during, or due to, the *Helium Shortage 2011–2013*, as a result of substitution and recycling.

In the years 2012 and 2013, 175 Mm^3 of helium are said to have been in demand worldwide. According to Garvey (2013), demand in 2013 corresponded to supply. Demand was at 32% for the USA, 31% for the Pacific region, 21% for Europe and 16% for the rest of the world, where growth in demand fell slightly to 3–5%/a.

The US helium expert Phil Kornbluth (2015) described 7 October 2013 as the *Helium Cliff*, which had to be climbed. On this date, the existing US legislation on helium stockpiling, and thus the financial support of the US Bureau of Land Management for maintaining the US helium storage network, ended. The *Helium Cliff* was overcome by the signing of the *Helium Stewardship Act of 2013* (see appendix: USA).

In 2014, global demand for helium is said to have fallen to 160–170 Mm^3 (depending on individual expert opinion). Supply is said to have been around 172 Mm^3 (cf. Section 5.1). Demand was 32% in the USA, 31% in the Pacific region, with particularly robust growth in demand of 5–7%/a, 21% in Europe, 12% in South America and 4% in the rest of the world (Africa, Middle East, India). Global demand growth in 2014 was estimated at 2–3%/a as was also forecast for 2015. The global decline in demand was attributed to increased recycling of gaseous helium, higher efficiency and substitution. According to Kornbluth (2016), these effects are estimated to have contributed to an approximately 10% decline in demand.

In 2015 and 2016, it is claimed, there was an oversupply of helium (cf. Section 6.1). Demand is said to have been at 164 Mm^3 and thus around 2 Mm^3 below the 166 Mm^3 supply. The surplus helium was temporarily stored in ISO containers (see Section 5.1) and in 2016, three helium units connected to the US Bureau of Land Management's (USBLM) storage network were deferred (see appendix: USA). In 2016, demand was split between 32% in the USA, 31% in the Pacific region, with high demand growth of 5–7%/a, 20% in Europe, 13% in South America and 4% across the rest of the world. Global demand growth was at 2–3%/a, as in previous years.

In 2017, global demand for helium was assumed to be 166 Mm^3 and thus, according to Garvey (2017), corresponded to supply. Demand was 32% in the USA, 32% in the Pacific region, 19% in Europe, 13% in South America and 4% in the rest of the world. Global growth in demand was estimated at a low 1%/a and the forecast for the coming years was 1.5%/a. As far as is known, the Qatar crisis in June 2017 (see appendix: Qatar) did not lead to a slump in helium demand.

According to Gubler et al. (2016), global growth in helium demand for the period 2010–2015 was a mere 0.7%/a but is forecast to increase to 2%/a for 2015–2020. For a number of Asian and other countries, however, the forecast growth in demand is almost twice as high. This regionally strong growth in demand is expected to be limited to China, India, South Korea, Taiwan and the Middle East, because of the local electronics and semiconductor industries and their LCD and optical fibre production facilities.

However, according to expert consensus, at least the demand for liquid helium for MRI should remain about the same in the coming years. Although modern MRIs continue to require less helium (cf. Sections 3.4 and 3.5), more and more hospitals are being equipped with MRIs in the emerging markets of India, China and Brazil. In the medium term, the effects of lower helium demand per device will be more or less cancelled out by an increasing number of devices.

Global demand for ^3He is estimated by the US Department of Energy to be 70,000 litres (= 70 m^3) annually. This will be halved in the coming years due to the substitution of ^3He in neutron detectors for security purposes (cf. Section 3.2.1), before another significant increase in demand is anticipated with the completion of the spallation neutron source facility at the Oak Ridge National Laboratory in Tennessee (Gubler et al. 2016).

4.2 Neon

The following brief description of the evolution in demand for neon is based entirely on the contributions of Richard Betzendahl – Betzendahl Gas Consultants LLC – in the gasworld journal (see bibliography) and has been updated after Spiritus & Betzendahl (2018):

Since the 1990s, the demand for neon has grown steadily due to its increasing use in lasers (cf. Sec-

Table 11: Absolute global demand for helium (in Mm^3) and growth in global demand for helium (in %/a) according to analyses by US experts, compiled from various papers in the gasworld journal.

	2001	2002	2003	2004	2005	2006	2007	2008
Demand	159							175
Growth				4 – 5		2 – 3	< 0	

	2010	2011	2012	2013	2014	2015	2016	2017
Demand	171	178	175	175	160 – 171	164	164	166
Growth					2 – 3	2 – 3	2 – 3	1

tion 3.2.2). In the early 2000s, demand continued to increase, not only because of the use of neon in lasers, but also in plasma televisions at that time. However, in 2009, demand for plasma televisions dropped relatively abruptly, which also affected demand for a number of years.

In absolute terms, demand for neon was estimated to be around 300 million litres (= 300,000 m³) in 1990, 214 million litres in 1995, 425 million litres in 2008, 352 million litres in 2012, and 477 million litres of crude neon in 2015. Crude neon contains an average of 50% neon. In the period 2014–2015 alone, growth in demand was 12%/a, meaning that demand exceeded supply for the first time during this period. In addition, users of neon stockpiled the noble gas regardless of price during this period, in order to maintain production under any circumstances (cf. Section 7). In the meantime, the price has stabilised due to robust supply growth and short-term recycling success (cf. Section 3.4), but demand continues to be very one-sided. 80–90% of global neon demand is driven by the demand for lasers and 70–75% of neon demand by the semiconductor industry's laser demand alone – a market that continues to grow at 8–10%/a, with a focus on China. For 2018, global crude neon demand is currently forecasting at approximately 690 million litres, and even 720–760 million litres of crude neon for 2020–2022.

According to Spiritus & Betzendahl (2018), global demand for neon increased by 6.3% annually between 2000 and 2015, and by as much as 9.0% between 2012 and 2017. Global demand for neon is expected to increase by a further 6.7% annually in 2017–2022. The use of neon in extreme ultraviolet lithography (EUV) for semiconductor production should be a market driver, at least until 2020. Only the well-known, but now smallest, sub-market, that of neon lighting, is expected to continue to decline significantly in the next few years (2017–2022: –5.6%).

4.3 Argon

In contrast to helium, but also unlike the much rarer noble gases neon, krypton and xenon, barely any data or analyses exist in the relevant specialist publications on the global evolution in the demand for argon. Because argon is required in large quantities, but by no means exclusively, in the steel production and processing, the demand for this noble gas correlates approximately with global steel production (see Fig. 23).

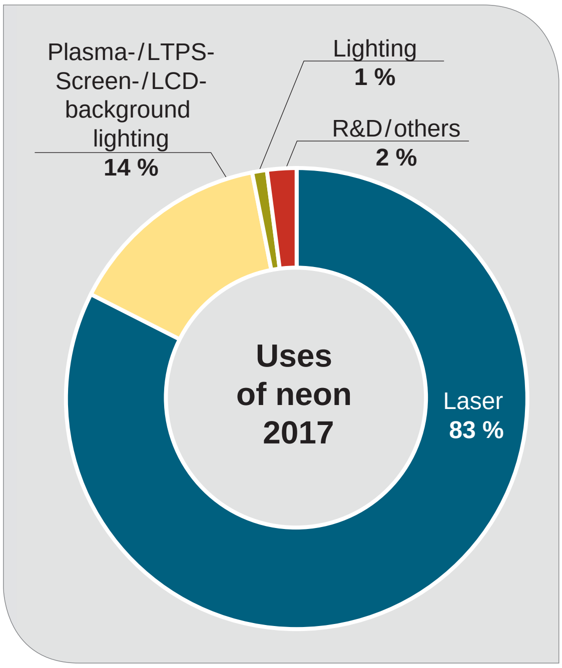


Fig. 22: Global neon demand distribution in 2017 (Spiritus & Betzendahl 2018).

In addition, developments in the global semiconductor industry (Fig. 24), in which argon is required as a protective gas, as well as the substitution efforts of helium consumers since the helium shortage of 2011–2013, must be taken into account, because they increasingly substitute argon for helium (cf. Sections 3.5 and 6.1). As a consequence, the demand for argon outside of the steel producing and processing industries continues to increase, which is why large multinational gas companies are attempting to maximise their argon capacity (Section 5.3).

According to Suresh et al. (2015), around 251 Mm³ of argon was used in Japan in 2015, 30% of which was used in the processing of metal products (protective gas for welding), 23% for the primary production of metals (steel production), 17% for electronics (predominantly in the semiconductor industry), 2% in the chemicals industry and 28% in other applications.

In the USA, around 47% of argon demand in 2015 was for protective gas in welding, 29% for steel production, 12% for the electronics/semiconductor

Fig. 23: Global steel production in million tonnes (Mt), source: World Steel Association.

Fig. 24: Global turnover in the semiconductor industry in US$ billions, source: Semiconductor Industry Association.

industry/solar cell production, 3% for manufacturing lighting elements and 9% for other applications (Suresh et al. 2016). In 2016, US industry required approximately 810 Mm³ of argon.

Also according to Suresh et al. (2016), China's demand was around 1.74 bn. m³ of argon in 2015, with growth in demand expected to reach 4.5%/a in the coming years. In 2015, 46% of demand was attributable to steel production, 21% to protective gas for welding, 15% to electronics, 10% to lighting and 8% to other applications.

In western Europe around 1.3 bn.m^3 of argon, and in Eastern Europe 355 Mm^3, are said to have been used in 2015. According to surveys performed for this study, German net consumption in 2017 was around 180 Mm^3. Use in the rest of the world is unknown, but the global argon requirement based on the usage given above can be estimated at > 5 bn. m^3/a.

4.4 Krypton

The following brief description of the evolution in demand for krypton is also based entirely on the contributions of Richard Betzendahl – Betzendahl Gas Consultants LLC – in the gasworld journal (see bibliography), updated after Spiritus & Betzendahl (2018):

In 1990, global demand for krypton was 17 million litres (= 17,000 m^3) and more than doubled by 1997, at 39 million litres. Since the mid-1990s, the sales market for krypton has grown, because it is (in addition to the much cheaper argon), primarily in Europe, the preferred filling gas in insulating glass windows. Krypton's global share of insulating glass production was estimated at 40–50% of the total sales market at that time, similar to today. By 2005, demand had again doubled to 82 million litres, with 48% of krypton production going into manufacturing insulating glass in that year. As a result of the global financial crisis beginning in late 2008, the construction boom in the USA began to stall and cheap fuel oil no longer offered a reason to save energy, insulating glass sales collapsed by 30–50% for a short period and thus also massively subdued the demand for krypton. To make matters worse, the major European gas companies had reportedly stockpiled several months' supply of krypton, which they gradually ran down due to lack of demand from their customers but did not replenish.

In addition, krypton was, and still is, very important for filling incandescent lamps. In the mid-2000s, global sales of lamps increased by 4%/a and by as much as 10–20%/a in developing countries. With the global financial crisis, this market also briefly collapsed, with the result that, by 2010, the total demand for krypton was around 15% below that of 2008, in which about 87 million litres had been in demand. Only the relatively small market for krypton for medical lasers displayed no weakness in the global recession at that time

Early in 2010, European insulating glass manufacturers were forced to supplement their reserves and the US government launched a tax saving programme for thermal insulation measures. However, this 5–10% increase in demand for krypton was short-lived and ebbed again by the end of 2012. In addition, in Europe, the USA and Australia, energy-saving lamps, which required less krypton, became established, but soon made way for LEDs, which no longer require krypton in their production and functioning. The effect was that the krypton market was not able to recover further. In addition, the producers still had an estimated 15–20 million litres of krypton in their warehouses.

According to Spiritus & Betzendahl (2018), global demand for krypton increased by 1.4% annually between 2000 and 2015, and by 6.8% between 2012 and 2017. In recent years, however, producers have been forced to increase their reserves. At the end of 2015, they are said to have accounted for more than half of annual production, i.e. more than 50 million litres. By the end of 2016, producers' reserves were at 80% of annual production, i.e. increased to 95 million litres, and are currently at around 80 million litres. Demand was and still is characterised by a steadily rising demand for

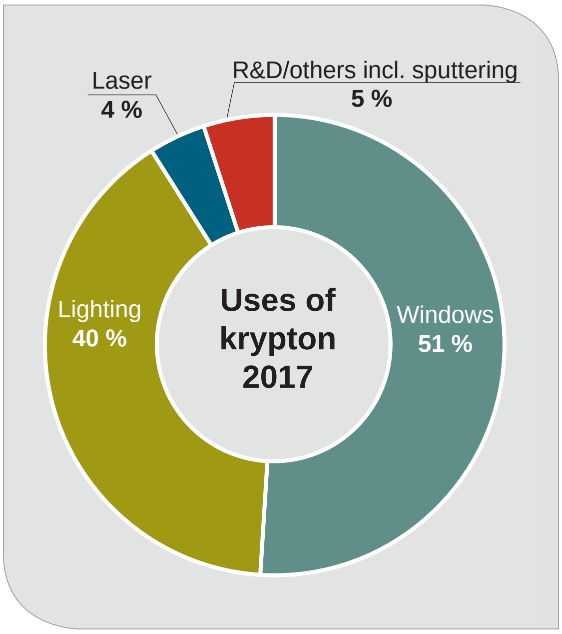


Fig. 25: Global krypton demand distribution in 2017 (Spiritus & Betzendahl 2018).

thermal insulation glazing (2017–2022: +2.7%), but at the same time with a declining market for light bulbs, especially halogen lamps, with krypton filling (2017–2022: –4.0%). In this submarket, the replacement of halogen bulbs for car headlamps is particularly relevant in Germany. Stronger growth, albeit with a much lower starting base (cf. Fig. 25), is expected to be achieved in the laser technology field (2017–2022: +5.9%) and in research and development (2017–2022: +6.4%), due to the continued low krypton price. Global demand for krypton is expected to increase by 0.6% annually in 2017–2022.

4.5 Xenon

The following brief description of the evolution in demand for xenon is also based entirely on the contributions of Richard Betzendahl – Betzendahl Gas Consultants LLC – in the gasworld journal (see bibliography) and has been updated after Spiritus & Betzendahl (2018):

Xenon is different to krypton in that, on the one hand, it is about ten times as rare, but on the other has many more applications, meaning that the global sales market for xenon is very volatile in detail, but cannot collapse entirely.

Similar to krypton and neon, xenon was also considered a strategic resource for satellite production in the former Soviet Union (see Section 5.2) but was not deployed in relevant quantities for military purposes.

In 1990, global demand for xenon was 2.2 million litres (= 2200 m^3), but almost doubled by 1995. During this period, the market for xenon lamps began to develop, which continues to employ significant amounts of this noble gas to this day. At the same time, xenon was so inexpensive that it was used as a cheaper (and higher-quality) substitute for krypton in the production of insulated glass windows.

In the late 1990s, xenon was increasingly used in telecommunications satellites as a manoeuvring fuel and individual requests from satellite manufacturers to supply up to 3 million litres of xenon briefly worried the xenon producers.

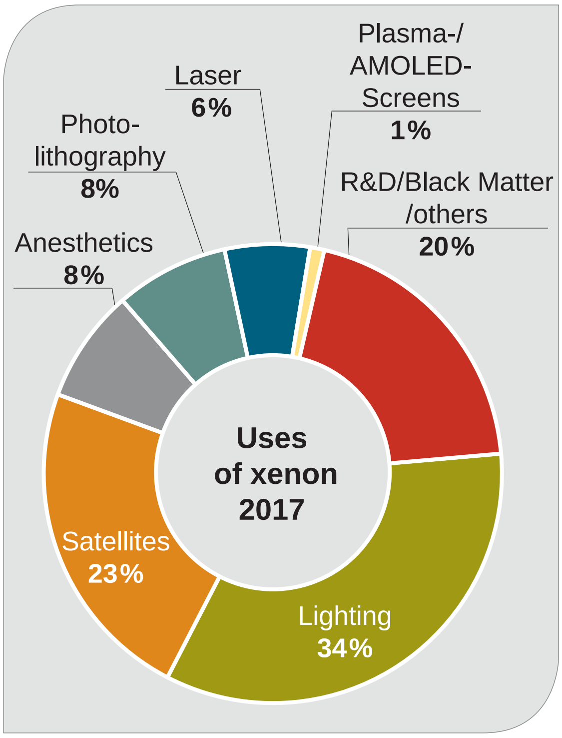


Fig. 26: Global xenon demand distribution in 2017 (Spiritus & Betzendahl 2018).

By 2005, the demand for xenon had risen to 8.3 million litres, and unexpectedly increased further to 11.1 million litres by 2008. The reasons for this surge in demand lay in a technology change from the production of plasma televisions instead of tube televisions, which demanded 2 million litres xenon/a (*Toshiba effect*). In addition, 1 million litres of xenon will have been used in 2008 solely for anaesthetic applications in Europe alone (gasworld 2008). In the same year, around 30% of global xenon production was already intended for laser applications.

As a result of the global financial crisis, the demand for xenon in almost all sales areas also dropped sharply by more than 20% between autumn 2008 and into 2010, and only recovered gradually from mid-2010 onwards. The decline in sales of xenon for lasers in the semiconductor industry was particularly strong, where 50–70% less xenon was demanded. On the other hand, the market for xenon for medical lasers was almost unaffected by the recession, similar to krypton. Between 2008 and the end of 2009, only 1 million litres of xenon/a were said to be in demand in the global electronics industry, as well as in the production of plasma televisions, instead of the previous 3 million litres xenon/a. However, this was also caused by a technological change in the production of plasma television sets, which required 50% less xenon per television.

At the end of 2010, the Russian government purchased 250,000 litres of xenon for its satellite programme, and overall xenon consumption also started to gradually increase again on the back of rising demand in China. Between mid-2011 and mid-2013, the demand for xenon for halogen lamps in the lighting industry increased to a market share of 2.5–3 million litres/a. Just as quickly as it had risen, however, this sales market collapsed again, because from 2014 the increasingly inexpensive LEDs prevailed as a light source. At that time, Osram had taken precautionary measures in stockpiling large volumes of xenon, but then ended up maintaining a surplus (Spiritus & Betzendahl 2018).

In recent years, the xenon market has been relatively stable, with increasing sales in basic research (research into dark matter), as well as satellite propulsion, and declining sales for conventional lamps. At present, a market for xenon in lasers is developing for the 3D photolithography process in semiconductor technology. This laser submarket is expected to require 2.4 million litres of xenon as early as in 2018, and 3.5 million million litres of xenon/a from 2019.

According to Spiritus & Betzendahl (2018), global demand for xenon increased by 3.6% annually between 2000 and 2015, and by as much as 6.8% between 2012 and 2017. Global demand for xenon is expected to increase by a further 3.0% annually in 2017–2022. Negative growth rates are predicted for the lighting market (–4.6% in 2017–2022) and for major research projects (–9.1% in 2017–2022), due to the completed procurement process. In contrast, demand for xenon in semiconductor fabrication and screen production (2017–2022: +22.2% and +14.9%, respectively) is expected to increase disproportionately.

The global satellite and aerospace industry, in particular, should be given special attention. From 2018, 882, and possibly as many as 2854, new satellites will successively enable global and permanent access to the Internet (*Oneweb*). Around 2.5 million litres Xe will be required by 2020 for this ambitious, but already partly funded, project. In addition, the Mars space programme may require 60 million litres of xenon in the next 15 years – if it is implemented and krypton or iodine not used alternatively as a manoeuvring fuel (see Section 3.5).

5 Supply

In the majority of cases, helium is a by-product of natural gas treatment in gasworks, natural gas liquefaction in LNG plants or air separation in air separation units (cf. Section 3.1.1). Its supply is therefore almost exclusively dependent on the global demand for natural gas and liquefied natural gas and, far more subordinately, on the regional demand for oxygen and nitrogen. To date, helium is only produced as the principal gas in very few plants in the USA and, in the future, possibly in Tanzania.

Argon is an important associated gas in around 1000 air separation units worldwide.

Neon or krypton are accompanying special gases in around 50, and xenon in more than 100, air separation units worldwide. However, these air separation units produce the rare noble gases in crude form only, which then must be purified to the pure gases required by industry in less than 20 processing plants worldwide.

5.1 Helium

The coefficient of expansion of gases when transitioning from the liquid to the gaseous state is very large and the factor for helium, for example, is 757. This means in practise that gaseous helium, although technically much lighter, can only be transported in much smaller quantities than liquid helium at the same volume. A typical ISO (*independent system operator*) container (see below) for liquefied helium contains around 29,000 m^3 of helium, while the largest trailer for transporting gaseous helium only has a volume of 8000 m^3.

Helium is therefore usually transported over long distances in liquid form at 99.999% He (5.0) (cf. Section 3.6) in ISO certified refrigerated containers, each holding up to 41,400 litres of helium. Globally, there are only two producers of these ISO containers, the US company Gardner Cryogenics, Inc, a subsidiary of the gas company Air Products & Chemicals, Inc., and Linde Engineering, who manufactures their containers (Helicon) at the Schalchen factory in Tacherting, Bavaria. Technically, these are multi-walled, stainless steel

Fig. 27: ISO refrigerated container for transporting liquid helium at Linde AG's Unterschleißheim factory. The two containers at the left were produced by Linde Engineering, the container on the right by Gardner Cryogenics, Inc., photo: BGR.

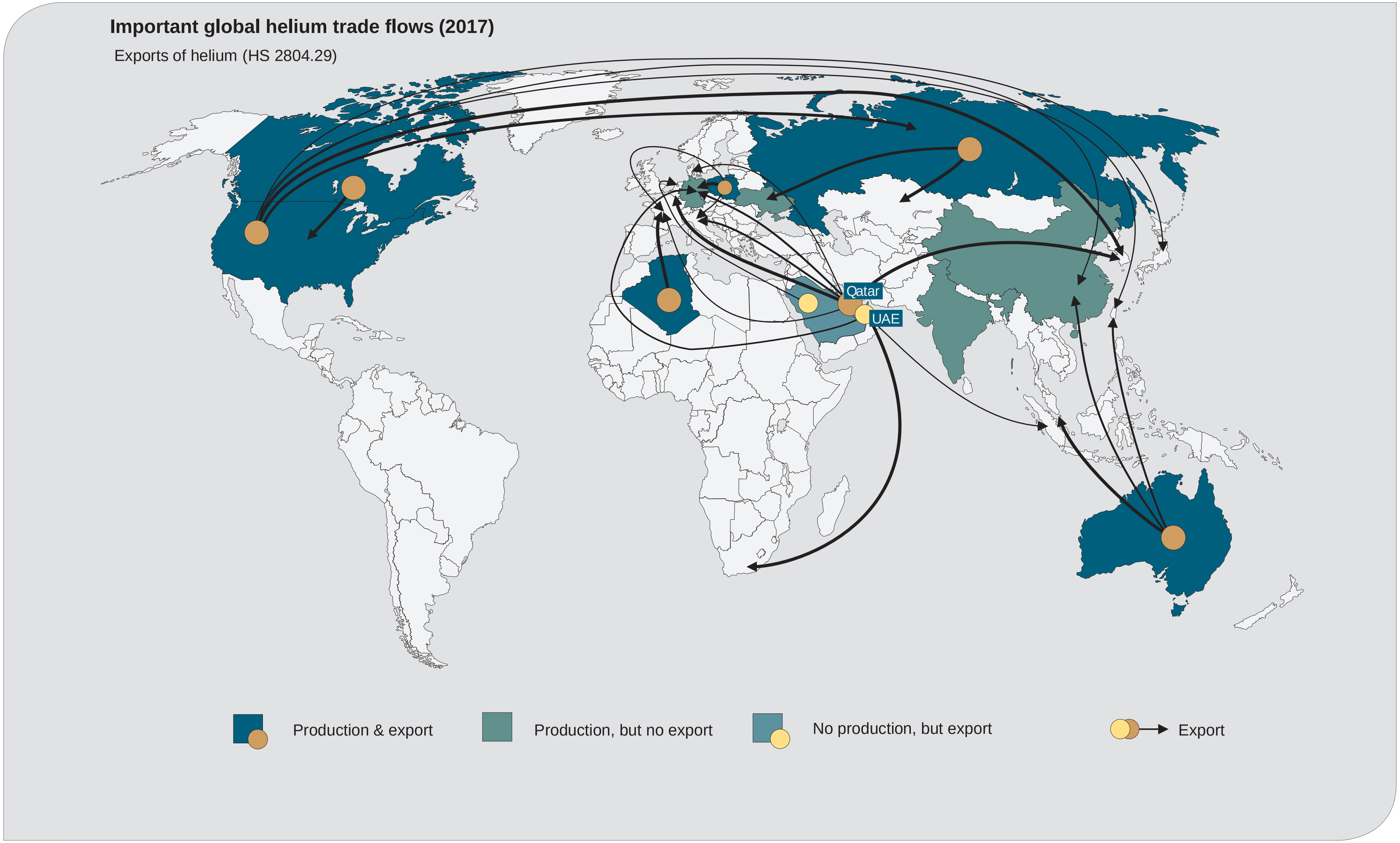


Fig. 28: Important global helium trade flows in 2017, after analysis of Global Trade Atlas data.

Fig. 29: Transport containers filled with 450 litres of liquid helium at Linde AG's Unterschleißheim factory, photo: Linde AG (with kind permission).

containers, pressurised to 5.2 bar, with the outer protective jacket also bring cooled by liquid nitrogen. In this way, refrigerated transport durations up to 45 days are possible. On arrival at the destination, the liquid-to-gas ratio is then about 50:50 and the gaseous helium must be re-liquefied. Globally, around 1000 of these ISO containers are in use, each with a value of US$120,000–$150,000.

The prohibitive cost of helium liquefaction does not allow large volumes of liquid helium to be held as reserves, meaning that helium is a *just-in-time* product. Virtually the entire volume of liquid helium that is not currently being produced or used is in circulation in ISO containers worldwide. A container with a destination in Europe is en route from/to the USA for approximately 40 days, from/to Algeria for approximately 16 days and from/to Russia for approximately 18 days. The closer the helium producer is to the consumer, the more cycles and thus transported volumes are possible per year (Gubler et al. 2016).

Small refrigerating containers of 250–1000 l capacity for domestic transport can be filled with liquid helium directly from the ISO containers. However, to date, helium and the other noble gases are generally transported over short distances in the gaseous state in tubular pressure vessels on trailers, in high-pressure cylinders and in what are known as dewars. Dewars are double-walled, stainless steel containers, in which the individual stainless steel layers are separated by an isolating vacuum.

The major international gas companies are bound to the few global helium producers almost exclusively via what are known as *take-or-pay* contracts, i.e. the companies are obliged to accept the guaranteed volume of helium, regardless of whether a sales market currently exists or not. Because, as stated above, it is only possible to store liquid helium at very high cost, in recent years some gas companies have decided to transfer the pure helium to which they are entitled – also at high cost – to the BLM helium pipeline system or to natural gas storage systems (Cliffside/USA, Gronau-Epe/Germany, in planning: Chayandinskoye and Tas-Yuryakhskoye/Russia) and to reinject it at these locations, thus stockpiling it as raw helium.

Alternatively, artificial gas storage systems can be used for helium storage, if they are sufficiently large. The German gas company Messer Group has concluded a long-term supply contract for liquid helium with the Russian company Cryor. Messer transports the helium from Orenburg in their own 40,000-litre, vacuum super-insulated tank containers to their European filling plants. At the Austrian Messer Group site in Gumpoldskirchen, near Vienna, Messer uses Europe's largest helium tank storage facility with a capacity of 113,000 litres. This allows the company to accept and temporarily store liquid helium during servicing works on the large hadron storage ring, LHC (see Section 3.2.1).

Global helium production data are listed in Table 12 (see appendix: country profiles) The production data for the helium producing countries since 2000 are given in Table 13 for comparison. The net crude helium extraction from the Cliffside helium storage facility in Texas, USA, is included, resulting in the global annual helium supply.

Table 12 shows that there are currently probably 53 helium plants worldwide (four of which are deferred) with a (currently available) production capacity of approximately 252 Mm^3 of pure helium

Table 12: Global helium production data to date, as far as known (see appendix: country profiles).

Country	Start	End	Origin	Number of helium plants	Total capacity [1] (mill. m^3)
Algeria	1994	active	Liquefaction of natural gas	2	33.2
Australia	2010	active	Liquefaction of natural gas	1	4.4
Canada	1917	1920	Processing of natural gas	1	n.a.
	1963	1977	Processing of natural gas	1	0.3 / 1.0
	2014	active	Processing of natural gas	2	2.2?
China	1970´s	active	Processing of natural gas	2	0.3
	1998	active	Air separation	7?	0,2
Germany	1970´s	n.a.	Processing of natural gas	1	< 0,1
	2014	active	Air separation	1	< 0,1
France	1969?	1978?	Processing of natural gas	1	0.2
India	2008	active	Processing of natural gas	1	0.1
Poland	1977	active	Processing of natural gas	1	4.2
Qatar	2005	active	Liquefaction of natural gas	2	55.5
Russia	1949	1978	Processing of natural gas	4	1.4 / 1.7
	1978	active	Processing of natural gas	7 [3]	8.8
	n.a.	active	Air separation	3?	0.1
Ukraine	n.a.	active	Air separation	2?	0.1
USA	1918	active	Processing of natural gas	9 [2], [3], [6]	143.2 [2]
				7 [4], [6]	19.9 [4]
				6 [5]	70.0 [5]

n.a. = not available

[1] Data on capacities may differ
[2] Grade-A
[3] Two currently deferred
[4] At 95–98% He
[5] Crude helium
[6] Of these, one each for 95–98% He and pure helium

(cf. Fig. 30), plus 19.9 Mm^3 helium at 95–98% He (crude helium as a preliminary product is ignored). In comparison, the global helium production capacity in 2010 according to Gubler et al. (2016) was 225.1 Mm^3 and 289.2 Mm^3 in 2015, and will probably increase to 363.7 Mm^3 by 2020. In contrast to this, it is estimated that 80,000 l (= 80 m^3) ^3He are produced annually.

It is apparent from the production statistics and the annual available helium supply (Table 13) that:

- The available volume of helium from the USA has been on the decline since 2013, but by no means to such an extent that it should cause concern. Although 28.0 Mm^3 of the helium produced in the USA in 2017 came from the Cliffside storage field, now being wound up, in previous years it was sometimes even less (cf. Fig. 55). This additional decrease in storage volume in the coming years can be compensated for by increased production in Algeria and Qatar, utilising the capacities already available there, and by the planned start of new production in Russia from 2021 (cf. appendix: Russia and Section 5.4).
- Since 2016, global imports of helium from Australia have been above the capacity ceiling of 4.4 Mm^3 stipulated for the helium facility there, meaning that this figure is either incorrect or we are dealing with re-exports of a considerable magnitude.
- There is no hint of a helium shortage in the years 2006–2007, at least on the basis of the available supply (*Helium Shortage 1.0*). A helium shortage for the years 2011–2013 (*Helium Shortage 2.0*, cf. Section 4.1) as a result of reduced supply is also only apparent for 2013. During this period, or rather year, a reduced demand for natural gas – and thus a lower supply of helium-rich natural gas – together with planned and unplanned servicing works in a number of helium facilities, should have resulted in reduced helium production.

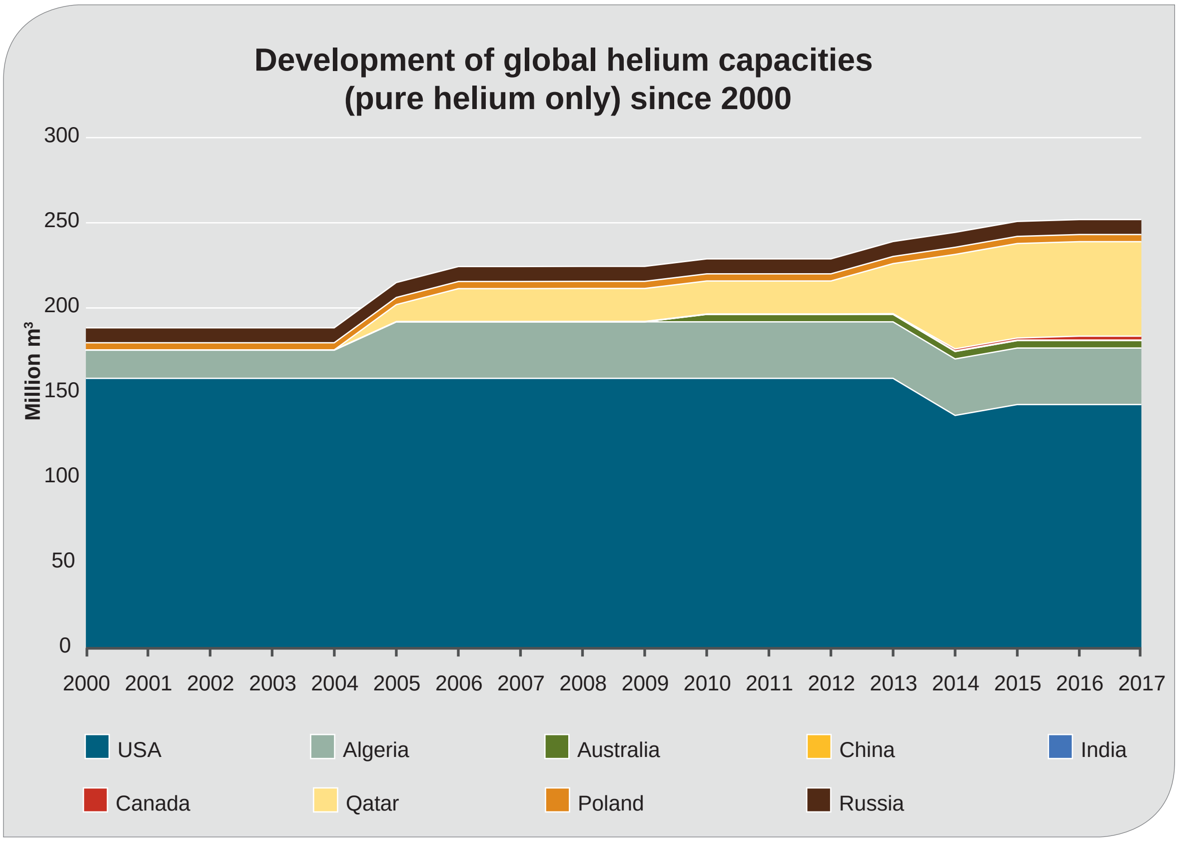


Fig. 30: Development of global helium capacities (pure helium only) since 2000.

***Table 13:** Global helium production (in Mm^3) since 2000 (see appendix: country profiles), plus net volumes of helium (in Mm^3), extracted from the Cliffside helium storage system in Texas/USA (source: USGS Minerals Yearbooks). In comparison, estimated global production of helium according to USGS Minerals Yearbooks.*

	2000	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**
Algeria	18.4	17.4	19.6	17.0	21.9	24.8	22.4	25.9	30.4
Australia	–	–	–	–	–	–	–	–	–
Canada	–	–	–	–	–	–	–	–	–
China[1]	0.1	0.1	0.1	0.1	0.1	0,1	0.1	0.1	0.1
Germany	–	–	–	–	–	–	–	–	–
India[1]	–	–	–	–	–	–	–	–	< 0.1
Poland	2.3	2.2	2.4	2.5	2.7	2.7	2.5	2.4	2.2
Qatar	–	–	–	–	–	1.3	7.0	10.9	12.1
Russia	5.3	5.3	6.3	6.5	3.5	1.6	3.9	4.9	5.0
Ukraine[1]	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
USA[2]	98.0	87.0	87.4	86.9	86.0	75,9	79.4	77.0	79.6
Storage withdrawal	28.6	44.9	39.7	35.1	44.0	57.1	57.7	60.7	49.9
World	**152.7**	**156.9**	**155.5**	**148.1**	**158.2**	**163.5**	**173.0**	**181.9**	**179.3**
World after USGS	117 [3]	106 [3]	109 [3]	144	154	160	166	171	175

	2009	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**	**2017**
Algeria	24.7	23.9	20.9	24.6	22.2	19.3	21.5	19.8	17.5
Australia	–	1.8	2.4	2.4	3.9	4.8	4.1	5.7	7.0
Canada	–	–	–	–	–	0.1	1.1	2.2	2.4
China[1]	0.1	0,1	0.1	0.1	0.2	0.2	0.2	0.2	0.2
Germany	–	–	–	–	–	< 0,1	< 0,1	< 0,1	< 0,1
India[1]	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Poland	2.7	3.1	3.4	3.3	3.0	2.8	2.8	2.9	3.2
Qatar	12.1	15.3	14.3	10.9	13.5	37.7	39.6	44.7	38.2
Russia	4.9	4.9	3.5	4.9	3.6	4.0	5.0	5.1	5.1
Ukraine[1]	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
USA[2]	78.0	75.0	70.7	72.8	68.9	75.2	71.8	*66*	63.0
Storage withdrawal	39.6	52.0	59.4	60.1	49.1	27.1	19.6	23	28.0
World	**162.2**	**176.2**	**174.8**	**179.1**	**164.4**	**171.3**	**165.8**	**169.7**	**164.7**
World after USGS	147	168	172	174	171	164	159	160	160

n.a. = not available

[1] Assumed

[2] Difference from sales of pure helium (Grade A) minus net withdrawal of raw helium from the Cliffside storage field (note: USBLM publishes different net withdrawal figures than USGS, e.g. for 2014, 28.3 Mm^3 instead of 27.1 Mm^3, for 2015, 21.2 million Mm^3 instead of 19.6 Mm^3, for 2016, 24.8 Mm^3 instead of 23 Mm^3)

[3] Net storage facility extraction not included

Fig. 31: Generalised map of global helium plant sites.

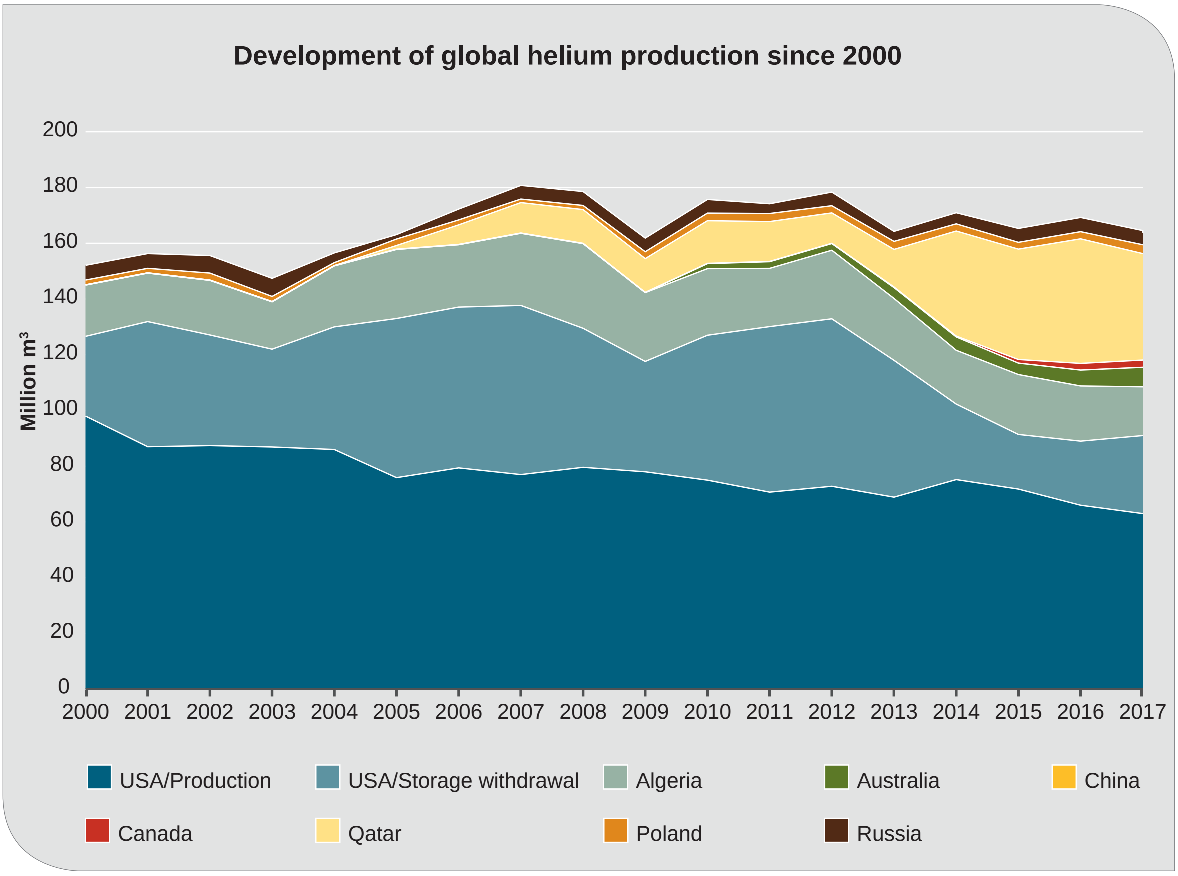


Fig. 32: Development of global helium production since 2000.

5.2 Neon

With the exception of Bahrain, Qatar, Panama and South Korea, all other countries in the world include their neon import and export data in those of the other speciality gases krypton and xenon, meaning that useful conclusions about the global neon market, in this case the neon supplier market, can only be inferred from South Korean import data, an important semiconductor and electronics producer.

According to the Korea Customs Service, 51,404 kg of neon or, possibly, neon-rich gas mixtures were imported in 2015, 63,599 kg in 2016 and 95,528 kg in 2017 (= 113,454 m^3 at 15 °C) (HS code 2804292000).

Supply countries in 2017 were the USA at 46.6%, Ukraine at 29.7%, China at 23.6% and Taiwan at 0.1%. The ratios were similar in the preceding years. In 2009, supplies from Ukraine ceased and then only increased only slowly thereafter. Former neon supplier countries to South Korea for a number of years included Germany, France, the United Kingdom, Hong Kong, Japan and Thailand.

The following brief description of the evolution in supply for neon is based almost exclusively on the contributions of Richard Betzendahl – Betzendahl Gas Consultants LLC – in the gasworld journal (see bibliography), updated after data in Spiritus & Betzendahl (2018):

Neon was regarded as a strategic resource in the former Soviet Union, because it was believed to be required for the intended production of laser weapons for missile and satellite defence purposes in the 1980s. Accordingly, all major air separation units in the Soviet Union were equipped with neon, but also krypton and xenon, enrichment facilities or, in some cases, purification plants (cf. Sections 5.4 and 5.5). The domestic Soviet supply of neon was extremely large but demand low.

Following the collapse of the Soviet Union, global crude neon production was approximately 500–600 million l/a (= 500,000–600,000 m^3/a). It was dominated by far by large-scale air separation units associated with metallurgical combines in Russia and Ukraine. Simultaneously, demand was estimated at around 300 million l/a (cf. Section 4.2). In the years between 1990 and 2012, therefore, most crude neon was not purified, but released into the atmosphere, because there was no customer base.

In 2007, as in previous years, global crude neon production was estimated at 575 million l/a. 70% of the available neon came from Russia and Ukraine, where three of the world's only five (two were located in the USA) crude neon purification plants were located. At this time, neon was, and continues to be, a globally traded noble gas.

In 2010, global production of crude neon was believed to have been around 545 million l/a, of which approximately 60% came from the CIS, showing a slight decrease. Three of the largest air separation units with crude neon production were associated with steel smelters in eastern Ukraine. The large Ukrainian neon producer Iceblick Ltd. (see appendix: Ukraine) assumed a slightly lower global supply of around 450,000 m^3 Ne/a at that time (Cockerill 2010).

In 2012, there were around 20 air separation units worldwide, with a crude neon capacity of approximately 575 million l/a; however, total production was only around 500 million litres. Eight purification plants for crude neon jointly provided a capacity several times that of actual production, i.e. some of the purification plants were also deferred this year.

The over-supply on the neon market, which had been prevalent since the 1980s, ended in July 2014 after several old air separation units with crude neon capacity were closed over a number of years and replaced by new ones without neon capacity. At the same time, steel production, and thus the demand for oxygen, in the eastern European steel industry declined significantly, as a result of which many air separation units also cut their production. Between 2012 and 2015, a total of four large air separation units in eastern Europe went out of operation and although initial neon capacities in China were added, the global crude neon capacity nevertheless fell by 125 million l/a by 2015. In mid-2014, another major air separation unit in Ukraine, accounting for 8% of the world's crude neon production, was shut down due to political unrest. In 2015, global crude neon production fell to 415 million l/a as a result. At the same time, demand rose to around 477 million l/a as a result of the strong demand on the laser market and the formation of clean-stock inventories by consumers (see Fig. 33). Worldwide, 18–20 air separation units with crude neon capacities were in operation, while simultaneously 5–6 plants (with 150 million litres of crude neon capacity) were deferred. 70–75% of the crude neon supply came from Ukraine. Six purification plants were operating worldwide, one in Odessa/Ukraine, one in Moscow/Russia and two in the USA (Burns Harbor/Indiana and Alpha/New Jersey).

Above all, due to new air separation units with crude neon capacities in China, the global crude neon supply had risen again to around 470 million l/a by 2016. In addition, several eastern European air separation units would be capable of producing (more) crude neon relatively quickly – which is currently being released into the atmosphere as a He/Ne mix – should demand pick up again. This is currently forecast for the end of 2018 on, because by then wafer production in China, and therefore the demand for neon as the most important laser gas in semiconductor production, is expected to increase significantly (cf. Section 4.2).

As of October 2017, Spiritus & Betzendahl (2018) identified 25 locations worldwide with air separation units with crude neon/helium capacities, and nine sites with neon purification plants. Given production of 720 million litres of crude neon in 2017, the theoretical capacity should be substantially higher, at 853 million l/a. However, the reliability of all these data has been disputed by German market participants (Anonymous, personal communication). Table 14 presents an updated, but also incomplete, overview of the relevant air separation units and Fig. 33 shows the global distribution of crude neon purification plants.

Table 14: Locations of air separation units with crude neon capacities and crude neon purification plants, according to Spiritus & Betzendahl (2018), Suresh et al. (2016), Internet research and Anonymous (personal communication).

Country	Location	Production	Purification
China	various/Hubei (9 x)	He/Ne	
	Wuhan/Hubei		He, Ne
	Ma'anshan/Anhui (3 x)	He/Ne	
	Tangshan/Hebei	He/Ne	Ne
	Handan/Hebei	He/Ne	Ne
	Panzhihua/Sichuan	He/Ne	
	Zhangjiagang/Jiangsu		Ne
	Huzhou/Zhejiang	He/Ne	Ne
	Nanxiang/Shanghai		Ne
	Guangzhou/Guangdong	He/Ne	Ne
	Shaoguan/Guangdong	He/Ne	Ne
	Nanjing/Jiangsu		
Germany	Leuna (2 x)	He/Ne	He, Ne
France	Le Blanc-Mesnil	He/Ne	He, Ne
Netherlands	IJmuiden	He/Ne	Ne
Russia	Moscow		Ne (inactive)
	Nischni Tagil	He/Ne	
	Lipezk	He/Ne	
	Orsk	He/Ne	
	Magnitogorsk	He/Ne (not used)	
Ukraine	Krywyj Rih	He/Ne	He, Ne
	Mariupol (2 x)	He/Ne	He, Ne
	Zaporizhia	He/Ne	
	Alschevsk	He/Ne (inactive)	
	Dzerzhinsky	He/Ne	
USA	Claymont, DE	He/Ne	
	Warren, OH	He/Ne	
	Pittsburgh, PA	He/Ne	
	La Porte, TX (2 x)	He/Ne	
	Burns Harbor, IN (2 x)	He/Ne	Ne
	Calumet, IN (3 x)	He/Ne	
	Bayport, TX	He/Ne	
	Alpha, NJ		Ne

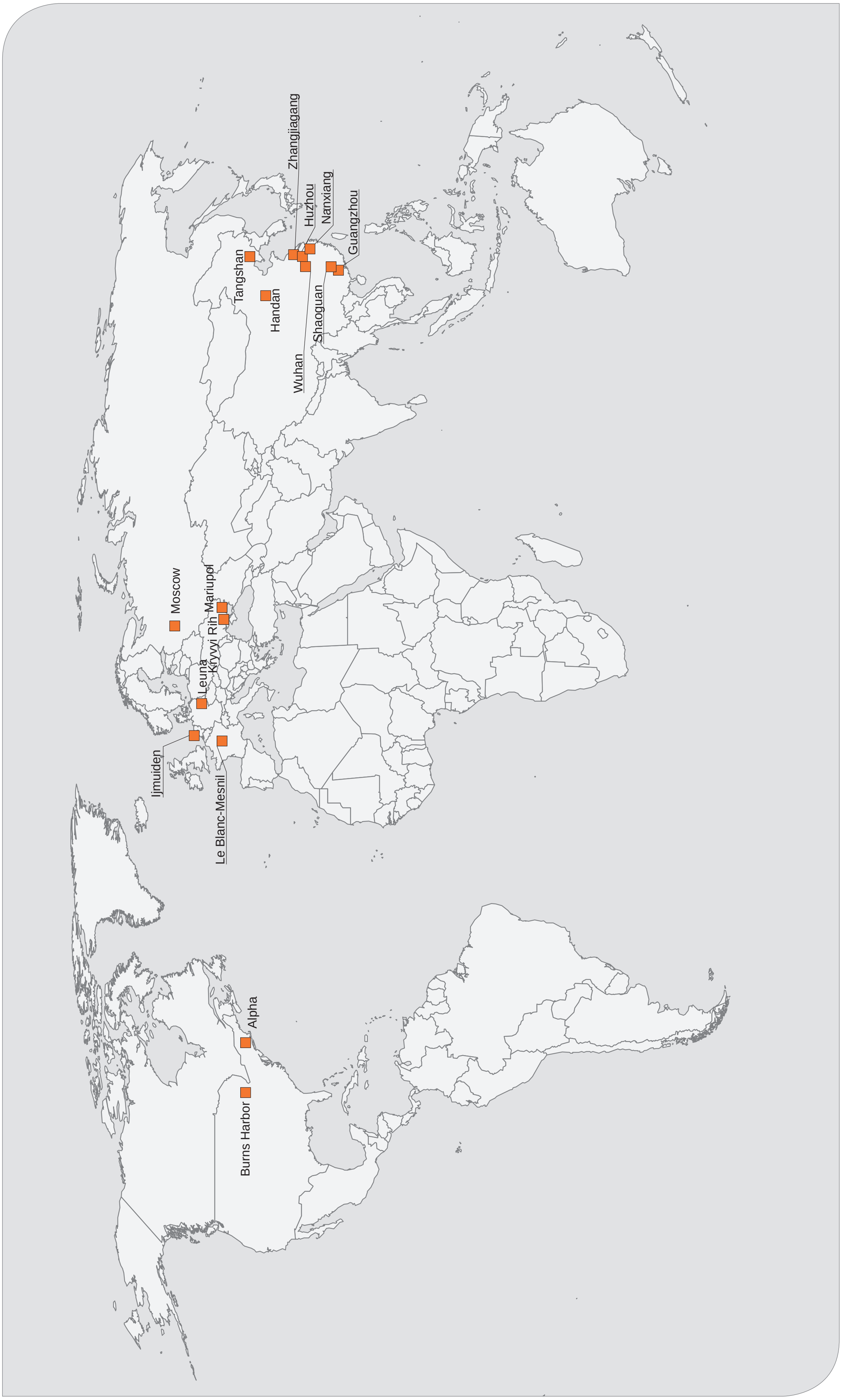


Fig. 33: Generalised map of crude neon purification plant sites.

5.3 Argon

According to Livonen (2006), global argon capacity in 2006 was around 18,500 t/d; the actual production volume, however, was lower. According to their analysis, global argon capacity corresponds to about 1.5% of global oxygen capacity. This was approximately 1.2 million t/d in 2006 and increased by 5–6% per annum over the ten years prior to this. However, it is reported to have already reached approximately 2 million t/d in 2012 (Clarke & Clare 2012). Assuming a further annual increase of 6%, global oxygen capacity would today be around 2.8 million t/d and argon capacity around 42,500 t/d, 15.5 million t/a or 9.3 bn. m^3/a.

More than 950 air separation units worldwide are equipped with argon columns (Table 15).

Even today, argon is considered a typical by-product of oxygen production in air separation units associated with steel smelters. Production of this noble gas therefore decreases and increases in line with regional or global steel production and thus with regional or global economic development. Regardless of this, however, argon is also produced in air separation units supplying ammonia and other chemicals works.

Fig. 34: In Germany, argon is supplied by a number of companies, here by Linde AG, photo: BGR.

In response to the global demand for argon, which has been growing outside the steel sector for around a decade, the large multinational gas companies have been attempting to maximise their argon capacities for several years. For example, argon capacity in the USA in 2011 was approximately 5000 t/d and has since grown by an average of 2%/a to the current level of about 5600 t/d. However, 90% of this growth occurred in the more recent period 2015–2017.

Table 15: Number of sites with air separation units with argon capacities in individual countries, as far as known, as of February 2016 (according to Suresh et al. 2016, supplemented by in-house research with regard to Germany).

Country	Number
America	
Argentinia	8
Bolivia	1
Brazil	59
Canada	23
Chile	10
Costa Rica	1
Dom. Republic	1
Ecuador	1
Guatemala	2
Mexico	14
Peru	5
Trinidad und Tobago	5
Uruguay	2
USA	222
Venezuela	5
total	**359**
Eastern Europe	
Belarus	2
Bosnia-Herzegowina	1
Bulgaria	3
Croatia	3
Czech Republic	6
Estonia	1
Hungary	5
Kazakhstan	1
Latvia	1
Lithuania	1
Macedonia	1
Poland	13
Romania	5
Russia	31
Serbia	2
Slovakia	2
Ukraine	10
Uzbekistan	2
total	**90**
Africa	
Algeria	2
Egypt	4
Kenya	1
Marocco	1
Rep. South Africa	6
Sudan	1
total	**15**
Western Europe	
Austria	5
Belgium	5
Danmark	1
Finland	3
France	5
Germany	46
Greece	2
Italy	2
Luxembourg	1
Netherlands	2
Norway	2
Spain	2
Sweden	2
Switzerland	2
United Kingdom	1
total	**81**
Asia	
Bangladesh	1
China	181
India	21
Indonesia	21
Japan	59
Malaysia	7
Philippines	4
Singapore	6
Rep. South Korea	32
Taiwan	25
Thailand	13
Vietnam	10
total	**380**
Middle East	
Bahrain	1
Iran	4
Israel	2
Kuwait	1
Qatar	2
Saudi Arabia	2
Turkey	7
total	**19**
Oceania	
Australia	3
total	**3**

5.4 Krypton

With the exception of South Korea, all other countries in the world include their krypton import and export data in those of the other speciality gases xenon, and generally also neon. However, South Korea is a major industrialised country and also an important semiconductor and electronics producer, meaning that its import data can be used to draw conclusions about the global krypton market, in this case the pure krypton supplier market. According to the Korea Customs Service, 6888 kg of krypton were imported in 2015, 17,014 kg in 2016 and 15,993 kg in 2017 (= 4562 m^3 at 15 °C) (HS code 2804293000).

Supply countries in 2017 were Ukraine at 45.1%, Russia at 34.9%, USA at 11.4% and China at 8.6%. In 2016 these figures were Russia at 73.9%, Ukraine at 13.7%, USA at 9.9% and China at 2.5%, and in 2015 Russia at 49.9%, USA at 24.4%, Ukraine at 16.3% and China at 9.4%.

The following brief description of the evolution in supply for krypton is based predominantly on the contributions of Richard Betzendahl – Betzendahl Gas Consultants LLC – in the gasworld journal (see bibliography), updated after data in Spiritus & Betzendahl (2018):

Krypton is a constituent of the column sump obtained in all air separation units (cf. Section 3.1) which, if used, is further enriched or separated into pure krypton and pure xenon in a number of treatment stages and in special plants.

Although krypton is much less in demand than xenon (cf. Sections 3.2.4, 3.2.5, 4.4 and 4.5), it is its coupled gas and accumulates in large quantities as xenon production increases. Only more recently have major gas companies been working to reduce the krypton ratio when producing krypton and xenon, or to eradicate xenon completely.

In the former Soviet Union, krypton and xenon were regarded as strategic resources, because they were required for the development of the post-WWII Soviet aerospace programme, primarily during the 1980s. Virtually all major air separation units, among others in Novomoskovsk, Lipetsk, Cherepovets, Chelyabinsk, Nizhny Tagil and Orsk in Russia, Enakiyevo, Kommunarsk, Kryvyi Rih, Makeyevka, Mariupol, Severodonetsk and Dneprodzerzhinsk in Ukraine, as well as Temirtau in Kazakhstan, were identically equipped with crude krypton/crude xenon plants (Pakhomov & Dubasov 2014). According to Lebedev & Pryanichniko (1993), around 11,000 m^3 (= 11 million litres) of crude krypton/crude xenon were produced in Ukraine in 1991. Production in all CIS states together was approximately 25,000 m^3.

However, in the majority of cases, operators of former soviet air separation units have no demand for krypton and xenon (and neon), leading them to offer their column sump (see Section 3.1.4) for sale to interested traders or directly to purification companies. As a result of their very good contacts to Russia, primarily the companies OOO *Akela-N* (Chimki), but also Chromium Ltd. (Moscow) or, in Ukraine, the previously mentioned company Iceblick Ltd., were able to conclude the majority of contracts over numerous years. Following the dissolution of Iceblick, new companies such as Cryoin Engineering Ltd. (Odessa), Ingas AE (Mariupol) and UMG RT Gas (Kiev) split the market for Ukrainian neon, krypton and xenon among themselves.

Until the global financial crisis in 2009, worldwide crude krypton/crude xenon production capacity was at around 135 million litres (of which 120 million litres was krypton) but had already fallen to around 100 million by the end of 2008 due to the sharp decline in global steel production – and the concurrent production from the associated air separation units. In 2009, approximately 85 million litres of krypton were produced.

In 2010, there were approximately 85 air separation units worldwide with a crude krypton/crude xenon capacity of 111 million litres, of which approximately 100 million litres were krypton. More than 80% of this was controlled by the gas companies Air Liquide SA, Praxair Inc., Linde AG and Iceblick Ltd. (see above). At that time Betzendahl assumed production figures of around 98 million litres of krypton, but continuously corrected this value downwards to 84 million litres. The large Ukrainian krypton producers Iceblick Ltd. (see appendix: Ukraine) at that time gave a much higher global supply of around 130,000 m^3 Kr/a in Cockerill (2010).

Crude krypton/crude xenon production, or rather, crude krypton/crude xenon capacity was distributed as follows in 2010:

Fig. 35: In Germany, pure krypton is produced by Linde AG in their Unterschleißheim factory, among others, photo: BGR.

- USA: approximately 12–14 million litres, of which 85% by Praxair Inc., declining production, of which the majority in old air separation units for supplying steel smelters;
- eastern Europe: approximately 32–34 million litres, of which 70% by Iceblick Ltd., gradually declining production, of which the majority in old air separation units for supplying steel smelters, peak production approximately 40 million l/a in 2005;
- western Europe: approximately 18–20 million litres, of which almost 100% by Air Liquide SA and Linde AG, constant production in large air separation units at steel smelters and chemicals works;
- Middle East/Africa: 14–16 million t, constant production, of which around 10 million litres (at 70% Kr) in the world‘s largest coal gasification plant in Sasol (now corrected substantially downwards, see appendix: South Africa);
- China/Asia: approximately 22–26 million litres, of which 15–20 million litres in China, robust growth, until 2013 growth in China by a further 10 million litres due to very large air separation units planned there, in addition four purification plants for krypton/xenon in China.

In 2012, there were around 100 air separation units with crude krypton/crude xenon capacities of around 110 million litres and an estimated production of 86 million litres of crude krypton at 70 locations. Around ten of a total of 17 known purification plants were in operation worldwide and produced pure krypton, including two in the USA.

In 2013, global crude krypton capacity was at 90 million litres and production was relatively constant at an estimated 87 million litres. However, in that year, global stocks were already at more than half of annual production and by 2016 they had increased to 80% of annual global production.

The global supply of krypton is expected to grow steadily thanks to new and larger air separation units in China and will probably be at more than 130 million l/a from 2018. In addition, the number of purification plants worldwide is expected to continue increasing, primarily in China.

As of October 2017, Spiritus & Betzendahl (2018) identified 63 air separation unit locations worldwide with crude krypton capacities, and 21 sites with purification plants. However, the reliability of these data is disputed by German market participants (Anonymous, personal communication). Table 16 presents an updated, but also incomplete, overview of the relevant air separation units and Fig. 36 shows the global distribution of krypton and xenon purification plants.

Table 16: Locations of air separation units with crude krypton/crude xenon purification capacities at various enrichment levels and of purification plants, according to Spiritus & Betzendahl (2018), Suresh et al. (2016), Internet research and Anonymous (oral communication).

Country	**Location**	**Production**	**Purification**
Austria	Linz	Kr/Xe	
Brazil	Ipatinga	Kr/Xe (mid 2018)	
Canada	Sault Ste. Marie, ON	Kr/Xe	
China	various/Anhui (2 x)	Kr/Xe	
	Ma'anshan/Anhui		Kr, Xe
	various/Hubei (9 x)	Kr/Xe	Kr, Xe
	Ningbo/Zhejiang (2 x)	Kr/Xe	
	Quanzhou/Fujian (2 x)	Kr/Xe	
	Xiangtan/Hunan (6 x)	Kr/Xe	
	Chongqing	Kr/Xe	
	Taiyuan/Shanxi	Kr/Xe	
	Jinan/Shandong	Kr/Xe	Kr, Xe
	Handan/Hebei	Kr/Xe	Kr, Xe
	Panzhihua/Sichuan (6 x)	Kr/Xe	Kr, Xe
	Xichang/Sichuan (2 x)	Kr/Xe	
	Huzhou/Zhejiang	Kr/Xe	
	Tangshan/Hebei	Kr/Xe	Kr, Xe
	Shaoguan/Guangdong	Kr/Xe	Kr, Xe
	Nanjing/Jiangsu	Kr/Xe	
	Yangzhou/Jiangsu	Kr/Xe	
	Yantai/Shandong (2 x)	Kr/Xe (mid 2019)	
Czech Republic	Vresova	Kr/Xe	
Finland	Tornio	Kr/Xe	
France	Le Blanc-Mesnil	Kr/Xe	Kr, Xe
	Dunkerque	Kr/Xe	
	Richemont	Kr/Xe	
	Moissy-Cramayel	Kr/Xe	
Germany	Ludwigshafen (2 x)	Kr/Xe	
	Duisburg-Ruhrort (2 x)	Kr/Xe	
	Duisburg-Hüttenheim (2 x)	Kr/Xe	
	Leuna (2 x)	Kr/Xe	
	Dormagen	Kr/Xe	
	Bremen (2 x)	Kr/Xe	
	Brunsbüttel	Kr/Xe	
	Marl	Kr/Xe	

Table 16 (continued).

	Eisenhüttenstadt (2 x)	Kr/Xe	
	Salzgitter	Kr/Xe	
	Gelsenkirchen	Kr/Xe	
	Oberhausen-Biefang (2 x)	Kr/Xe	
	Hürth (2 x)	Kr/Xe	
	Unterschleißheim		Kr, Xe
	Krefeld-Gellep		Kr, Xe
Japan	Kashima	Xe	
	Kakogawa	Kr/Xe	Kr, Xe (2019)
	Oita	Kr/Xe	Kr, Xe
Netherlands	IJmuiden	Kr/Xe	
Romania	Galati	Kr/Xe	
Russia	Tscherepowez	Kr/Xe	
	Balashiha		Kr, Xe
	Murom		Kr, Xe
	Moscow (2 x)		Kr, Xe
	Saretschny		Kr, Xe
	Jekaterinburg	Kr/Xe	
	Nischni Tagil	Kr/Xe	
	Lipezk	Kr/Xe	
	Orsk	Kr/Xe	
	Magnitogorsk	Kr/Xe	
	Norilsk	Kr/Xe	
	Tscheljabinsk	Kr/Xe	
	Dzerzhinsk	Kr/Xe	
Slovakia	Kosice	Kr/Xe	
Rep. South Africa	Secunda	Kr/Xe	
UAE	Abu Dhabi	Kr/Xe	
Ukraine	Krywyj Rih	Kr/Xe	
	Mariupol (2 x)	Kr/Xe	Kr, Xe
	Severodonetsk	Xe	
	Zaporizhia	Kr/Xe	
	Odessa		Kr, Xe
	Alschevsk	Kr/Xe (no production)	
USA	Alpha, NJ		Kr, Xe
	Arroyo, WV	Kr/Xe	
	Beulah, ND (2 x)	Kr/Xe	
	Burns Harbor, IN (2 x)	Kr/Xe	Kr, Xe

Table 16 (continued).

	Calumet, IN (3 x)	Kr/Xe	
	Gary, IN (1 x)	Kr/Xe	
	Ecorse, MI	Kr/Xe	
	Groves, TX	Kr/Xe	
	La Porte, TX (2 x)	Kr/Xe (+ mid 2019)	
	La Porte, TX	Xe	
	Texas City, TX (2 x)	Kr/Xe	
	Dear Park, TX (2 x)	Kr/Xe	
	Garfield, UT	Kr/Xe	
	Cleveland, OH	Kr/Xe	
	Freeport, TX	Kr/Xe (mid 2019)	

5.5 Xenon

With the exception of South Korea, all other countries in the world include their xenon import and export data in those of the other speciality gases krypton, and generally also neon. However, South Korea is a major industrialised country and also an important semiconductor and electronics producer, meaning that its import data can be used to draw conclusions about the global xenon market, in this case the pure xenon supplier market. According to the Korea Customs Service, 3370 kg of xenon were imported in 2015, 6536 kg in 2016 and 11,771 kg in 2017 (= 2135 m^3 at 15 °C) (HS code 2804294000).

In 2017 supplier countries were the USA at 64.5%, France at 22.6%, Ukraine at 4.9%, Japan at 4.3%, China at 3.2% and other countries at 0.5% (Russia, Czech Republic, Austria, Taiwan). In 2016 these were the USA at 55.2%, Ukraine at 21.7%, France at 18.7% and other countries at 4.4% (Japan, China, Russia, Austria) and in 2015 they were France at 41.5%, the USA at 27.7%, Russia at 14.3%, Japan at 8.2%, Ukraine at 6.9% and other countries at 1.4% (China, Austria, Taiwan, Czech Republic).

The following brief description of the evolution in supply for xenon is based predominantly on the contributions of Richard Betzendahl – Betzendahl Gas Consultants LLC – in the gasworld journal (see bibliography), updated after data in Spiritus & Betzendahl (2018):

Xenon is a constituent of the column sump obtained in all air separation units (cf. Section 3.1) which, if used, is further enriched or separated into pure krypton and pure xenon in a number of treatment stages and in special plants.

Around 40% of the world's xenon is produced in air separation units that supply oxygen to chemical plants rather than steelworks. The best-known example is the Sasol coal gasification plant in South Africa (see appendix: Republic of South Africa).

Only a few years ago, 75% of global krypton and xenon production was controlled by the three major international gas specialists Air Liquide SA (France), Praxair Inc. (USA) and Linde AG (Germany), including the Ukrainian company Iceblick Ltd. Iceblick was founded in 1992 by companies in Russia, Kazakhstan and Ukraine, and was the world's second largest producer of pure krypton and xenon, dominating the former Soviet heavy noble gases market (see appendix: Ukraine). The remaining 25% of the market for krypton and xenon were shared by several other steel smelters in China and Russia, a chemicals company in South Africa (see above), the gas companies Air Products & Chemicals, Inc. (USA), Messer Group GmbH (Germany) and Taiyo Nippon Sanso Corporation (Japan), as well as around half a dozen smaller air separation units in eastern Europe. The Chinese share of global xenon production has increased in recent years.

Fig. 36: Generalised map of crude krypton and crude xenon purification plant sites.

As discussed above, krypton and xenon were regarded as strategic resources in the former Soviet Union. According to Lebedev & Pryanichnikov (1993), around 11,000 m^3 (= 11 million litres) of crude krypton/crude xenon were produced in Ukraine in 1991. In all CIS states together, production was approximately 25,000 m^3 of crude krypton/crude xenon with a total of approximately 1800 m^3 (= 1.8 million litres) of xenon content.

In 2007, there were approximately 75 air separation units worldwide with crude krypton/crude xenon production capacities, which typically each produced around 1.25 million litres Kr/a and 110,000 litres Xe/a. Ten purification plants were able to produce 99.999% pure Xe or at 99.999% pure Kr from the crude krypton/crude xenon gas mixtures. Global xenon capacity was around 10 million l/a, and production was 9.0 million litres.

One year later, 80 air separation units are claimed to have been able to produce crude xenon (gasworld 2008). At the end of 2008, global production capacity was 100 million litres crude krypton/crude xenon and increased into 2009 to 135 million l (of which 14 million litres were xenon). Simultaneously, global production was around 9.7 million litres xenon.

In 2010, there were approximately 85 air separation units worldwide with a crude krypton/crude xenon capacity of 111 million litres, of which approximately 11 million litres were xenon. More than 80% of this was controlled by the gas companies Air Liquide SA, Praxair Inc., Linde AG and Iceblick Ltd. (see above). Regardless of the recession, production is claimed to have been 9.7 million litres of Xe. The large Ukrainian krypton producers Iceblick Ltd. (see appendix: Ukraine) at that time, however, gave a much higher global supply of around 12,000 m^3 (= 12 million litres) Kr/a in Cockerill (2010).

See Section 5.4 for the regional distribution of global crude krypton/crude xenon capacities in 2010, as well as the known locations of air separation and purification plants with xenon production.

In 2012, there were 70 sites with around 100 air separation units having crude krypton/crude xenon capacities of approximately 108 million litres of Kr/Xe gas mixture and a production volume of an estimated 9.8 million litres at that time, now adjusted to 9.2 million litres of crude xenon content. At least ten of a total of 17 known purification plants were in operation worldwide and produced pure xenon, including two in the USA.

In 2013, global capacity for crude xenon once again reached 9.8 million litres and production was also at this level.

As of October 2017, Spiritus & Betzendahl (2018) identified 63 locations worldwide with air separation units with crude xenon capacities, and 21 sites with purification plants. However, the reliability of these data is disputed by German market participants (Anonymous, personal communication). Table 16 presents an updated, but also incomplete, overview of the relevant air separation units and Fig. 36 shows the global distribution of krypton and xenon purification plants.

Similar to the situation for krypton, the global supply of xenon is expected to grow steadily thanks to new and larger air separation units in China and will probably reach 13 million l/a in 2020 and continue to increase thereafter.

In addition, around 3 million litres of xenon used in dark matter research in the USA, the EU and China have not been used and will be available to the market again after the end of research activities.

5.6 Projects (helium)

Although the atmosphere contains around 370 million tonnes of helium and the Earth‘s crust is constantly outgassing new helium, the world helium requirement of around 75 t He/d cannot be met by air separation units alone. Due to the low helium content of the air of 5.24 ppm (Table 3), more than 100 km^3 of air would need to be separated every day to generate this global helium demand. Several power stations would be needed to provide the power for this. If helium were the only valuable gas, the current cost of production by air separation would be 60–100 times the cost of separation from natural gas. According to calculations made by Clarke & Clare (2012), a maximum of 2% of global helium production could come from air separation units in 20 years, but only if all new, larger plants were converted with immediate effect for He/N production.

The production of helium from natural gas, whether as a by-product or, in some cases, as a regional primary product from methane-rich, nitrogen-rich or carbon dioxide-rich natural gas, or from residual gases in natural gas liquefaction, will therefore remain indispensable for a long time. Nevertheless, helium from geothermal sources, as currently being explored in Tanzania (see appendix: Tanzania), may also make an important contribution to the future global helium supply.

According to Gubler et al. (2016), global helium resources were 58.82 bn. m^3 on January 1, 2016 and helium reserves 10.295 bn. m^3. Yakutseni (2014) estimated global helium reserves (categories: A + B + C1 according to Russian classification) contained in natural gas at 66.74 bn. m^3 as of January 1, 2009, of which approximately 36 bn. m^3 was helium in natural gas with concentrations > 0.15% He.

In the mid-term, the US Geological Survey (USGS) and the US Bureau of Land Management (USBLM) (see appendix: USA) plan to calculate the global helium reserves and, by the end of 2018, to recalculate US helium reserves. As of 31 December, 2006 global helium reserves were estimated to be 31.3 bn. m^3 (of which 10.1 bn. m^3 in Qatar, 8.2 bn. m^3 in Algeria, 6.8 bn. m^3 in Russia, 2.0 bn. m^3 in Canada and 1.1 bn. m^3 in China). By December 31, 2017, USBLM had analysed 22,100 natural gas samples from 27 countries in order to calculate helium reserves more accurately.

An independent calculation of global helium reserves in the context of this study is unfortunately not possible, because insufficient baseline data are available on many of the US natural gas fields. In addition, the figures for the helium content of important potential natural gas fields, the natural gas of which is already being liquefied (Libya, Indonesia), have not been published.

An overview of the known, because published, helium projects and planned helium installations is given in Table 17 (see appendix: country profiles). However, whether these projects or installations will all be realised – and meet deadlines – only time will tell. Any helium plants located in Indonesia or Iran, which are repeatedly the subject of speculation in the professional press, are absent from the list.

With around 10 trillion m^3 in 2016, Indonesia has the world‘s fourteenth largest natural gas resources and was 12th in global natural gas production at 74 bn. m^3. Most of the natural gas is exported and Indonesia became the fifth largest exporter of liquefied natural gas in the world in 2017. The helium content of the current domestic natural gas supply has not been published and the fate of the residual gas from the eight currently operating LNG plants is unknown. Two additional LNG plants are currently under construction and three are planned. However, due to the robust increase in domestic demand for natural gas, it is estimated that Indonesia requires around US$32 billion by 2025 to expand its natural gas infrastructure. Also, because of the high capital requirement for other, more urgent, investments, it is unlikely that the country will invest in additional helium facilities.

Similar to the Qatari section of the large South Pars/North Dome natural gas field, the Iranian section also bears helium that may be produced by liquefaction in Iran. According to Gubler et al. (2016), the Iranian helium reserves are estimated at 10 bn. m^3. Nor does the Iranian National Petroleum Authority (NIOC) plan to build its own helium facility, however, due to lack of capital.

However, Mohr & Ward predicted that this noble gas would not become scarce within the next 100 years due to the geological availability of helium – however, this was based on flawed USGS production figures and numerous assumptions about helium production in the various US states.

Table 17: Comparative list of known helium projects or planned helium plants.

Country	Natural gas field or plant name	Company	He-content or planned capacity	He-grade	Planned start of production
Kazakhstan	Amangeldy, Anabay, Ayrakty, Kumyrly, Nord Ucharal, Ucharal-Kempirtobe	JCS KazTransGas	37.7 mill. m^3	0.22 – 0.69 %	open
Qatar	Helium 3	Qatargas	11.1/11.8 mill. m^3/a	0.05 % (LNG)	2019
Russian Federation	Kovykta, Chayanda	PAO Gazprom	4.4 bill. m^3 5 bill. m^3	0.24 – 0.28 % 0.50 – 0.54 %	until 2021
	Amur GPP		19.4 mill. m^3/a 19.4 mill. m^3/a 21.2 mill. m^3/a		2021 2022 2024
Russian Federation	Yaraktinsky	Irkutsk Oil Company	7 mill. m^3/a		2021
Republic South Africa	Virginia (Free State)	TETRA 4 (Pty) Ltd.	21 – 28 mill. m^3 650,000 m^3/a	3 – 4 %	H1 2019
Tanzania	Rukwa	Helium One Ltd.	1.5 bill. m^3	8 – 10.2 %	open
USA	St. John (Arizona)	IACX Energy LLC	0.2 mill. m^3/a	0.009 – 0.134 %	open
USA	Pinta Dome (Arizona)	IACX Energy LLC	0.4 mill. m^3/a	5.4 – 9.8 %	open
USA	Woodside Dome (Utah)	IACX Energy LLC	1.7 mill. m^3/a	0.7 – 1.5 %	open
USA	Dry Piney Creek (Wyoming)	QEP Resources, Inc.	19.4 mill. m^3/a	0.6 %	Q3 2019

Natural gas liquefaction

In 2016, around 1086 bn. m^3 of natural gas, and thus 30% of the world's natural gas amounting to 3620 bn. m^3, were traded across borders (BGR 2017), of which around 347 bn. m^3 (32%) was liquefied natural gas (LNG). The number of LNG exporting countries rose again to 18 in 2016 when Angola and Egypt resumed production (IGU 2017). More than 70% of LNG demand came from Asia, most notably from Japan, which, as the world's largest LNG importer, imported nearly one third of the global supply in 2016.

Europe is the second largest importer of LNG. It currently has 25 large LNG landing terminals for liquefied natural gas regasification, 23 of which are within the EU and two in Turkey. The European terminals are located in Belgium, France, Greece, the United Kingdom, Italy, Lithuania, the Netherlands, Poland, Portugal, Spain and Turkey. In 2016, the total regasification capacity of the 25 European plants was 216 bn. m^3. This corresponds to about 40% of gas use in the region.

Early in 2017, around 340 Mt/a were nominally available in 78 LNG plants, i.e. around 457 bn. m^3 of liquefaction capacity. Around 68% of nominal total capacity was distributed among the six countries Qatar, Australia, Malaysia, Indonesia, Algeria and Nigeria. 29 LNG plants with a total capacity of 114.6 Mt/a were under construction worldwide at the beginning of 2017, and a further 123 plants with a total capacity of 879 Mt/a, 76% of which are located in the USA, were planned.

According to the International Gas Union (IGU 2017), Qatar was again the world's largest exporter of LNG in 2016, with an export volume of 77.2 Mt (104 bn. m^3), followed by Australia with 57 Mt (76 bn. m^3) and Malaysia with 24.9 Mt (33 bn. m^3). Qatar has the world's third largest natural gas reserves after Russia and Iran, accounting for just over 12% of global reserves. More than 60% of its marketed natural gas production, which amounted to 165 bn. m^3 in the previous year, was shipped worldwide in the form of LNG. The country accounted for around 30% of the LNG market in 2016 and has now announced its intention to increase its annual natural gas liquefaction capacity by 30% to 100 Mt/a by 2025 at the latest.

However, Qatar is competing with other countries that also aim to increase their LNG volumes. For example, Australia has made significant investments in its LNG export facilities in recent years and could replace Qatar as the world's largest LNG exporter in the next few years. In addition, in 2016, the USA began exporting liquefied natural gas from shale gas production.

Currently, only a few LNG plants in Algeria, Australia and Qatar produce helium as a by-product. An additional helium plant in Qatar has been announced.

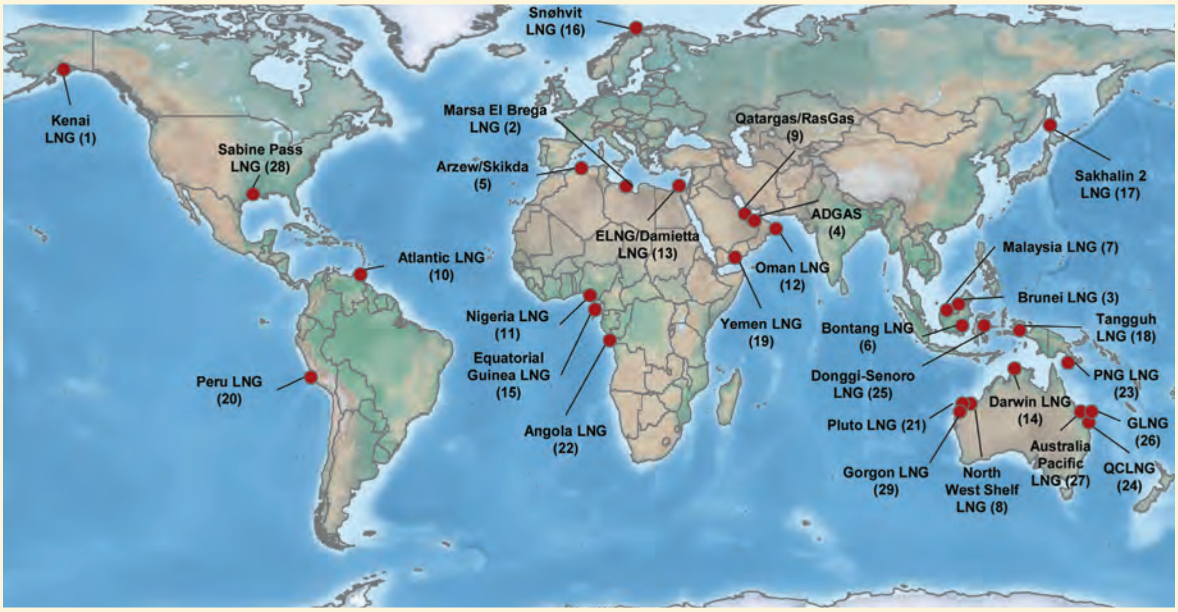


Fig. 37: Generalised map of current global LNG facilities, from IGU (2017). The figures following the plants are reference numbers and are not relevant here.

6 Supply and demand balance

6.1 Helium

Because the costs for cooling, transporting and storing noble gases in liquid form are high, but gases in the gaseous state require an extremely large amount of space (cf. Section 5.1), many analysts simply assume that the demand for noble gases, especially helium, as a rule approximately corresponds to supply. Only in exceptional situations, when customers complain about sharply rising prices or even delivery bottlenecks, are arguments sought to explain this obvious imbalance in supply and demand. During the period 2011–2013, when helium was not available to all users worldwide in sufficient quantities, this was unanimously explained (Dawson 2011, Garvey (2011), Cockerill 2013c, Kornbluth 2015) by insufficient supply due to the low demand for natural gas and the associated lesser supply of helium-rich natural gas, non-producing, new helium plants outside the USA and unforeseen servicing of helium plants in the USA (cf. Section 5.1). However, possible changes in the demand behaviour of helium users, on the other hand, were not taken into consideration.

It is striking that almost all helium experts – most of whom are based in the USA – use USGS supply data (demand = supply) in their analyses and thus arrive at the same conclusions. Employees from individual helium-producing gas companies then comment in support of these conclusions in interviews, without pointing out any possible deficiencies in the analyses. Only very few analysts, e.g. Frobes (2017), point out that something is wrong with the initial figures.

Because, as demonstrated in Section 5.1, the previously published global helium production statistics contain errors, and assuming demand = supply (see above), including the absolute demand data quoted in Section 4.1 for the sake of completeness, it would make more sense to study relative demand behaviour in more detail with regard to supply and demand accounting.

There was a global helium shortage during the 2006–2007 period. However, during these years the absolute supply of 173 Mm^3 and 182 Mm^3 of helium, respectively, was strikingly high, meaning that demand must have even exceeded these figures.

Garvey (2009) concluded that there was a helium shortage not only in 2006 and 2007, but that this continued until the onset of the global financial crisis in autumn 2008. Only in the first quarter of 2009 did the supply exceed demand by an estimated

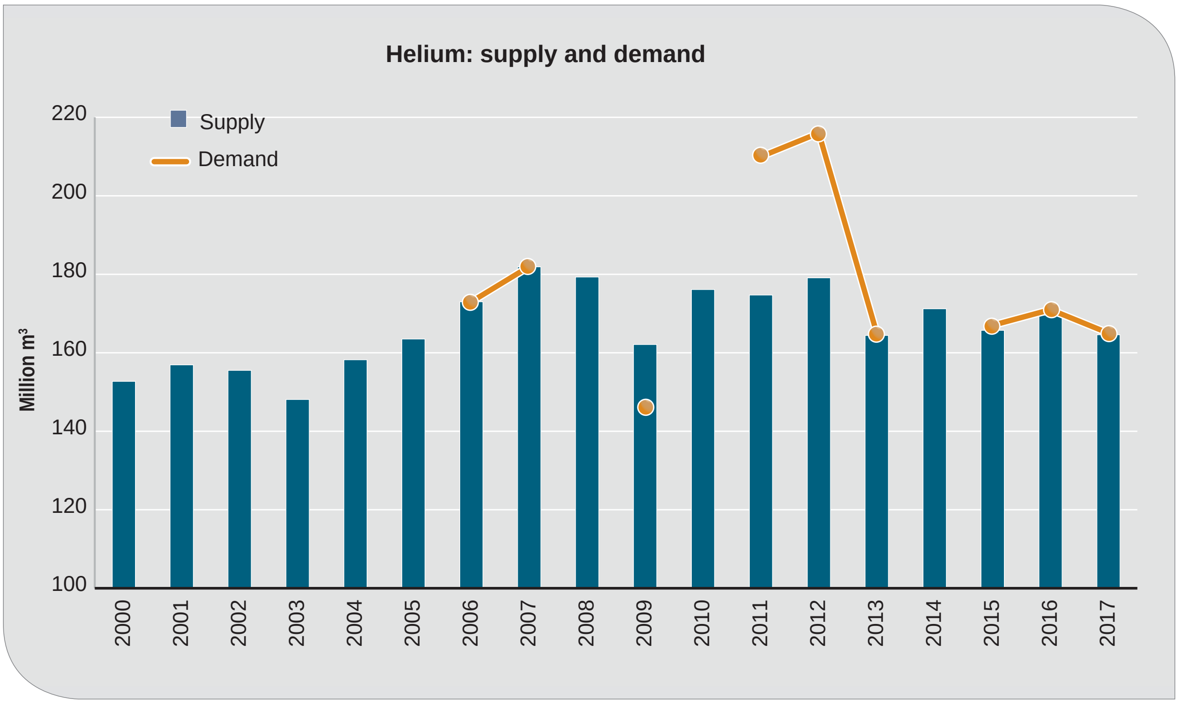


Fig. 38: Helium: supply and inferred demand since 2000.

10%, when demand fell sharply. Because supply was approximately 162 Mm^3 during the whole of 2009, it is possible to derive a demand of approximately 146 Mm^3.

According to Kornbluth (2015), global helium supply was 20% or more below demand in the period 2011–2013. Accordingly, demand during 2011–2012 would have been 210–215 Mm^3 and approximately 200 Mm^3 helium in 2013. According to Garvey (2013), however, demand in 2013 corresponded to the available supply and would therefore have only been approximately 165 Mm^3 helium.

There is claimed to be an oversupply of helium on the global market since 2014, which is said to be due to new capacities in Qatar, Algeria and Russia, as well as a lack of servicing shutdowns among large producers.

In 2015 and 2016, supply is said to have surpassed demand by approximately 2 Mm^3, which would be equivalent to a demand of 168–172 Mm^3 helium.

According to Garvey (2017b), the global demand for helium in 2017 corresponded to supply and was therefore approximately 165 Mm^3.

Because previous analyses by global helium experts are based on partially incorrect data and assumptions, accounting for supply and demand over the last few years is only possible to a very limited extent (see Fig. 38). Primarily, the lack of any reliable demand data prevents a more detailed evaluation.

It can be assumed that the unchecked use of helium temporarily outstripped supply in the years leading up to the global financial crisis of 2009, even though the greatest global helium supply of 181.9 Mm^3 was achieved in 2007. Only a short time after the global financial crisis, consumption rose again to new record levels, but this time supply could no longer keep pace. Thanks to committed substitution and recycling, users were able to significantly reduce their demand by 2013–2014. The previously very high demand for helium has not been achieved again in recent years, which is less likely to be due to a low interest in this noble gas than to user fears of renewed scarcity. Short-term supply bottlenecks discussed in many media, such as during the Qatar crisis in June 2017, prevent potential users from returning to helium as the preferred industrial gas.

6.2 Neon

The following description of the evolution in supply and demand accounting for neon is based entirely on the contributions of Richard Betzendahl – Betzendahl Gas Consultants LLC – in the gasworld journal (see bibliography) and has been supplemented using data in Spiritus & Betzendahl (2018):

By the time of the global financial crisis in 2009, global neon supply significantly exceeded the only slowly increasing demand. With the global financial crisis and for a few years following this, demand for neon declined primarily as a result of the significant decline in plasma television production, but neon supply also fell, in line with the reduced global production of neon as a speciality gas in air separation units.

Beginning in 2012, demand for neon increased sharply due to the strong demand for lasers in semiconductor manufacturing. With a simultaneous decline in neon production in eastern Europe (cf. Section 5.2), demand began to outstrip supply from July 2014 onwards. At the same time, there was a change of ownership in the market-dominating Ukrainian company Iceblick Ltd. at the end of 2004, whereby the new president attempted to enforce extreme prices (cf. appendix: Ukraine). All these events led to panic buying by the major neon consumers, i.e. semiconductor producers who met their demand directly from neon purification plants and who overbid each other with regard to prices. In addition, reserve purchases led to short-term and extreme price increases (cf. Section 7.2). It was important to the buyers to avoid a shutdown of their semiconductor production under all circumstances.

As a result of the very high demand and the extreme prices, air purification plants with neon capacities in Russia, Ukraine and China increased their production at short notice and deferred plants were reactivated. Within a year, by mid-2016, global neon production increased by more than 40%, once again significantly exceeding demand, which has since been reduced by recycling (see Section 3.4).

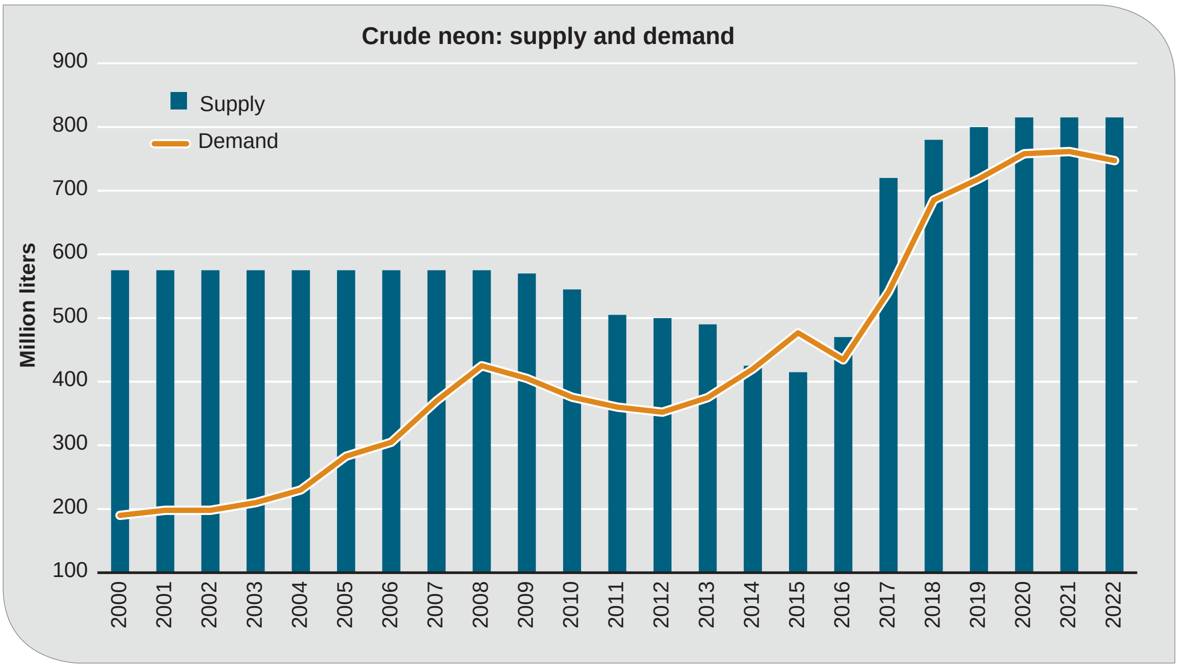


Fig. 39: Crude neon: supply and demand since 2000, including forecast of future development, sources: Betzendahl (various years, see bibliography), Spiritus & Betzendahl (2018) and anonymous (personal communication).

In July 2016, Linde Group announced its plans to increase its crude neon capacity by 40 million litres/a by expanding its air separation unit in La Porte, Texas. In addition, further air separation units in Russia and China will be equipped with neon capacities, meaning that supply will continue to increase. However, this is also predicted for demand, which will be shaped by the opening of, and demand from, new semiconductor factories in China. In the period 2020–21, therefore, shortage on the global neon market may again be the result.

6.3 Argon

No current and reliable analyses of argon‘s global supply and demand have been published. In contrast to all other noble gases, argon is produced regionally in sufficient volumes and is therefore not a globally traded industrial gas. If the gas companies identify an increasing regional demand for argon, they plan to equip future air separation units (retrofitting old plants is too complex and too expensive) with argon columns and then, if necessary, to purchase this gas from the air separation unit operators as merchandise.

The current global demand for argon is at least 5 bn. m^3/a (see Section 4.3), but supply should exceed 9 bn. m^3/a (see Section 5.3), meaning that argon shortages, which are occasionally reported, will only be short-term and regional in extent.

6.4 Krypton

The following description of supply and demand accounting for krypton is based entirely on the contributions of Richard Betzendahl – Betzendahl Gas Consultants LLC – in the gasworld journal (see bibliography) and has been supplemented using data in Spiritus & Betzendahl (2018):

For many years, with the exception of the 2007–2009 period, the global market for krypton has been characterised by oversupply and is likely to remain so for a long time to come. This is due to the fact that krypton is obtained exclusively as a by-product of the coveted xenon, which in turn is around ten times as rare. At the same time, the demand for krypton is very unilaterally dictated by the insulating glass industry, which uses krypton as an insulating filling gas. Incandescent lamp filling, formerly krypton‘s second largest sales market, only faltered with the development of energy-saving lamps but has now largely collapsed due to the rapid penetration of the light bulb market by LEDs. Nevertheless, here in Germany, for example, the

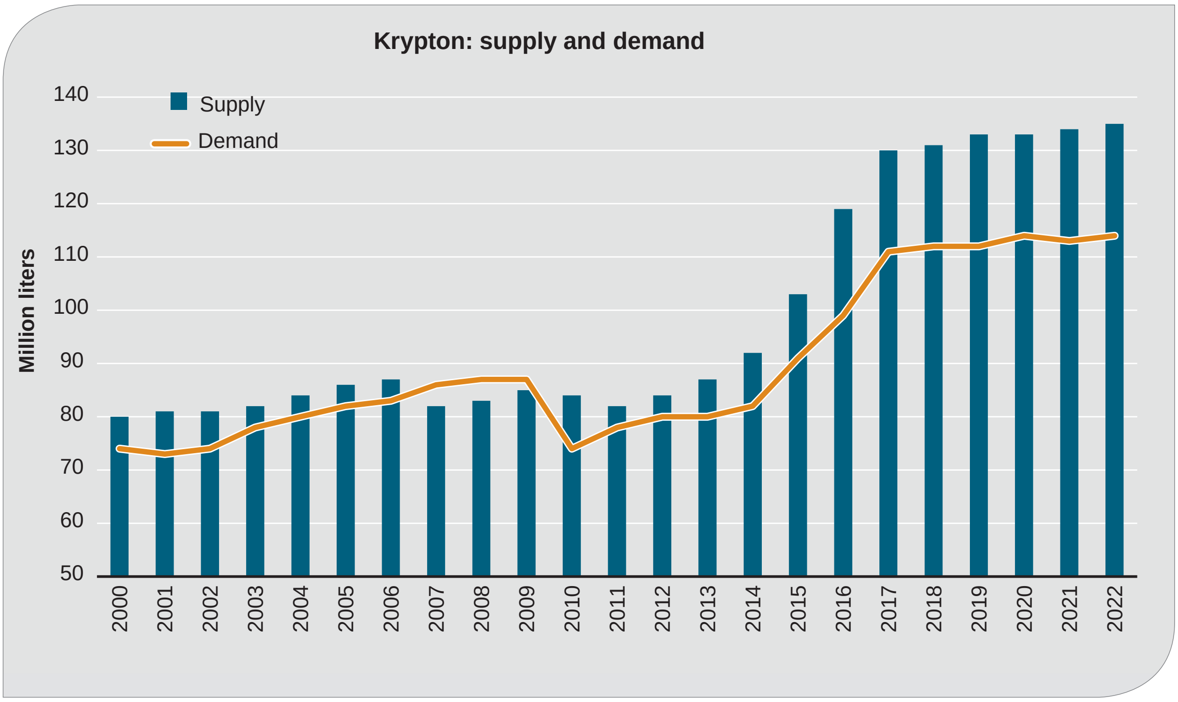


Fig. 40: Krypton: supply and demand since 2000, including forecast of future development, sources: Betzendahl (various years, see bibliography) and Spiritus & Betzendahl (2018).

sales market for halogen lamps with krypton filling for car headlights still retains some importance. The producers are said to store a very large volume of krypton, which will last for many production months, and thus does not lead to an increase in production being anticipated.

In the years leading up to the global financial crisis of 2009, all sales markets were strong and the supply of krypton was even briefly below demand. With the recession, however, the global construction boom collapsed, heat-insulating glass was no longer in such high demand and when the recession was over, energy-saving lamps were prescribed in many countries.

6.5 Xenon

The following description of the evolution in supply and demand accounting for xenon is based entirely on the contributions of Richard Betzendahl – Betzendahl Gas Consultants LLC – in the gasworld journal (see bibliography) and has been supplemented using data in Spiritus & Betzendahl (2018):

The global xenon market was characterised by a slight oversupply until the mid-2000s. In the years following this, until the global financial crisis, new applications for xenon were constantly being added, such that demand exceeded the barely

Fig. 41: Xenon – the most valuable and critical noble gas, photo: BGR.

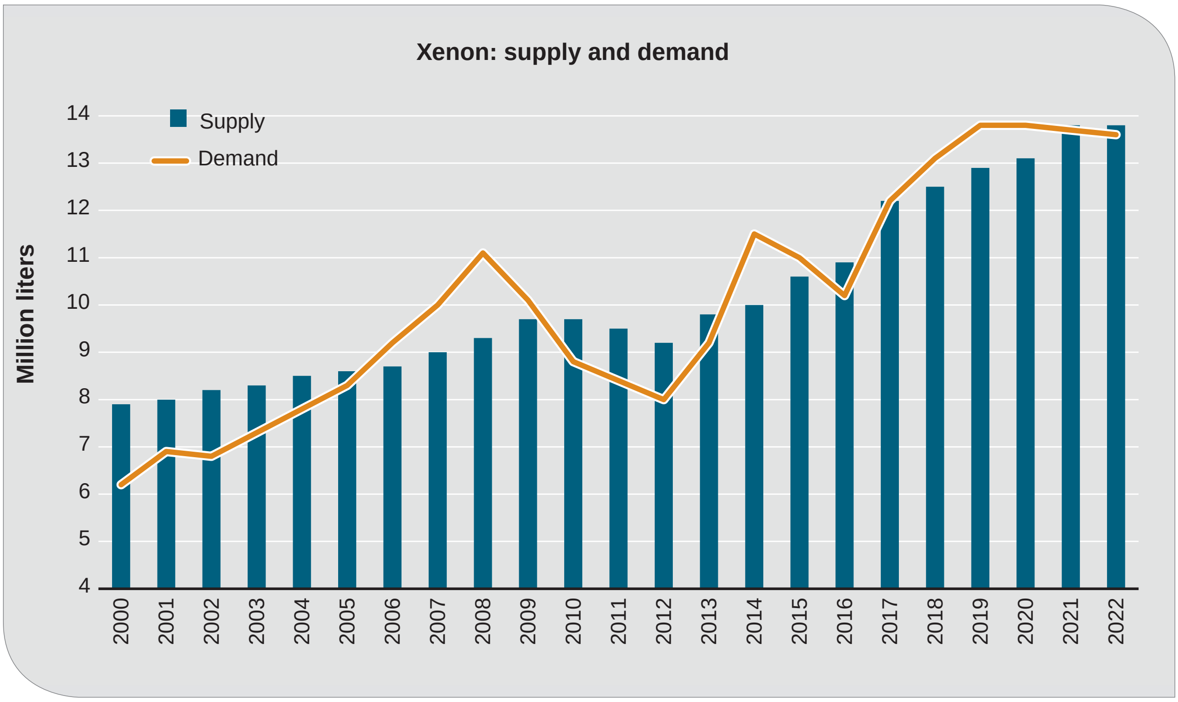


Fig. 42: Xenon: supply and demand since 2000, including forecast of future development, sources: Betzendahl (various years, see bibliography), Spiritus & Betzendahl (2018) and anonymous (personal communication).

increasing supply, in some cases significantly. During this time, the use of xenon and neon in plasma television production began, as well as the early use of xenon, krypton and neon for lasers in semiconductor production, both applications that required large volumes of xenon. In the years 2007 and 2008, in particular, this resulted in a scarcity that led to corresponding price increases (cf. Section 7). In the course of the global recession, xenon demand declined, and to a lesser degree, supply.

Only at the end of 2012, with the use of xenon as a filling gas for halogen lamps, did a promising new market for this noble gas develop which, however, was very short-lived, contrary to expectations. It was not until 2014 that the demand for xenon was again higher than the global supply. From mid-2015 on, there was again an oversupply of xenon, which was, however, for a limited time only. With the use of xenon in basic research and in an ever-increasing number of satellites, but above all in new laser processes in semiconductor manufacturing, demand is already outstripping supply.

7 Price trend

With the exception of helium, prices for all noble gases (and all other industrial gases) are individually negotiated between consumers and producers. Here, the regional competition market, the required volume, the duration of the supply contract, the regional energy costs, the operating duration of the air separation units and the transport distance between air separation unit and take-off point have the largest influence. In addition, the type and number of transportation and storage containers required or leased play a role in pricing.

7.1 Helium

The major international gas companies are bound to the few global helium producers almost exclusively through what are known as *take-or-pay* contracts. This form of contract requires companies to take or pay for the amount of helium they are guaranteed, regardless of whether there is a sales market or not.

The delivery and take-off prices agreed in the contracts between the helium producers and the gas companies are not published, but there are indicators for their approximate value, because they are oriented around the price data of the US Bureau of Land Management (USBLM). Often these are purchase agreements with price escalation clauses coupled to the USBLM price (see below), which are concluded over a period of 20 years. Future price escalation clauses have not yet been decided, because USBLM will presumably no longer publish prices in the future (cf. appendix: USA).

In its annual Minerals Yearbooks (intermittent) USGS publishes:

- since 1925, official prices for helium (at 98.2% He, later 99.995% He, now 99.997% He) from government-owned helium plants for government customers, and including private customers since 1938 (cf. Cai et al. 2012)
- since 1973, estimated prices for pure helium (at 99.995% He, now 99.997% He), as asked for in the USA by private helium producers
- since 1999, official USBLM prices for crude helium when selling to government customers
- since 2012, official USBLM prices for crude helium when selling to private customers

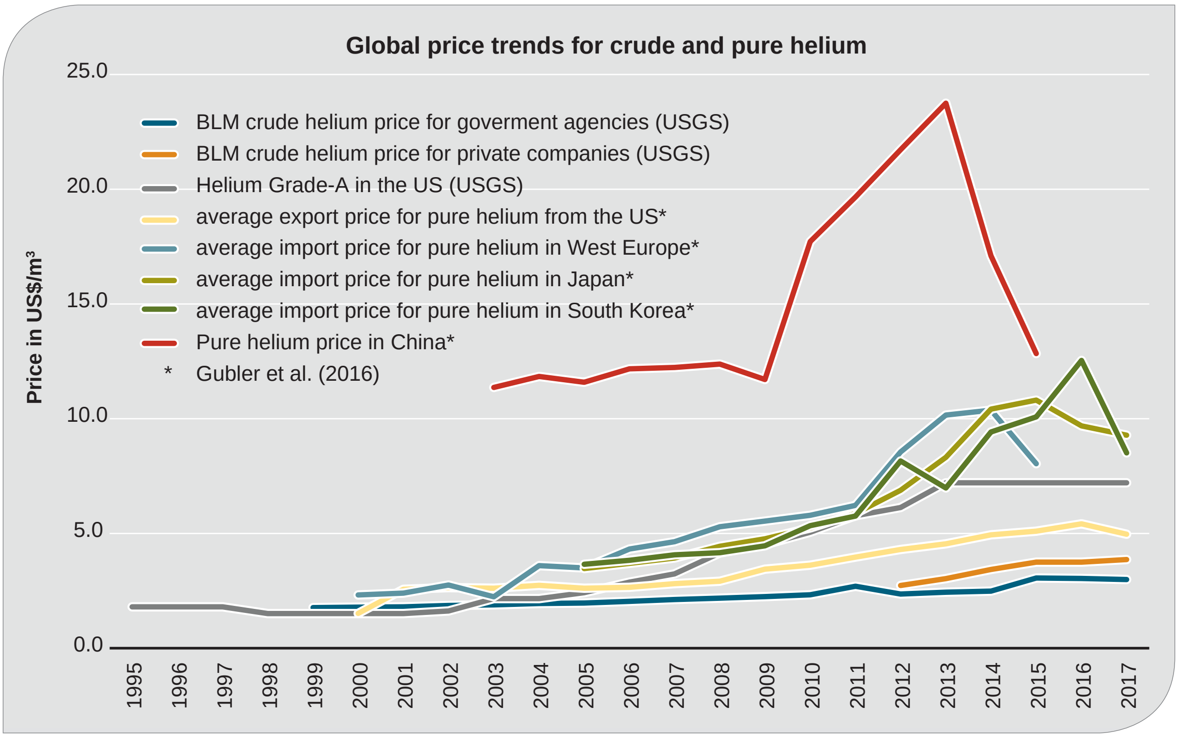


Fig. 43: Price trend for crude and pure helium since 1995, according to USGS and Gubler et al. (2016), supplemented.

Gubler et al. (2016) also researched:

- the average export price for pure helium from the USA since 2000
- the average import price for pure helium to western Europe since 2000
- the average import price for pure helium to Japan since 2005
- the average import price for pure helium to South Korea since 2005
- the average domestic price for pure helium in China since 2003

The development of these very diverse helium prices is shown in Fig. 43.

In comparison, the average German import price for helium in 2017 was €6.43/m^3.

In addition, from the literature, the historical price of helium in 1915 ($61,000/m^3) and in 1921 ($17.30/m^3, later reduced to US$6.27/m^3) is known, as well as the average revenue of the USBLM helium auctions in recent years (cf. appendix: USA):

- 1st auction on July 30, 2014: auctioned, 2.6 Mm^3 crude helium, average revenue US$5.82/m^3
- 2nd auction on August 26, 2015: auctioned, 7.6 Mm^3 crude helium, average revenue US$3.74/m^3
- 3rd auction on July 20, 2016: auctioned, 11.1 Mm^3 crude helium, average revenue US$3.86/m^3
- 4th auction on July 19, 2017: auctioned, 13.9 Mm^3 crude helium, average revenue US$4.29/m^3
- 5th auction on August 31, 2018: auctioned, 5.8 Mm^3 crude helium, average revenue US$10.09/m^3
- 6th auction in September 2018: auctioned, 2.5 Mm^3 crude helium, average revenue US$6.31/m^3

Historically, the price for ^{3}He was US$100–200/l, increasing in mid-2009 to US$1000–1200/l following reports of the scarcity of this helium isotope, reaching US$3000/l in autumn 2009, US$3900/l in 2013 and back to US$2000/l in 2016 (Gubler et al. 2016).

7.2 Neon

The price trend for neon is known from the contributions of Richard Betzendahl – Betzendahl Gas Consultants LLC – in the gasworld journal (see bibliography), updated after data in Spiritus & Betzendahl (2018):

According to this data, the average wholesale price of neon remained relatively constant at US$0.10/l for many years, then doubled to trebled in the years 2012–2014 as a result of increasing demand, and exploded by a factor of one hundred in 2015 (to US$3.00/l, spot prices up to US$5.00/l) (see Sections 4.2, 5.2 and 6.2), only to quickly return to values of US$0.10–0.20/l, and US$0.08/l in September 2017. A general price increase trend up to US$0.30/l is forecast – with minor fluctuations – for the coming years up to 2022.

7.3 Argon

The historical price trend for argon is unknown and probably varies greatly from region to region. According to Suresh et al. (2016), prices increased in 2014 by 10–25% and a further 15–20% in 2015.

Internet research revealed that the current prices in the USA vary greatly and are currently (as of 2017–2018) between US$8.80 and US$19.10/m^3 for private customers or an average of US$12.50/m^3.

According to Suresh et al. (2016), these large price differences can also be explained by the complex price calculation system, illustrated using the example of major customers in Canada. Here, in 2015, CDN$750/m^3 were charged as a monthly baseline fee, plus CDN$4.00/m^3 for the first 1500 m^3, plus a possible further CDN$2.00/m^3 for the next 2500 m^3, plus another possible further CDN$1.20/m^3 for any argon volume over and above this.

7.4 Krypton

The price trend for krypton is known from the contributions of Richard Betzendahl – Betzendahl Gas Consultants LLC – in the gasworld journal (see bibliography), updated after data in Spiritus & Betzendahl (2018):

Characterised by a long period of oversupply and thus falling to stable prices, the price of krypton recovered by 10–20% in the first quarter of 2007 and was at a wholesale price of US$0.30–0.50/l for 2007 as a whole. A strong increase in krypton

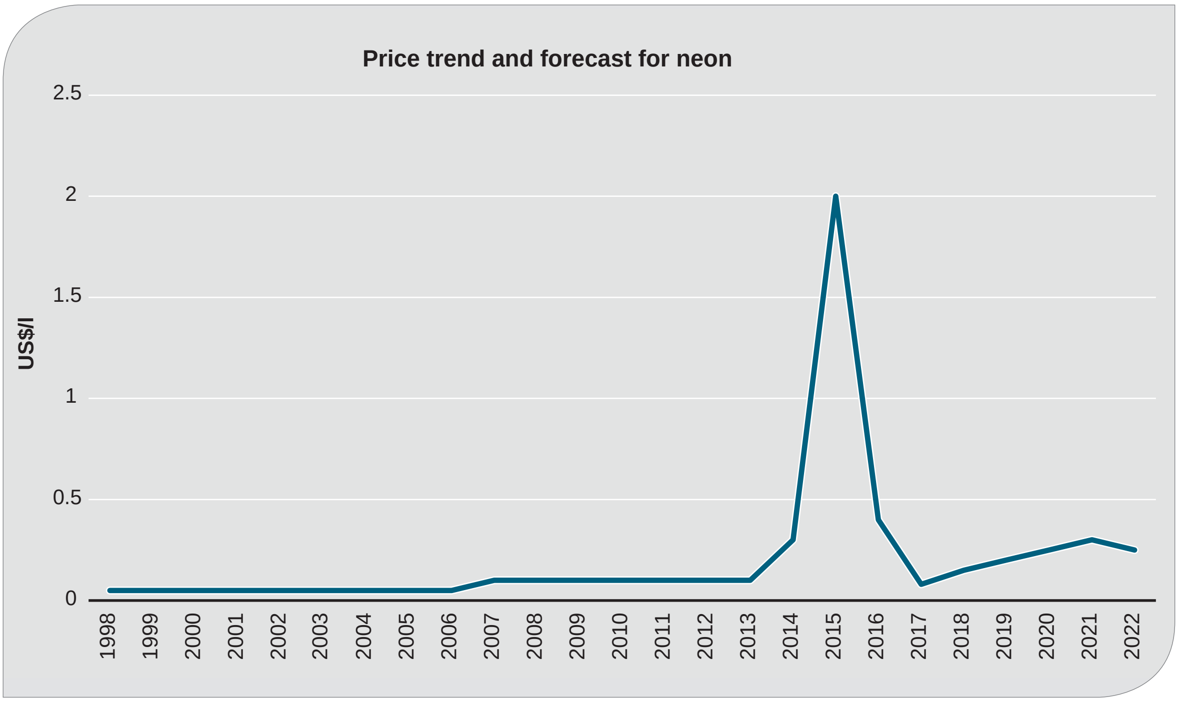


Fig. 44: Price trend and forecast for pure neon (wholesale price) in US$/l since 1998, according to Betzendahl (various years, see bibliography) and Spiritus & Betzendahl (2018).

demand for filling insulating glass panels in 2008 led to a wholesale price increase to an average of US$1.90/l and a maximum of US$2.50/l in the fourth quarter of 2008. Due to the collapse of the global construction industry during the 2009 recession, the price fell to US$1.15–1.75/l in the middle of that year, and even to US$0.75/$1.10 in the following year. Since then, the widespread elimination of krypton as a filling gas in lighting led to another sharp price decline to US$0.08/l (as of September 2017), which may be long-term. The producers‘ stocks are overflowing (cf. Section 4.4), demand is low and production of the coveted xenon as a co-product cannot be reduced rapidly everywhere.

According to market participants, the price for krypton in Germany is currently (as of summer 2018) approximately €0.10/l.

7.5 Xenon

The price trend for xenon is known from the contributions of Richard Betzendahl – Betzendahl Gas Consultants LLC – in the gasworld journal (see bibliography), updated after data in Spiritus & Betzendahl (2018):

The xenon price is characterised by exceptionally large price fluctuations as a result of the very small market volume with few producers, but at the same time continuously new applications, some with highly relevant volumes. The low concentration of xenon in the air only allows economic production in large air separation units and expanding production is only possible in conjunction with high planning and start-up costs.

As late as 1984, xenon was an exceedingly rare and sought-after, and therefore very expensive, speciality gas in the West, costing around US$20.0/l. With the collapse of the Soviet Union, enormous Soviet stocks entered the global market and the price fell to US$1.0/l in the years 1990/91. The market was constantly saturated by new sales from ex-Soviet stocks for many years afterwards.

In 2007, demand continued to outstrip supply as a result of new and constantly growing applications, with the wholesale price for xenon increasing by 50% from US$3.0–US$5.0/l in the first quarter of 2007 alone and reaching US$20/l due to very strong demand at the end of 2007. In 2008, prices were up to US$20.0–30.0/l, averaging US$28.0/l.

With the global recession, this overheated xenon price also dropped again and was at US$6.0–

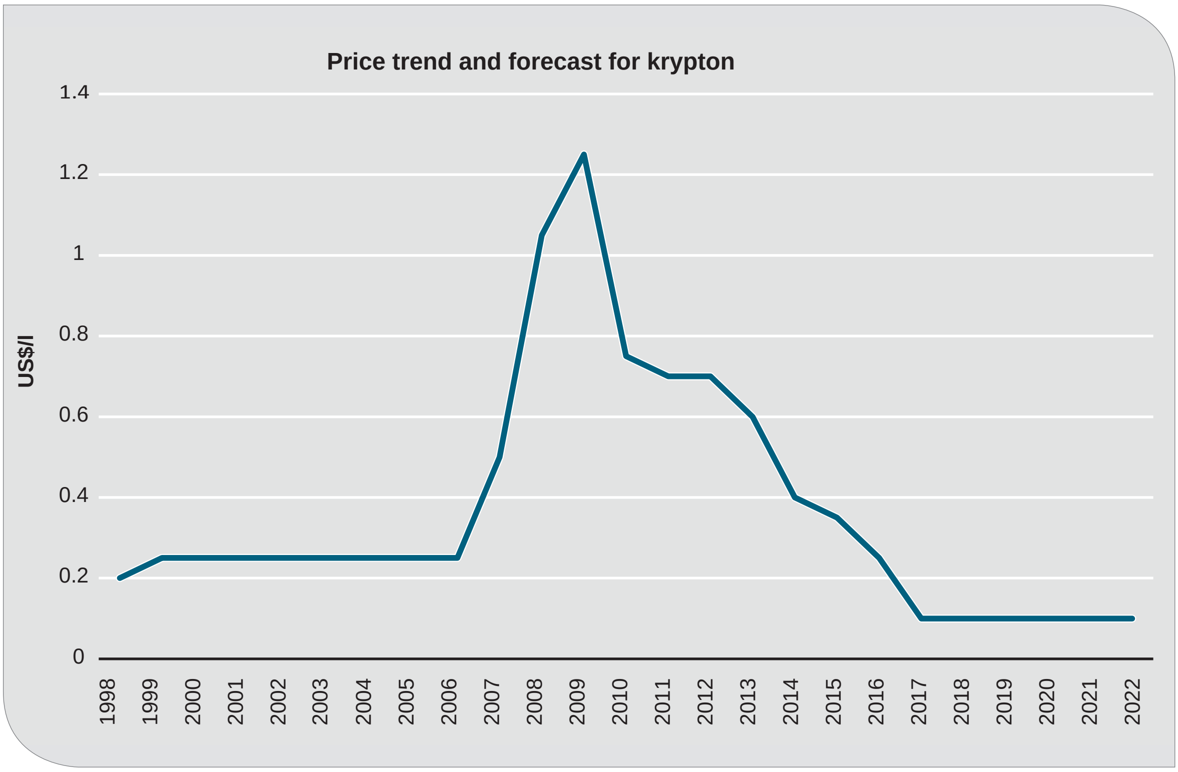


Fig. 45: Price trend and forecast for krypton (wholesale price) in US$/l since 1998, according to Betzendahl (see bibliography) and SPIRITUS & BETZENDAHL (2018).

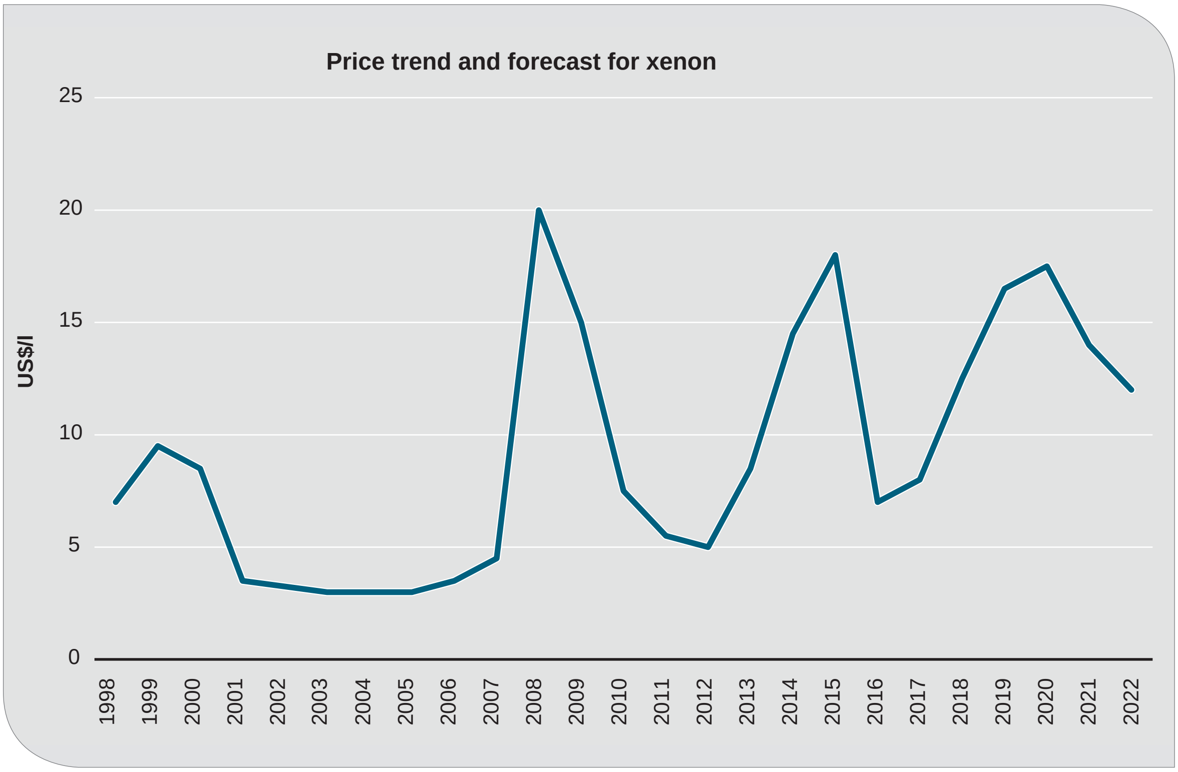


Fig. 46: Price trend and forecast for xenon (wholesale price) in US$/l since 1998, according to Betzendahl (see bibliography) and SPIRITUS & BETZENDAHL (2018).

8.0/l in 2010. In subsequent years, however, the demand for xenon increased again and in 2014 the global supply was exceeded again and prices reached up to US$18.0/l. With prices of US$6.0–8.0/l in 2016, the demand and thus the price of xenon has increased again significantly since then. In September 2017, the wholesale price reached US$11.0/l. According to market participants, the price for xenon in Germany is currently (as of summer 2018) approximately €11.00/l.

Robust demand is predicted for the coming years, but from 2020 onwards this will be offset by increasing capacities, especially in Chinese air separation units. This should lead to short-term price increases up to US$20/l, but in the medium term should again lead to a calming in the market price of xenon.

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Appendix

Country profiles

Algeria

Helium

As of December 31, 2016, Algeria had 4501 bn. m^3 of natural gas reserves or 26,720 bn. m^3 of natural gas resources. This ranks the North African country 11th in global reserves and 7th in global resources. Its annual production in 2016 amounted to 93.2 bn. m^3 of natural gas. This corresponds to 2.6% of global natural gas production or 9th worldwide. Since production began in the early 1960s, Algeria has produced around 2483 bn. m^3 of natural gas. The largest Algerian natural gas field is Hassi R'Mel with an average content of 0.19% He in the natural gas.

In 1964, Algeria became the world's first producer of liquefied natural gas (LNG) when it commissioned a natural gas liquefaction plant in Béthioua, near Arzew, on the Mediterranean coast. Here, liquid helium, among other things, has also been produced commercially since 1995 and exported primarily to Europe since the end of 1995. If the supplying LNG-2 plant in Arzew can provide sufficient volumes of helium-rich residual gases, an annual production of 16.6 Mm^3 of gaseous helium or 2800 t of liquid helium can be achieved. However, this does not appear to have been the case for some time (D.N. Baciu, Linde AG, personal communication). The helium plant is owned by the *Helios S.p.A. – Société pour la Construction et l'Exploitation d'une Helium Liquide et d'Azote* joint venture, founded in 1991, 51% of which is owned by the state-owned Algerian company *Sonatrach S.p.A.* and 49% by the *Helap S.p.A.*joint venture (shareholders are Air Liquide S.A./France and Air Products and Chemicals, Inc./USA). Plans have been in place for a decade to build a second helium facility in Arzew (Reinoehl 2012).

In 2005, a second helium plant was opened in a natural gas liquefaction plant in Skikda, also on the Mediterranean coast, some 510 km east of Algiers, near the three existing LNG facilities, some of which have been in operation since 1971. This Helison Production S.p.A. helium plant was built by Linde Engineering, went into production in April 2007 and is 51% owned by the German Linde AG and 49% by Algeria's Sonatrach S.p.A. Linde are entitled to 50% of helium production. The helium plant's annual capacity (depending on source) is 3000 t liquid helium or 16.6 Mm^3 of gaseous helium at > 99.999% He. At the same time, however, the associated LNG system can only supply residual gas with a maximum content of 12.5 Mm^3 He/a (D.N. Baciu, Linde AG, personal communication).

Algeria's helium production figures have not been published. Some media only report that the helium plant in Skikda allegedly produced 3 Mm^3 of helium in the year it opened (2007).

The remaining production data given in Table 18 are US Geological Survey estimates, whereby the estimates since 2010 differ according to USGS author and are obviously not harmonised.

The production data are compared to overall global imports of helium from Algeria (or France, because a large proportion of Algeria's helium is landed in Marseilles) according to the Global Trade Atlas.

Table 18: Total global helium import volume from Algeria and France (in Mm^3), according to the Global Trade Atlas (t and ft^3 converted to m^3) and US Geological Survey (USGS) estimates of Algerian helium production.

	1995	1996	1997	1998	1999	2000	2001	2002
Imports								
- from Algeria	n. a.	n. a.	10.55	10.85	12.09	10.41	9.08	10.81
- from France	0.05	0.54	2.07	6.32	8.20	8.00	8.30	8.76
- total	n. a.	n. a.	12.62	17.17	20.29	18.41	17.38	19.57
Estimate USGS	10	15	15	16	16	10	17	17
	2003	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**
Imports								
- from Algeria	11.97	14.27	15.16	12.22	14.70	14.59	12.35	10.10
- from France	5.04	7.64	9.59	10.18	11.21	15.77	12.32	13.80
- total	17.01	21.91	24.75	22.40	25.91	30.36	24.67	23.90
Estimate USGS	17	17	17	15	20	20	20	20
	2011	**2012**	**2013**	**2014**	**2015**	**2016**	**2017**	**2018**
Imports								
- from Algeria	11.97	14.27	15.16	12.22	14.70	14.59	12.35	11.30
- from France	8.91	10.30	7.06	7.05	6.82	5.24	5.13	5.82
- total	20.88	24.57	22.22	19.27	21.52	19.83	17.48	17.12
Estimate USGS	20/17	15/17	15/25	16/25	10	10	14	14

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Australia

Helium

In Australia, there are several sedimentary basins in which helium has been identified as an accompanying gas in natural gas. Some examples are:

Amadeus Basin (central Australia):
- Constant natural gas extraction from sandstones in the Palm Valley natural gas field with an average of 0.15% He
- In 1992, pilot production from a fault in quartzite underlying salt, which delivered 1750 m^3 daily of nitrogen-rich wet gas containing 7.2% He
- In 2014, two pilot productions from wells in a jointed granite underlying salt, which initially delivered up to 14,700 m^3/d, but significantly lower levels of natural gas containing up to 12% He after only a few minutes

North Perth Basin (Western Australia)
- Woodada natural gas field with an average 0.21% He. Reserves: 3.5 Mm^3 He (proven reserves) in addition to 4 Mm^3 He (possible resources), currently no production

Canning Basin (Western Australia)
- Meda: explored natural gas accumulation with 0.50% He, production unlikely

Gunnedah Basin (New South Wales)
- Wilga Park: explored natural gas accumulation with 0.45% He, production unlikely

McArthur Basin (Northern Territory):
- Pilot production of natural gases with high methane and He, but low CO_2 content, undergoing exploration

Helium production in Australia began at Wickham Point near Darwin, Northern Territory, in March 2010, despite the numerous occurrences of domestic Australian helium. At that time, BOC Ltd., a subsidiary of Linde AG, opened a plant which since then has been able to extract helium from He-rich residual gases (with an average of 3.0% He, 0.1% H_2, 3.2% CH_4, 93.6% N_2) from a neighbouring ConocoPhillips natural gas liquefaction plant. The liquefied natural gas comes from the Bayu Undan field in the offshore Bonaparte Basin in the Timor Sea. This natural gas field is located around 250 km south-west of Suai on Timor-Leste and 500 km north-west of Australia at a water depth of approximately 90 m. The assumed reserves amount to 88 bn. m^3 natural gas (with 0.013–0.28% He and 0.18% He on average) and are sufficient for production over approximately 25 years. Natural gas production in the Bayu-Andan field began in April 2004, and the natural gas liquefaction plant in Darwin, connected by pipeline, was commissioned in February 2006.

The helium plant in Darwin was built by the Swiss company Linde Kryotechnik AG and has an official capacity – depending on the source – of 4.16 Mm^3 or 5.6 Mm^3 of gaseous helium per year at 99.999% He. According to D.N. Baciu (Linde AG, personal communication), the capacity is 4.44 Mm^3 and annual production also remains constant at this capacity. However, the plant obviously does not supply customers in Australia, as was originally announced, but almost exclusively customers in Southeast Asia (primarily Malaysia and South Korea) and New Zealand. The production data since opening have not been published. However, global imports of helium from Australia according to the Global Trade Atlas are listed in Table 19 (note: total imports of helium from Australia in 2016 and 2017 are well above the installed helium capacity and cannot be explained at this time). By comparison, domestic Australian helium demand is between 500 and 850 t/a, corresponding to 3.0–5.1 Mm^3/a.

Table 19: Total global helium import volume from Australia according to Global Trade Atlas (in m^3 or t, 1 t He approximately corresponds to 5988 m^3 He at 15 °C and 1 bar pressure).

	2010	2011	2012	2013	2014	2015	2016	2017
m^3	141.773	548.595	627.745	925.121	41.863	176.078	181.846	1.137.347
t	269	305	292	490	799	658	920	977
Sum in mill. m^3	1.75	2.37	2.38	3.86	4.83	4.12	5.69	6.99

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Canada

Helium

Investigation of the helium content in Canadian natural gas reservoirs dates back to the years 1916–1918, when the British Admiralty showed an interest in Canadian helium for airships. In 1917, a helium pilot plant came into production in Hamilton, Ontario, drawing on the local Blackheath natural gas reservoir at 0.34% He. After numerous setbacks, it began to produce helium gas at 87% He. However, because insufficient natural gas was soon available, the plant was decommissioned in autumn 1918 and transported to Calgary, Alberta.

In Calgary, natural gas from the Bow Island natural gas field was tapped, with a helium content of 0.36%. Following a series of setbacks, commercial helium production began there in autumn 1919 and lasted until 17 April of the following year. During this brief period, around 1700 m^3 helium were produced at a purity of 60–90%. When sufficient helium was again available from the USA following World War I and demand dropped drastically, the plant was once again decommissioned.

In October 1958, an exploration well was sunk near Aikens in south-western Saskatchewan, approximately 14.5 km north of the small town of Swift Current. At a depth of around 2000 m it encountered a natural gas reservoir with a composition of 96.57% N_2, 1.90% He, 0.99% CO_2, 0.23% Ar and 0.31% other gases. The initial natural gas pilot production achieved up to 140,000 m^3/d.

In February 1960, in a different well around 150 km south-east of Swift Current, near Wood Mountain (now Mankota), a second, similar, natural gas reservoir with a composition of 96.35% N_2, 1.08% He, 0.29% Ar and 2.28% CH_4 was found. Natural gas pilot production was between 460,000 and 570,000 m^3/d. Another well, sunk in the same reservoir in December 1960, yielded natural gas with a composition of 94.40% N_2, 1.38% He, 2.87% CH_4 and 1.20% H_2. At the time, the helium resources of the two natural gas reservoirs at Aikens and Wood Mountain were estimated at 25–50 Mm^3 by the Saskatchewan geological survey (Lee 1962).

In December 1963, a processing plant went into production north of Swift Current, exploiting four producing wells which, according to a publication by the Canadian scientist M. M. Yurkowski (Yurkowski 2016b), produced 57.2 Mm^3 of natural gas until it was closed in 1977, estimated to contain approximately 1.4% helium (corresponding to about 800,000 m^3 helium). It is worth noting that, at a conference a few months prior to this, the same scientist (Yurkowski 2016a) gave a remaining operating period of 1964–1975 and a precise production volume of "464,181 mscf" (thousand standard cubic feet, corresponding to 12.875 Mm^3) helium. According to the U.S. Geological Survey Minerals Yearbooks, helium production in the Canadian plant in the period 1963–1977 was around 10.5 Mm^3 Helium.

The capacity of the plant operated at the time by Canada Helium Ltd. (shareholders: British American Oil, British Oxygen and Canadian Liquid Air) was initially 330,000 m^3 helium/a and was increased to 1 Mm^3 helium/a in 1967. The plant was decommissioned in 1977 when the discharge head of the reservoir fell and water ingress followed. In June 2014 Canada Helium Inc. and Quantum Helium Management Corp. recommenced natural gas production at the Wilhelm site from the recommissioned reservoir north of Swift Current. No helium production figures have yet been published.

In January 2016, North America Helium Inc. began exploration of another prospective helium reservoir in south-western Saskatchewan, on the border to Alberta. Royal Helium Corporation, Jasper Mining Corporation, Navis Resources Corporation and Thor Resources also investigated potential helium reservoirs in Canada (Forbes 2017, Grynia & Griffin 2016).

A few months later, in August 2016, the US company Weil Group Resources, LLC, opened a second helium plant in Saskatchewan. This plant, in Mankota, utilises natural gas from the reservoir discovered there in 1960 and has a capacity of > 1.1 Mm^3 helium/a, to be separated from around 100 Mm^3 natural gas/a. The helium produced there at a purity of 99.99% is marketed by Linde Group, who also designed the plant. In November 2017, Weil Resources also announced their intention to build a helium liquefaction plant with the name CryoHub™ in Medicine Hat, Alberta, pointing to a positive start to production. Presumably, the aim is to also supply the domestic market with the liquid helium produced there.

The production volumes of the two helium plants in Canada newly opened since 2014 have not been published. However, the total global imports (almost exclusively to the USA) of helium from Canada according to the Global Trade Atlas are given in Table 20. In comparison, domestic demand is between approximately 2500 and 3500 t of liquid helium (corresponding to approximately 15–21 Mm^3 gaseous helium).

Table 20: Total global helium import volume from Canada, slightly modified after Trade Atlas (in Mm^3).

	2014	**2015**	**2016**	**2017**	**2018**
Million m^3	0.09	1.11	2.22	2.36	0.55

Argon

According to Suresh et al. (2016), Canada's argon production capacity in February 2016 was approximately 2950 t/d. Argon columns were in operation at 23 sites, some with several air separation units.

Krypton, xenon

According to Betzendahl & Spiritus (2018), crude krypton/crude xenon are also produced in Praxair Canada Inc.'s air separation units at the Sault Ste. Marie site in Ontario, which have a total capacity of 2700 t O_2/d.

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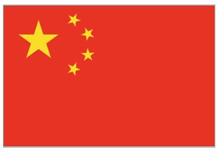
China



Helium

Chinese industry's helium demand, which cannot be covered by domestic production, is high and growing robustly. China began to invest in domestic helium production as early as the early 1960s as a result of the US embargo and an increase in domestic military demand became apparent. The helium levels in domestic natural gas reservoirs were first studied for this purpose. Data on the genesis, tectonics and noble gas isotope ratios of numerous Chinese sedimentary basins are available in Yongchang et al. (1996). In particular, to date some economic geology data for the approximately 180,000 km^2 Sichuan Basin, which apparently has the highest helium content (Jian et al., 2015), have been published:

Sichuan Basin, eastern Sichuan Province

- Southern Sichuan Basin with the large natural gas fields Weiyuan, Ziliujin and Washi, averaging 0.24% He;
  Weiyuan natural gas field, originally with proven reserves of 40 bn. m^3 of natural gas at 88–93% CH_4, 4.8–15.3% N_2 and 0.12–0.22% He, and 0.40% He maximum, averaging 0.16% He, discovered 1964, almost exhausted
- Eastern Sichuan Basin, average 0.04% He
- Central Sichuan Basin, average 0.03% He
- Western Sichuan Basin, average 0.02% He

Helium has only been produced on an industrial scale from 3 km deep wells on the Weiyuan natural gas field since the 1970's, in a helium plant operated by Chengdu Natural Gas Chemical Plant General, a subsidiary of the Petro-China Southwest Oil and Gasfield Company. The annual production volume is said to have been only 50,000 m^3 of helium and, because of the low helium content of the natural gas, the cost of production exceeded the cost of imported helium. In order to at least make Chinese science and the military more independent of helium imports, Chengdu Natural Gas Chemical Plant General began construction of a further helium plant developed by them in 2010, in Dongxing City, Sichuan Province, at an investment cost of 110 million Yuan (approximately €12 million). In April 2012, the plant is said to have produced helium for the first time in a trial run – but it is not known whether industrial production has started. According to Gubler et al. (2016), plant capacity is 285,000 m^3 He/a and utilisation is 40–50%.

In order to reduce dependence on US helium imports, Chinese market participants propose (Dongxiang 2014):

- moving to helium from Qatar and Australia
- developing helium joint ventures with Russia
- holding strategic helium reserves
- beginning helium recycling and
- producing helium as a by-product in domestic natural gas liquefaction facilities.

It is worth noting that in May 2016 the fourth-largest Chinese steel concern, Wuhan Iron and Steel (WISCO), announced their intention to build an additional air separation unit in central China with the aid of Linde AG, in addition to two existing facilities. Here, the aim is to produce or treat around 230,000 m^3 of neon annually, in addition to helium.

The US company Air Products & Chemicals, Inc. also commissioned a new air separation unit in Chongqing City in April 2017, supplying a local semiconductor manufacturer with nitrogen, oxygen, hydrogen, argon and helium.

In 2017, the Chinese imported 3629 t (corresponding to 20.3 Mm^3) of helium, 51.3% of which came from Qatar, 36.4% from the USA and 11.2% from Australia.

Argon

According to Suresh et al. (2016), argon was produced in least 181 air separation units in China in early 2016, in addition to oxygen and nitrogen. In 2015, around 1.745 bn. m^3 argon was used, against production of 1.771 bn. m^3. 1.7 Mm^3 of argon were imported in 2015 and 28.4 Mm^3 exported.

The German company Messer has been present in China since 1994 and is a pioneer there among international gas suppliers. To date, 17 operating companies have been founded in three core regions, occupying a leading position in Hunan, Yunnan and Sichuan, as well as Jiangsu, Zhejiang and Guangdong. Messer China has invested in more than 30 air separation units nationwide to supply steelworks and other industries with the necessary industrial gases oxygen, nitrogen and argon. All of Messer's Chinese air separation units are equipped with argon columns.

At the end of 2015, Linde Group operated 25 air separation units in China, including 13 equipped with argon columns, and announced that it would build six additional large plants for Shenhua Ningxia Coal Industry Group Co. Ltd. and Shenhua Logistics Group Co. Ltd. in Yinchuan in the Ningxia Hui Autonomous Region of north-west China. These new plants will together have a capacity of over 10,000 t O_2/d, 6000 t N_2/d and 700 t Ar/d.

Neon, krypton, xenon

According to Wuhan Iron and Steel (WISCO), China's fourth-largest steel group, they were the largest producer of noble gases in China in 2015, with a 70% market share. WISCO runs three air separation units with a total air separation capacity of 450,000 m^3/h and produces argon, neon, helium, krypton and xenon from air.

Chinese polyurethane manufacturer Ningbo Wanhua Polyurethane currently operates two air separation units built by Linde Gas Ningbo. The plants, commissioned in 2010, have a daily capacity of 800 t of liquid O_2 and N_2, and also produce krypton and xenon for the open market.

The Shougang Group is also one of China's largest steel companies. As early as 1998, the group's own engineering company built a first air separation unit with an oxygen capacity of 30,000 m^3/h, which also produces N_2, Ar, Kr, Xe and He. In 2005, a second, similar plant with an oxygen capacity of 35,000 m^3/h (including N_2, Ar, crude Kr/Xe and He), and in 2009 a third, similar plant in Jingtang with oxygen capacities of 2 x 75,000 m^3/h (including N_2, Ar, crude Kr/Xe and He), were added.

In March 2012, the German gas company Messer announced that its Chinese subsidiary Hunan Xianggang Messer had signed a partnership agreement with a Chinese company to build a krypton-xenon plant in Xiangtan, Hunan Province. The new plant can produce 9.4 kg of a gas mixture (*thick soup*) consisting of 90% Kr and 10% Xe, in addition to 24 t of liquid oxygen.

In June 2015, Messer opened a krypton and xenon purification plant in Panzhihua, Sichuan province. The plant has a capacity of 5 million litres of krypton and 450,000 litres of xenon with purities of 99.999%.

Further crude krypton/crude xenon to pure gas purification plants were built by the Russian gas specialist PJSC *Cryogenmash* in 2011 for the Jinan Iron and Steel Works, now merged into the Shandong Iron and Steel Group Co. Ltd. (daily capacity 960 litres Xe and 10,800 litres Kr) in Jinan, and a year later in Handan.

Fig. 47: The krypton and xenon purification plant in Panzhihua, Sichuan Province, of Hunan Xianggang Messer, photo: Messer Group GmbH (with kind permission).

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France

Helium

The helium contents of French natural gases are not published and are therefore presumably economically irrelevant.

In contrast, the noble gas content of the majority of French thermal waters was analysed as early as the beginning of the 20th century and published in a variety of works. Rogers (1921) provided a summary, which identified 55 sources with contents up to 10.16% He and up to 1.643% Ar. The highest helium levels or yields at that time are listed in Table 21.

Table 21: Noble gas content and annual helium discharge of French thermal waters at the beginning of the 20th century, according to Rogers (1921).

Spring	Location	Department	He-grade %	Ar-grade %	He-delivery l/a
Lithium	Santenay	Côte-d'Or	10.16	n. a.	5182
Carnot	Santenay	Côte-d'Or	9.7	n. a.	17.845
Fontaine Salée	Santenay	Côte-d'Or	8.40	n. a.	n. a.
Romaine	Maizières	Côte-d'Or	5.92	0.92	1080
Ys	Grisy	Saône-et-Loire	2.18	1.18	n.v.
Lymbe	Bourbon-Lancy	Saône-et-Loire	1.84	1.20	10.074
Reine	Bourbon-Lancy	Saône-et-Loire	1.75	1.15	n. a.
Parc Sainte-Marie	Nancy	Meurthe-et-Moselle	1.60	1.29	n. a.
César	Néris	Aller	0.97	0.88	33.990
Choussy	La Bourboule	Puy-de-Dôme	0.01	0.10	3048

According to the U.S. Geological Survey Minerals Yearbooks, between 0.2 and 0.4 Mm^3 helium were produced annually in a helium plant near Paris between 1973 and 1978. Sears (2015) cites helium production in 1971 of 0.2 Mm^3 for this plant. Jones & Stacey (1974) even report two helium plants in France, which are said to have produced helium in 1974 in a plant with a total capacity of 420,000 m^3 helium/a. The helium is reported to have been extracted from natural gas from the Netherlands. According to Yakutseni (2014), a helium plant in France has been producing helium since 1960 – this source is again reported to be the natural gas imported from the Dutch Groningen natural gas field.

A plant operated by what was then *Gaz de France* for denitrifying natural gas from Groningen, which began operations in late 1968 in Alfortville, near Paris, can be confirmed. A connected helium plant with a capacity of 0.2 Mm^3 helium/a was in production later, probably in 1969. The Alfortville gas plant was shut down in the 1980s, as the supply of Russian gas increased. The volumes are unknown, as is the duration of helium production at this plant. The main helium customer was the French Ministry of Defence. The Groningen natural gas field went into production in 1963 and contains 0.037–0.055% He, averaging 0.045% He. Russian gas first reached France in 1975.

Since 1989, the French industrial gas company Air Liquide SA has been producing up to 18 m^3 of a helium-neon mixture every hour at its air separation unit in Le Blanc-Mesnil near Paris, where it is also processed. The global helium activities of Air Liquide SA are also controlled from Le Blanc-Mesnil and Jebel Ali, in UAE.

French helium imports stood at 13.97 Mm^3 in 2017, 37.6% from Algeria, 2.7% (2016: 26.2%) from Qatar, 4.3% from Poland, 7.1% from the USA and 48.3% indirectly from 14 other countries, including Germany (32.9%), in particular.

Krypton, xenon

In 1988, a production facility for up to 2 m^3 crude krypton/crude xenon per hour was commissioned in the air separation unit in Le Blanc-Mesnil, near Paris. A crude krypton/crude xenon mixture is also produced in the Air Liquide air separation unit in Moissy-Cramayel, south-east of Paris.

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Germany

Helium

German natural gas fields, coal mines and thermal springs have been repeatedly investigated and evaluated for their suitability for industrial helium production since the late 1930s. To date, however, helium has only been produced in the former GDR, beginning in the early 1970s.

Mayer-Gürr (1938) reported the helium content of numerous natural gas wells, mine air (coal shafts) and spring gases (from thermal springs) from across Germany. At generally extremely low, and therefore uneconomic, yields the highest helium levels then known were in natural gas wells at Mühlhausen (Thuringian Basin, up to 0.16% He) and in coal shafts in the former Ewald coal mine (Herten/North Rhine-Westphalia, in production 1877–2000, up to 0.23% He), as well as in thermal waters in the former Künzing sulphur baths (Passau, Bavaria, 0.26% He), Maxquelle in Bad Dürkheim (1.5–2% He), Baden-Baden mineral spring(s) (0.85% He), Wiesbaden mineral spring(s) (1.7–4.9% total noble gases), the former Heidelberg thermal spring (silted up since 1957, 0.65% He) and the Bad Wildbad thermal springs in the Black Forest (0.71% He).

In addition to 0.71% helium, the thermal springs of Bad Wildbad are also said to contain 1.56% argon. Here, at least the helium content of the Wildbad thermal waters was determined shortly after the element was discovered. The local thermal waters originate in a granite at a depth of 2500–3000 m and are 7500–12,000 years old. Up-to-date analyses on the inert gas yield of these sources are not available, as in almost all German baths, due to the high analysis costs.

In Bad Dürkheim, Rhineland-Palatinate, the old *Maxquelle*, drilled as early as 1859, had to be replaced at a different location by the *Neubohrung Maxquelle* in 1970–71. This 351 m deep well essentially yields deep, NaCl-bearing water, the origin of which can be found in the deep Tertiary salt deposits of the Upper Rhine Graben. However, no further noble gas analyses have been carried out during the last 30 years (personal communication with *Stadtwerke Bad Dürkheim GmbH*).

The numerous thermal waters exploited in Baden-Baden are assumed to be of more recent origin and represent precipitation penetrating the Bunter Sandstone (Lower Triassic) to great depths through joints, being heated there and rising again through faults. In addition, highly mineralised water is incorporated from pores and joints in the deeper subsurface. However, according to Rogers (1921), the gases in Baden-Baden's thermal water galleries only contain a maximum of 0.015% He. In recent years, no further major analyses of healing waters in Baden-Baden, which also analysed noble gases,have been carried out (personal communication with *Carasana Bäderbetriebe GmbH*).

Wiesbaden's thermal waters are also formed by precipitation penetrating fissure systems at great depth and being both heated around ancient magmatic chambers and enriched with gases there. According to Käss & Käss (2008), of Wiesbaden's five thermal springs with the highest noble gas data in use, the *Schützenhofquelle* leads with 0.9% Ar and 0.4% He, followed by the *Salmquelle* with 0.6% Ar and 0.2% He, the *Kochbrunnen* with 0.7% Ar and 0.09% He and the *Große Adlerquelle* with 0.4% Ar and 0.08% He (all 1996 data). The last major healing water analyses were performed in 2009 and 2016 and retruned 0.8% Ar and 0.35% He for the *Schützenhofquelle* (2009), 1.0% Ar and 0.09% He for *Kochbrunnen* (2016) and 0.3% Ar and 0.08% He (2009), and 0.4% Ar and 0.06% He (2016) for *Große Adlerquelle* (personal communication with *mattiaqua Wiesbaden*).

Data on helium levels in 126 hydrocarbon exploration wells in north-west Germany were listed in a publication by Benzel (1975). 71 analyses displayed values of 0.01–0.04% He, 46 analyses returned values of 0.05–0.09% He and 42 analyses of 0.10–0.58% He. Due to the low volume of available data it was not possible for the author to demonstrate regional and geological relationships between He distribution in north-west Germany or to assign He levels to even a few individual geological structures.

Some of the highest He levels (0.42–0.53% He) were found in wells in the Alfeld-Elze/Hildesheimer-Wald natural gas field south of Hannover, discovered in 1972. They were abandoned and dismantled in the 1990s but recommissioned in 2015. In 2016, they produced 29.8 Mm³ of natural gas.

At that time, Schmidt (1977) quantified the helium resources in the Salzwedel/Peckensen natural gas field (in production since 1969) in the western *Altmark* at 350 Mm³ with levels at 0.18–0.24% He. This resource is reduced by 16 Mm³ of helium annually as a result of the annual production of around 8 bn. m³ of natural gas.

Thuringia's natural gas reservoirs contained between 0.08 and 0.17% He with helium resources at the time of approximately 6 Mm³. Elevated concentrations of helium were identified in the *Fahner Höhe* and *Langensalza* natural gas fields, with 0.8% He and 0.6% He, respectively. The joint helium resources of these two, albeit not economically exploitable, fields were around 2 Mm³.

The Rüdersdorf natural gas reservoir east of Berlin, discovered in 1964 and abandoned in 1992, had 0.3% He (and 93% N_2, but only 6% CH_4) and originally a recoverable resource of 1.5–2.0 Mm³ helium. Based on this natural gas content, *VEB Technische Gase Leipzig* began operating a helium plant in the early 1970s, which produced around 50,000 m³ of helium annually. According to Schmidt (1977), it was intended to expand this to 100,000 m³ helium/a. This elevated production was intended to cover the GDR's domestic helium demand until post-1980. The date to which this helium plant continued to produce is unknown.

In addition to oxygen and nitrogen (primary products), argon has also been produced in an air separation unit in Leuna since 1959. Linde AG took over the site on 01/03/1991, where two air separation units with

Fig. 48: In addition to oxygen, nitrogen and argon, the air separation unit in Leuna also produces crude neon, crude krypton/crude xenon and helium, photo: Linde AG (with kind permission).

a daily separation capacity of around 7000 t air now also produce, in addition to argon, crude neon (since 2008–2009), crude xenon/crude krypton (since 2010–2011) and helium (since 2014).

Air Liquide Helium Services S.A., a subsidiary of the French Air Liquide S.A, has used a salt cavern in the Epe brine field between Gronau-Epe and Ahaus-Graes in western Münsterland for helium storage since July 2016. The cavern used, S72, was created by brine extraction in the years 2004–2011, is at a depth of 1181–1376 m and has a volume of 281,000 m^3. It can accept up to 47 Mm^3 helium, approximately corresponding to Air Liquide's annual European demand. The liquid helium is delivered in tankers, evaporated to a gas and then fed into the cavern under pressure, where it successively displaces the brine there. It is worth noting that the helium storage operating schedule approval procedure for Gronau-Epe was completed in only nine months (Lübbers et al. 2018).

Neon

Crude neon has been produced in the two Linde AG air separation units in Leuna since the turn of 2008–2009. One of the few global, and the only European, neon purification plants is also located at this site. It is said to be the largest pure neon purification plant in the world (Anonymous, personal communication). However, neither the crude neon volume, nor the pure neon production figures for the Leuna site, have been published. Assuming full utilisation of their inferred capacity, Spiritus & Betzendahl (2018) conclude an annual production of 36 million litres of crude neon or 120 million litres of pure neon. For 2017, production of approximately 40 million litres of crude neon with an approximate content of 20 million litres of neon is assumed (Anonymous, personal communication).

Argon

Based on Suresh et al. (2016), and kindly reviewed by the German market participants, 67 air separation units (ASU) are operated in Germany by 13 companies at a total of 49 sites, of which 46 ASUs are equipped with argon columns at the following 36 sites (cf. Fig. 49):

- Duisburg-Hüttenheim: two ASUs operated by Air Liquide Deutschland GmbH
- Dortmund-Hörde: two ASUs operated by Air Liquide Deutschland GmbH, argon capacity 40 t/d
- Frankfurt a.M.: ASU operated by Air Liquide Deutschland GmbH
- Gelsenkirchen: ASU operated by Air Liquide Deutschland GmbH, commissioned 2001
- Kornwestheim: ASU operated by Air Liquide Deutschland GmbH
- Oberhausen-Biefang: two ASUs operated by Air Liquide Deutschland GmbH, 2nd plant commissioned 2013, argon capacity 180 t/d
- Stade: ASU operated by Air Liquide Deutschland GmbH
- Hattingen: ASU operated by Air Products GmbH
- Wilhelmshaven: ASU operated by Air Products GmbH
- Bremen: two ASUs operated by Linde AG (ArcelorMittal steel production)
- Buna/Schkopau: two ASUs operated by Linde AG
- Duisburg-Ruhrort: five ASUs operated by Linde AG, three with argon columns, commissioned 2012 (ThyssenKrupp steel production)
- Eisenhüttenstadt: three ASUs operated by Linde AG, two with argon columns, commissioned 2017 (ArcelorMittal steel production)
- Gablingen: ASU operated by Linde AG
- Hamburg-Finkenwerder: ASU operated by Linde AG
- Herne: ASU operated by Linde AG
- Leuna: two ASUs operated by Linde AG, beginning of argon production 1959, since 1989 production of pure argon at 99.999% Ar
- Marl: ASU operated by Linde AG

- Salzgitter: two ASUs operated by Linde AG, one with argon column, also produces pure argon at 99.9999% Ar (Salzgitter Flachstahl GmbH steel refining)
- Stolberg: two ASUs operated by Linde AG, one with argon column
- Worms: ASU operated by Linde AG
- Salzgitter: ASU operated by Messer Industriegase GmbH (Salzgitter AG steel production)
- Siegen: ASU operated by Messer Industriegase GmbH, commissioned 2009, argon capacity 12 t/d (steel production by Deutsche Edelstahlwerke Specialty Steel GmbH & Co. KG)
- Biebesheim (Rhine): ASU operated by Praxair Deutschland GmbH
- Völklingen-Dillingen: three ASUs operated by Praxair Deutschland GmbH, two with argon columns
- Dormagen: ASU operated by Praxair Deutschland GmbH
- Hürth: two ASUs (one in standby) by Praxair Deutschland GmbH, argon capacity 70 t/d
- Hörstel: ASU operated by Westfalen AG, commissioned 1993
- Laichingen: ASU operated by Westfalen AG, commissioned 2001
- Trostberg: ASU operated by AlzChem AG (metal processing)
- Ludwigshafen: three ASUs operated by BASF SE, two with argon columns
- Frankfurt-Höchst: ASU operated by Infraserv GmbH & Co. Höchst KG (Chemiepark Höchst)
- Wetzlar: ASU operated by Buderus Edelstahl GmbH
- Friedrichshafen: ASU operated by Sauerstoffwerk Friedrichshafen GmbH, producing pure argon at 99.9999% Ar
- Dettelbach: ASU operated by Sauerstoffwerke Friedrich Guttroff GmbH, commissioned 2006
- Brunsbüttel: ASU operated by Yara Brunsbüttel GmbH (ammonium synthesis)

According to the Federal Statistical Office, ten companies in Germany produced 243.0 Mm^3 of argon in 2017, with a value of €98.3 million (40.4 cents/m^3), cf. Table 22. However, research among the producing German gas companies in the context of this study revealed 13 companies that together produced 233.1 Mm^3 of argon in 2017.

Table 22: Argon production in Germany, according to the Federal Statistical Office (Technical Series 4, No. 3.1).

Year	Production (mill. m^3)	Value (mill. €)	Value (€/m^3)
2009	186.7	75.6	0.41
2010	219.1	100.9	0.46
2011	224.1	91.6	0.41
2012	228.1	86.8	0.38
2013	222.8	90.7	0.41
2014	226.0	95.0	0.42
2015	224.7	91.8	0.41
2016	240.7	95.9	0.40
2017	243.0	98.3	0.40
2018	258.5	105.2	0.41

Fig. 49: Generalised map of air separation unit (ASU) sites with argon production in Germany. Several ASUs may be producing for different companies at any one site.

Krypton, xenon

As far as is known, both crude and pure krypton and xenon are produced at the following sites in Germany:

- Ludwigshafen: two of three air separation units (ASUs) by BASF SE, production of highly enriched crude krypton/crude xenon
- Gelsenkirchen: ASU operated by Air Liquide Deutschland GmbH, production of pre-enriched crude krypton/crude xenon
- Duisburg-Hüttenheim: two ASUs operated by Air Liquide Deutschland GmbH, production of pre-enriched crude krypton/crude xenon
- Oberhausen: two ASUs operated by Air Liquide Deutschland GmbH, production of pre-enriched and highly enriched crude krypton/crude xenon
- Krefeld-Gellep: Air Liquide Deutschland GmbH plant, purification of highly enriched crude krypton/crude xenon from the Oberhausen plant to pure krypton and pure xenon
- Duisburg-Ruhrort: five ASUs operated by Linde AG, in two ASUs production of pre-enriched crude krypton/crude xenon, highly enriched crude krypton/crude xenon in one ASU and partly purified crude krypton/crude xenon
- Leuna: two ASUs operated by Linde AG, production of highly enriched crude krypton/crude xenon
- Marl: ASU operated by Linde AG, production of pre-enriched crude krypton/crude xenon
- Bremen: one of two ASUs operated by Linde AG, production of pre-enriched crude krypton/crude xenon
- Eisenhüttenstadt: two ASUs operated by Linde AG, production of pre-enriched crude krypton/crude xenon
- Salzgitter: two ASUs operated by Linde AG, production of pre-enriched crude krypton/crude xenon
- Brunsbüttel: ASU operated by Yara Brunsbüttel GmbH, production of pre-enriched crude krypton/crude xenon
- Hürth: ASU operated by Praxair Deutschland GmbH, production of partially enriched crude krypton/crude xenon
- Dormagen: ASU operated by Praxair Deutschland GmbH, production of partially enriched crude krypton/crude xenon
- Unterschleißheim: Linde AG plant (see Fig. 51), purification of pre- and partially enriched crude krypton/crude xenon from the ASUs Salzgitter (Linde), Marl (Linde), Duisburg-Ruhrort (Linde), Bremen (Linde), Eisenhüttenstadt (Linde), Hürth (Praxair), Dormagen (Praxair) and Brunsbüttel (Yara), as well as highly enriched crude krypton/crude xenon from the ASUs Leuna (Linde) and Duisburg-Ruhrort (Linde) to pure krypton and pure xenon.

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Fig. 50: Generalised map of air separation unit (ASU) sites with crude krypton and crude xenon production in Germany. Several ASUs may be producing for different companies at any one site.

Fig. 51: View of part of the crude krypton and crude xenon purification plant at Linde AG's Unterschleißheim plant, photo: BGR.

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India

Helium

India has no natural gas reservoirs with relevant helium content. The option of extracting helium from monazite sands (1 m^3 He per t monazite) and the gas content of thermal waters have therefpre primarily been investigated in detail to date (Das et al., 2005, Chaudhuri et al. 2015).

Around 300 thermal springs are known in India, which occur within three belts:

1) East India: Bihar, Assam and Orissa
2) West coast of India: Ratnagiri, Thane, Colaba and Surat
3) Himalayan mountain range: Jamunotri (Uttaranchal), Gangotri and Monikaran (Kullu Valley, Himachal Pradesh)

Two known groups of thermal springs near Bakreswar (West Bengal) and Tantloi (Jharkand) contain gases with elevated levels of noble gases but are simultaneously low yield. These two groups are 25 km apart and around 250 km from Kolkata. The gases in the thermal water springs at Bakreswar average 92.20% N_2, 1.40% He (1.88% He max.), 2.07% Ar, 0.90% O_2 and 3.43% CH_4. The gases in the thermal water springs at Tantloi are of very similar composition: 92.00% N_2, 1.26% He (2.77% He max. in wells), 2.40% Ar, 1.14% O_2 and 3.20% CH_4.

Other thermal waters in India contain < 1.0% He. Pilot plants aimed at utilising the gas supply do exist, but they were developed at university level and are not economically viable. The same applies to a pilot plant at the Kuthalam site near Mayiladuturai in Tamil Nadu, where natural gas containing 88.5% CH_4, 9.86% heavy hydrocarbons, 1.18% N_2, 0.4% CO_2 and 0.06% He has been collected and processed since early 2008. The throughput capacity of this small plant is 50 m^3 gas/h and helium production at 99.0% He is 18 l/h, corresponding to a maximum of approximately 100,000 m^3 helium/a. Output is approximately 61%.

To date, India therefore relies almost entirely on helium imports. These amounted to 580 t in 2017 (corresponding to approximately 3.47 Mm^3) and 88% came either directly or indirectly from Qatar.

Argon

In India, numerous ammonium plants are equipped with argon treatment facilities, where between 20 and 40 t Ar can be produced daily. In addition, Suresh et al. (2016) identified at least 21 air separation units equipped with argon columns.

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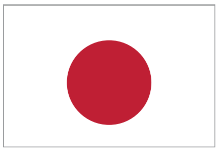
Japan



Helium

Japan does not produce helium and relies entirely on imports of this noble gas. These amounted to 1719 t in 2017 (corresponding to approximately 10.3 Mm^3) with 75.3% originating from the USA and 24.7% from Qatar. To reduce its enormous dependence on these two countries, Japan plans to develop a strategic supply relationship with Russia and to procure helium over the long term from eastern Siberian natural gas reservoirs.

Argon

Japan is an important producer and consumer of argon. According to Suresh et al. (2016), air separation units equipped with argon columns were in operation at 59 sites with a total capacity of approximately 40,700 m^3 Ar/h, corresponding to 356 Mm^3 Ar/a, as of February 2016. In 2016, 268 Mm^3 of argon were produced in Japan, with an increasing trend, with 96% in liquid form.

Krypton, xenon

The Japanese company Air Water Inc. announced that, in addition to their crude xenon production in the air separation unit in Kashima, they also intend to produce xenon and krypton, probably in a purified form, at their air separation unit in Kakogawa beginning in April 2019. The production capacity in the Kakogawa plant is expected to be 1,103,600 litres Xe annually, but only 88,909 litres Kr.

Kazakhstan

Helium

As of December 31, 2016, Kazakhstan had 1907 bn. m^3 of natural gas reserves or 4179 bn. m^3 of natural gas resources. This ranks the central Asian country 18th in global reserves and 6th in global resources. Its annual production in 2016 amounted to around 22 bn. m^3 of natural gas. This corresponds to 0.6% of global natural gas production or 32nd worldwide. Since intensive natural gas production began in the late 1960s, Kazakhstan has produced around 578 bn. m^3 of natural gas.

Kazakh natural gas contains vastly different levels of helium (Table 23).

Table 23: Helium content in natural gas fields in Kazakhstan, from Worldbank (1997).

Region	Natural gas field	Reserves / Resources of natural gas Categories: A+B+C (mill. m^3)	Helium grade %
Aktjubinsk	Kzilojskoe	1488	0.03 – 0.15
Atyrau	Imashevskoe	78,679	0.1
Zhambyl	Ayrakty	2079	0.2 – 0.3
	Amangeldy	8143	0.2
	Kumyrly	1533	0.7
	Pridorojnoe	7396	0.2
Jezkazgan	Kumkol	8710	0.1 – 0.2
	Ortalik	665	0.2 – 0.3
West Kazakhstan	Karachaganak	1,322,390	0.0
Mangistau	Central-/East-Prorva	25,410	0.01 – 0.02
	Kansu	4313	0.1

The Karachaganak natural gas/condensate field is located in north-western Kazakhstan and is one of the world‘s largest natural gas condensate fields. It covers an area of 280 km^2, was discovered in 1979 and went into production in 1984. The estimated resources (as 2017) are around 1704 bn. m^3 natural gas and 13.3 bn. barrels of natural gas condensate and crude oil. It is currently being run by the international consortium Karachaganak Petroleum Operatung B.V. with Royal Dutch Shell plc and ENI S.p.A. as operators.

Treatment of the Karachaganak natural gases, the helium levels of which are unpublished but presumably very low, takes place in PAO Gazprom‘s Russian gas plant in Orenburg. It is connected with Karachaganak through five, 140 km long pipelines and also comprises a helium plant (see Russia). In 2016, 8.934 bn. m^3 of natural gas were supplied to Orenburg from Karachaganak.

At the end of 2012, the Kazakh JCS KazTransGas group issued a global call for tenders for a feasibility study for an integrated gas production and treatment plant in Kazakhstan (Tuleshow 2012). The group has large reserves of nitrogen/methane/helium-rich natural gases in the Amangeldy, Anabay and Ayrakty fields in the Zhambyl region of southern Kazakhstan (0.22–0.26% He, C1 resources: 10.9 Mm^3 helium) and Kumyrly (0.694% He, C1 resources: 10.6 Mm^3 helium) and nitrogen/helium-rich natural gases in the North Ucharal (0.46% He, C1 resources: 1.9 Mm^3 helium) and Ucharal-Kempirtobe fields (0.68% He, C1 resources: 14.2 Mm^3 helium). As far as they have been explored, the natural gas fields there contain total C1 resources of at least 37.7 Mm^3 helium. Nitrogen, helium and methane from these natural gas fields will be refined domestically in the future and the pure gases primarily exported to China.

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Poland

Helium

As of December 31, 2016, Poland had 91 bn. m^3 of natural gas reserves or 1224 bn. m^3 of natural gas resources. This ranks our neighbouring country 53rd in global reserves and 50th in global resources. Its annual production in 2017 amounted to 5.0 bn. m^3 of natural gas. This corresponds to less than 0.2% of global natural gas production or 51st worldwide. Small quantities of natural gas were produced in Poland as early as the 1920s. The cumulative volume was around 274 bn. m^3 by the end of 2017.

The search for natural gas reservoirs began in the 1960s in the Polish lowlands and was soon successful. 152 natural gas reservoirs are currently known in this region, of which 79 were producing in 2017. 16 reservoirs in the Zielona Góra-Rawicz-Odolanów region comprise natural gas with a high nitrogen content (> 40%) and enhanced helium levels (0.22–0.42%). Of these, nine were producing in 2017; the most important is the Bogdaj–Uciechów field with reserves of 3.37 bn. m^3 of natural gas and 11.68 Mm^3 of helium. The total helium reserves (categories: A+B) in Poland as of 31/12/2017 were 24.01 Mm^3.

To reduce the high nitrogen content in many newly discovered natural gas fields in the Polish lowlands, a denitrification plant with an integrated helium plant was built at the central Odolanów site, which went into production in 1977 and is also capable of liquefying natural gas. Today, the Odolanów plant, of which the state-owned Polish Oil & Gas Company (*Polskie Górnictwo Naftowe i Gazownictwo SA* – PGNiG SA) owns the majority, continues to produce both liquid nitrogen, and gaseous and liquid helium. The capacities are 4.2 Mm^3 of gaseous helium/a and 420 t of liquid helium/a, respectively, which have not, however, been achieved for some years due to decreasing natural gas production or lower utilisation (Table 24). Here, too, the helium content of the helium-rich natural gases processed here has fallen from the original 0.42% to below 0.18% today.

In 2017, 3.172 Mm^3 of helium were produced in Odolanów, of which, however, only 0.75 Mm^3 originated from natural gas fields with enhanced helium levels (see above) (PGI 2018).

Until 2017 and 2018, only partial helium production figures from natural gas fields with enhanced helium levels have been published by the Polish Geological Institute. However, PGNiG SA kindly made their complete helium production data available for the purpose of this study (Table 24).

***Table 24:** Helium production in Poland since 1989 (in Mm^3) from natural gas fields with enhanced helium levels, according to the POLISH GEOLOGICAL INSTITUTE (PGI 2018), as well as total helium production since 2000 (in Mm^3), according to PGNiG SA (kind written communication).*

	1989	**1990**	**1991**	**1992**	**1993**	**1994**	**1995**	**1996**	**1997**	**1998**
PGI	4	3	2.5	2	3	3	2	1.3	1.3	1.3
PGNiG	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.
	1999	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**
PGI	1.3	1.22	1.37	1.43	1.26	1.29	1.22	1.15	1.12	1.03
PGNiG	n. a.	2.27	2.22	2.30	2.51	2.71	2.67	2.47	2.36	2.24
	2009	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**	**2017**	**2018**
PGI	1.05	1.01	0.91	0.91	0.84	0.81	0.80	0.78	0.75	0.75
PGNiG	2.69	3.14	3.40	3.31	2.99	2.81	2.83	2.86	3.17	3.08

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Qatar

Helium

As of December 31, 2016, Qatar had 24,073 bn. m^3 of natural gas reserves or 2000 bn. m^3 of natural gas resources. This ranks the country 3rd in global reserves; on a global scale, resources are only minor. Its annual production in 2016 amounted to around 165 bn. m^3 of natural gas. This corresponds to 4.6% of global natural gas production or 4th worldwide. Small quantities of natural gas were produced in Qatar as early as the 1960s, with a total of around 1772 bn. m^3 to date.

Globally, Qatar is the second largest natural gas exporter and the largest producer and exporter of liquefied natural gas (LNG). The production of liquefied natural gas in Qatar began in 1981 with the commissioning of two LNG plants at the Ras Laffan industrial site. Qatargas was founded in 1984 with the remit to market the liquefied natural gas from its now four producing operations

- Qatargas 1 (shareholders: Qatar Petroleum – 65%, ExxonMobil Corp. – 10%, Total S.A. – 10%, Mitsui & Co. Ltd. – 7.5% and Marubeni Corp. – 7.5%), commissioned 1984, 3 LNG plants
- Qatargas 2 (shareholders: Qatar Petroleum – 70% and ExxonMobil Corp. – 30%, and Qatar Petroleum – 65%, ExxonMobil Corp. – 18.3% and Total S.A. – 16.7%), commissioned 2009, 2 LNG plants
- Qatargas 3 (shareholders: Qatar Petroleum – 68.5%, ConocoPhillips Co. – 30%, Mitsui & Co. Ltd. – 1.5%), commissioned 2010, 1 LNG plant
- Qatargas 4 (shareholders: Qatar Petroleum – 70%, Royal Dutch Shell plc – 30%), commissioned 2011, 1 LNG plant

The liquefied natural gas produced by Qatargas comes from the approximately 9700 km^2 South Pars/North Dome natural gas field, located in the Persian Gulf and discovered in 1971, whereby the South Pars section (approximately 3700 km^2) belongs to Iran. South Pars/North Dome is by far the largest natural gas field on the planet, with the greatest reserves. The latter comprises around 34,200 bn. m^3 of natural gas and 16 billion barrels of natural gas condensate.

The helium content of the natural gas is very low and averages 0.05%. However, the recoverable helium reserves in North Dome are estimated to be approximately 10 bn. m^3 due to its sheer size. Qatargas and RasGas assume that this volume corresponds to around 26% of known global helium reserves.

The second largest producer of liquefied natural gas in Qatar was RasGas Company Ltd., founded in 2011 and merged with Qatargas on 01/01/2018. Its producing operations were:

- Ras Laffan I, commissioned 1999, 2 LNG plants
- Ras Laffan II, commissioned 2004/2005/2007, 3 LNG plants
- Ras Laffan III, commissioned 2009/2010, 2 LNG plants

Qatargas operates two helium plants in the Ras Laffan industrial complex:

- Helium 1, commissioned August 2005, capacity: 19.4 Mm^3 helium/a, distributed by BOC Group Inc. (Linde AG) and Air Liquide America LP
- Helium 2, commissioned June 2013, capacity: 36.1 Mm^3 helium/a or 17.3 t helium/d, distributed until 2032 by Air Liquide America LP – 50%, Linde AG – 30% and Iwatani Corp. – 20%

The liquefied helium produced in Helium 1 and particularly in the large liquefaction plant in Helium 2 is 99.999% pure.

Erection of a third helium plant, Helium 3, was announced as early as the inauguration ceremony for Helium 2 in December 2013. It will have a capacity of 11.1 or 11.8 Mm^3 helium/a and, following delays, go into production in 2019 at the latest. Air Liquide America LP was selected as the distribution partner in late 2015.

For a while, there was even speculation about the construction of a fourth helium facility.

On 5 June 2017, Saudi Arabia, Egypt, Yemen, Bahrain, the Maldives and the United Arab Emirates (UAE), whose port of Jebel Ali exports much of the helium from Qatar, announced a trade embargo against Qatar. A week later, due to the extremely limited storage capacity, Qatar shut down its two helium facilities. The two plants were restarted on 2 July 2017 and some of the helium has since then been redirected through various ports, e.g. the port of Hamad near Doha, the capital of Qatar.

Production volumes of helium in Qatar have been published in part, whereby the production data from Qatargas (in million ft^3) and RasGas (in Mt) are contradictory (Table 25). It is possible to more reliably derive the volumes of helium produced since commissioning of the first helium plant in 2005 using the global import data of helium from Qatar according to the Global Trade Atlas. In this case, however, Qatar's neighbouring countries of (UAE, Oman, Saudi Arabia) should also be included as potential exporting countries (Table 26).

Table 25: Helium production in Qatar in Mm^3 (converted from ft^3) according to Qatargas annual reports or in t (converted to Mm^3, 1 t He corresponds to approximately 5988 m^3 He at 15 °C and 1 bar) according to RasGas sustainability reports.

	2005	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**
Million m^3	n. a.	n. a.	n. a.	n. a.	n. a.	6.1	5.9
t	n. a.	n. a.	n. a.	n. a.	1900	1800	1800
= Million m^3	n. a.	n. a.	n. a.	n. a.	11.4	10.8	10.8
	2012	**2013**	**2014**	**2015**	**2016**	**2017**	**2018**
Million m^3	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.
t	1900	2870	3300	3700	n. a.	n. a.	n. a.
= about mill. m^3	11.4	16.6	19.8	22.2	n. a.	n. a.	n. a.

Fig. 52: Just under a quarter of the world's helium was produced In Qatargas' huge LNG facilities in Ras Laffan, Qatar in 2017, photo: www.qatargas.com.

Table 26: Total global helium imports from Qatar, Saudi Arabia and the United Arab Emirates (UAE) according to Global Trade Atlas (in Mm^3 and t, 1 t He corresponds to approximately 5988 m^3 He at 15 °C and 1 bar), in comparison to USGS estimates of helium production in Qatar.

Year	Qatar		Saudi-Arabia		UAE		Total	USGS
	mill. m^3	t	mil. m^3	t	mill. m^3	t	mill. m^3	mill. m^3
2005	0.08	35	0.29	4	0.02	119	1.34	0.2
2006	0.65	496	0.15	6	0.04	534	7.04	4.4
2007	1.70	837	0.12	5	1.25	470	10.93	7.1
2008	0.89	1503	0.06	1	0.14	339	12.13	12.7
2009	2.72	1248			0.03	319	12.13	20
2010	3.55	1441			0.13	494	15.27	20
2011	2.14	1218	0.79	14	0.14	649	14.33	20
2012	3.04	808	0.99	15	0.17	301	10.93	20
2013	3.86	933		104	0.24	535	13.51	38
2014	13.15	3247		60	0.84	652	37.70	46
2015	14.22	3089	0.07	30	2.97	606	39.57	49
2016	17.37	2922	0.01	43	5.69	645	44.69	50
2017 1)	11.69	3435	0.22	31	3.65	316	38.23	45
2018 1)	14.04	2054		10	0.16	201	27.87	45

1) *In 2017, 27,066 m^3, and in 2018 106,379 m^3 of helium from Qatar were imported by Germany via Oman (note: this does not mean that only 27,066 m^3 of helium (equivalent to exactly one ISO container) reached Germany in 2017 via the transit country Oman, but that all other imports from Oman, which were considerably larger according to Linde AG (personal communication), were assigned by Customs to the country of origin UAE.)*

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Russian Federation

Helium

As of December 31, 2016, the Russian Federation (short: Russia) had 47,777 bn. m^3 of natural gas reserves or 152,050 bn. m^3 of natural gas resources. This ranks this country 1st in both global reserves and global resources. Its annual production in 2016 amounted to around 641 bn. m^3 of natural gas. This corresponds to 17.7% of global natural gas production or 2nd worldwide. It was not until after WW II that large volumes of natural gas were produced in Russia, cumulating to around 23 trillion m^3 of natural gas at the end of 2016.

According to Stepanyuk (1995), geological exploration of potential helium reservoirs began in Russia as early as the 1920s. More than 200 natural gas fields were evaluated up to the 1990s, but significant reserves could only be identified in the regions of Orenburg and Astrakhan in southern Russia and in southern Siberia (Irkutsk and Krasnoyarsk regions), as well as natural gas reserves with elevated helium levels (0.20–0.56% He) in the Republic of Sakha in eastern Siberia. In 1949, commercial helium production began in the town of Uchta, Republic of Komi, in north-western Russia, based around the local Voyvozh natural gas reservoir (@ 0.06–0.15% He). Previously, in 1933–1935, a pilot helium treatment plant had been built in the village of Melnikowo (Tomsk Oblast) (Andreev 1995). In the 1950s and 1960s, the gas plants in Moscow, and later Minnibaevo (Republic of Tatarstan) and Otradny (Samara Oblast), were supplemented by small helium plants. Up to 1.7 Mm^3 of helium were recovered annually from these four helium plants (according to Andreev 2005, up to 1.4 Mm^3 of helium). All of these plants were closed in 1978 following the start of production in Orenburg, see below.

In 1966, in the south of Russia, not far from the then Kazakh Soviet Socialist Republic, the first section of the large Orenburgskoye oil and gas condensate field was discovered in Osnovnaya . A gas plant, which went into production in 1974, was built west of the city of Orenburg to utilise the rich hydrogen sulphide (1.8%) and nitrogen (5.4%) in the natural gas (@ 0.055% helium) from this field. In January 1978, a connected helium plant was commissioned in the village of Kholodnye Klyuchi. A year later, the large Karachaganak natural gas condensate field was discovered in present-day Kazakhstan (see there) and also connected to the Orenburg gas plant in 1984 after production commenced.

The Orenburgskoye oil and gas condensate field has supplied more than 1200 bn. m^3 of natural gas since it was developed and the Orenburg gas plant over 35 Mt of sulphur and 172 Mm^3 of helium, among other things. As at December 31, 2016, the field's remaining category A+B+C1 reserves and resources amounted to 648.9 bn. m^3 of natural gas, 202.5 Mt of crude oil and 55.7 Mt of natural gas condensate. Orenburgskoye's peak natural gas production was during the 1980s when, close to maximum capacity, around 45 bn. m^3 (maximum 48.7 bn. m^3) of natural gas and 3.2 Mt of natural gas condensate/crude oil were extracted or processed annually. The helium produced was largely utilised by the Soviet mechanical engineering industry and only subordinately by the defence industry (Andreev 1995). In 1990, peak of helium production was reached at 9.2 Mm^3. Production at Orenburgskoye has been slowing since 1986 but has fallen significantly since 2000. In 2016, natural gas production there was 15.65 bn. m^3.

Today, the Orenburg gas plant, as Gazprom dobycha Orenburg, LLC, belongs to the Russian PAO Gazprom group. Current processing capacity is 37.5 bn. m^3 of natural gas. The helium facility in Orenburg consists of seven individual plants (five of which are producing) with a maximum throughput of 18 bn. m^3 of natural gas (currently limited to 15 bn. m^3 of natural gas) and an annual helium capacity of 8.8 Mm^3. Helium is produced with purities of 99.99% He and 99.995% He. The impurities are traces of N_2, H_2, CH_4, O_2, Ne and Ar, which could not, or cannot, be removed using Russian technology. A helium liquefaction plant with a capacity of 500 l/h (other sources: 700 l/h) has been operating in Orenburg since 1993. In July 2004, this ageing plant was replaced by a new helium liquefaction plant, which was installed by Linde Kryotechnik AG. The plant will produce liquid helium with a purity of 99.9999% at a capacity of 4000 l/a (around 500 t/a or 3 Mm^3/a, other sources: 4.2 Mm^3/a). According to their data, Gazprom sold 3.32 Mm^3 gaseous helium and 289.56 t of liquid helium in 2017.

The helium production figures for Orenburg since the year 2000 have also been published in detail by the PAO Gazprom operating group (Table 27).

According to Russian state sources (MINISTRY 2014), Russia's helium production capacity is nowhere near exhausted. For example, around 3.6 Mm^3 of helium may have been produced in Orenburg in 2013, but this could have been 4.1 Mm^3 more in the same year. In addition, 10.2 Mm^3 of helium escaped from 160 other helium-bearing Russian natural gas fields unused into the atmosphere in the same year.

Table 27: Helium production in Orenburg, Russia since 2000 (in Mm^3), after PAO Gazprom.

2000	2001	2002	2003	2004	2005	2006	2007	2008
5.27	5.34	6.29	6.47	3.45	1.64	3.84	4.87	5.04
2009	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**	**2017**
4.89	4.86	3.53	4.92	3.57	4.00	4.97	5.05	5.10

Great potential is seen in the natural gas fields in southern and eastern Siberia discussed above. According to YAKUTSENI (2014), the helium resources of the natural gas deposits previously explored in eastern Siberia alone amount to around 16 bn. m^3.

The resources of the Sobinskoye-Paiginskoye natural gas condensate field in the Krasnoyarsk Territory, which has still been insufficiently explored, are estimated at 130 bn. m^3 of natural gas with 26.29% N_2 and 0.60% He, corresponding to a helium content of 780 Mm^3.

The Yurubchenko-Tokhomskoye natural gas field, discovered in 1972 and producing since 2012, is also located in the Krasnoyarsk region. It contains proven reserves of 330 bn. m^3 of natural gas with 6.39% N_2 and 0.18% He, i.e. reserves of 594 Mm^3 of helium.

The Kovyktinskoye (Kovykta) natural gas condensate field, near Lake Baikal, 350 km north-east of Irkutsk, was discovered in 1987. It contains reserves or resources (categories A-C1) of 86 Mt of recoverable natural gas condensate and 1563 bn. m^3 of natural gas at 0.24–0.28% He, i.e. a helium content of approximately 4.4 bn. m^3.

The following oil and gas condensate fields, among others, are located in the Republic of Sakha:

- Srednebotuobinskoye, in production since 2014, with reserves or resources (categories A – C2) of 162 Mt crude oil/natural gas condensate and 182 bn. m^3 of natural gas at 2.93% N_2 and 0.2–0.6% He, i.e. approximately 0.4–1.1 bn. m^3 of helium.

and

- Chayandinskoye or Chayanda, in production (natural gas) since 2015, with reserves or resources (categories A-C1) of 1000 bn. m^3 of natural gas at 6.44% N_2 and 0.50–0.54% He, i.e. around 5 bn. m^3 helium, of which 1.4 bn. m^3 should be recoverable.

In August 2015, PAO Gazprom group began construction of a large gas plant, the Amur Gas Processing Plant (GPP), near the town of Svobodny, in the Amur region, for the treatment of natural gas from the Siberian Kovykta and Chayanda natural gas reservoirs, and including its licence share from Srednebotuobinskoye. It covers an area of more than 850 ha at an estimated overall cost of €Bn11.5. It is aimed to go into partial production in 2021 (19.4 Mm^3 helium/a), 2022 (adding 19.4 Mm^3 helium/a) and be complete by 2024. The natural gas reservoirs are connected by the *Power of Siberia* pipeline network. The prime contractor for separating valuable industrial gases from the natural gas is Linde AG. Following completion of commissioning, Amur GPP should have a processing capacity of 42 bn. m^3 natural gas/a and have a helium plant with a capacity of 60 Mm^3/a maximum. The liquefied helium will be transported (via a road yet to be built) to the port of Vladivostok and be exported from there. Due to its regional proximity and economic growth, the most important customer for the majority of the gases produced will be China. In addition, planning is underway for an underground helium storage field, similar to the US Cliffside storage field, in the region of the salt structures in the Chayandinskoye and Tas-Yuryakhskoye natural gas fields, whereby the necessary geological exploration has already been completed.

The Irkutsk Oil Company also announced that it intends to commission a helium plant in 2021, based around its Siberian Yaraktinsky oil field, located about 200 km north of Ust-Kut. This should have an annual capacity of 10 million litres of liquid helium, corresponding to about 7 Mm^3 of gaseous helium.

According to Suresh et al. (2016), helium is also produced in the air separation units in Yekaterinburg, in Novokuibyshevsk and probably in Cherepovets.

Russia uses an estimated 3.5 Mm^3/a of helium, of which slightly more 1 million litres/a is liquid helium.

Neon, argon, krypton, xenon

According to Suresh et al. (2016), there are 31 known air separation unit sites at which argon is also produced in Russia.

Crude krypton, crude xenon and presumably crude neon are produced in the air separation unit in Cherepovets.

The Lipezk steel smelter air separation unit produces around 810 m^3 of a crude krypton/crude xenon mixture monthly.

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South Africa

Helium

The Republic of South Africa is the largest consumer of natural gas in Africa, relying largely on imports, primarily from neighbouring Mozambique. Exploration of the few natural gas deposits has been driven for many years in the country, where mainly offshore exploration was successful. The largest natural gas field discovered to date is Ithubesi, 105 km offshore of North Cape Province, with proven reserves of 15 bn. m^3 of natural gas. Potential shale gas reserves are estimated at 7.510 bn. m^3 (world rank 9).

To date, only one natural gas field has been developed onshore, the 1870 km^2 Virginia natural gas field, or Free State gas field, near Virginia, in the vicinity of the town of Welkom, midway between Johannesburg and Bloemfontein. Virginia contains proven reserves of around 690 Mm^3 of natural gas with 3–4% He, corresponding to a helium content of 21–28 Mm^3. In May 2016, Linde AG was commissioned by a regional subsidiary to erect a helium plant and sell the helium from this reservoir. The plant will begin production in the first half of 2019 and have a capacity of 650,000 m^3 helium/a.

However, South African demand for helium is considerably higher, differs greatly from year to year and in 2015, for example, was 7.0 Mm^3 and 9.0 Mm^3 in 2016, but only 3.0 Mm^3 in 2017.

Argon, krypton, xenon

In Secunda, around 130 km east of Johannesburg, the petrochemicals company Sasol operates the world's largest commercial coal gasification plant. The plant is supplied by five coal mines in Mpumalanga. The coal is gasified with the aid of large volumes of oxygen and numerous primary materials for the petrochemicals industry are produced from the gas via a large number of intermediate stages. 15 air separation units with an overall capacity of 41,900 t O_2/d (including currently the largest single air separation unit in the world with a capacity of 5000 t O_2/d) or around 13 Mt O_2/a generate the necessary oxygen. The total argon capacity is 150 t/d. Crude krypton/crude xenon are separated in 14 of the air separation units. In 1999, the existing krypton/xenon enrichment plant was also expanded by Air Liquide SA on behalf of Sasol and now has an annual capacity of 9.5 million litres (= 9500 m^3) of krypton and 2.5 million litres (= 2500 m^3) of xenon in the form of a crude krypton/crude xenon gas mixture (*thick soup* with a Kr:Xe ratio of 4:1, cf. Section 3.1.4). According to Spiritus & Betzendahl (2018), however, the actual production of this largest source of Kr/Xe worldwide is around 7 million litres annually, which are exported for processing in their entirety to France by Air Liquide.

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Tanzania

Helium

In correspondence dated 03/11/2004, the Federal Ministry for Economic Cooperation and Development (BMZ) approved the BGR proposal dated 20/10/2004 for the implementation of a sub-measure within the framework of the Studies and Expert Fund for Geo-Sector Projects (Geo-SFF) with the working title “Sustainable use of non-metallic resources in East Africa”. It was decided as part of this sub-measure to survey the countries of Malawi, Tanzania and Ethiopia.

On 25/01/2006, BMZ approved an increase in funds and extension of the project until 31/12/2007. Within this extended period, the Tanzanian government was to receive an investor’s manual entitled “Industrial Minerals of Tanzania. A Progress Report”.

The investor’s handbook with the final title “Industrial Minerals in Tanzania. An Investor’s Guide” (Elsner et al., 2008) was completed in January 2008 and 1850 printed copies made available to the Tanzanian government in April 2008.

In November 2013, the two geologists Thomas Abraham-James and Josh Bluett were travelling through Tanzania en route to a gold deposit. On the back seat they found a copy of the investor’s handbook discussed above and their attention was drawn to the chapter on “Helium and other natural gases” (pp. 92–94). The following, helium-bearing, thermal waters were named in this chapter, based on older literature sources:

Mbeya District:
- Nyamosi with natural gas at 17.9–18.2% He

Mara District:
- Maji Moto Musoma with a yield in the well of 200 l natural gas/h at 13.2–13.5% He

Singida District:
- Gonga, 64 km north-east of Saranda with natural gas at 8.9% He
- Mponde, 48 km north of Saranda with natural gas at 4.4–10.2% He
- Hika, 11 km north of Saranda with natural gas at 6.7% He
- Takwa with natural gas at 7.0% He

Dodoma District:
- Manyeghi, 137 km north-west of Dodoma, with natural gas from 320 m deep diamond cored wells at 4.4–6.7% He, 1.2–1.6% Ar, 89.3–93.0% N2 and 0.6–1.8% CO_2

In addition, highly saline waters near Uvinza, Kigoma District, natural gas bore 2.5% He, 1.2% Ar, 1.7% CO_2 and 94.6% N_2.

On this basis, the geologists then founded *Helium One Ltd*. on the British Virgin Islands with the aid of investors and acquired numerous *Exclusive Prospecting Licenses* across a total area of 4500 km^2 in the sub-areas Rukwa (at approx. 90% N_2 and 8–10.2% He), Eyasi (6.0% He max.) and Balangida (10.6% He max.) in a variety of Tanzanian sections of the East African Rift Valley. However, the company concentrated on the region around Rukwa in Mbeya District in the south-east of Tanzania, because older seismic data and the results from crude oil wells were available for that area. In May 2016 they estimated the recoverable helium resources in this area at a total of 700 Mm^3 (low estimate), 2.7 bn. m^3 (best estimate) and 8.9 bn. m^3 (high estimate) in more than 28 individual fields. Given improved data, a probable resource of 1.5 bn. m^3 helium was published in October 2017 (Owen-Jones 2017). In addition, *Helium-One Ltd*. gives 2.7 bn. m^3 helium as the prospective recoverable helium resource (*unrisked prospective recoverable helium volume* (P50)).

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Ukraine

Argon

According to Suresh et al. (2016), 10 air separation unit sites at which argon is also produced are known in Ukraine. However, this figure is probably higher, because of the very high argon demand of the Ukrainian steel industry.

Helium, neon, krypton, xenon

One of the world's largest suppliers of heavy noble gases was the company Iceblick Ltd., founded in 1990 and disbanded in 2016, with its headquarters in Odessa and access to a production facility and purification plant in both Moscow and Odessa (Rare Gases International Group). In addition, Iceblick represented several special gas companies in Russia (OOO Zenon Gas and Chromium Ltd.), Ukraine (Airgas Ltd.), Kazakhstan and the USA. Highly purified (5.0, 6.0) xenon, krypton and neon were sold, but also gaseous and liquid helium, gas mixtures and isotopic fractions of neon (^{22}Ne, ^{21}Ne, ^{20}Ne). Ten years ago, in 2007, Iceblick Ltd. still enjoyed global market shares of 70% for neon and 25% for krypton and xenon. By 2010 these market shares had fallen to 65% and 17%, and 65% and 15% in 2012, and by 2015 to a still very high 50% for neon.

From the end of 2014 on, an internal dispute about the direction of Iceblick arose (Spiritus & Betzendahl 2018). A new owner attempted to force extreme prices on the market. The former president, Dr. Vitaly Bondarenko, who has possession of all supplier and customer contacts, then left his former company and founded a new company, Cryoin Engineering Ltd., also in Odessa. Iceblick Ltd. is now no longer active, while Cryoin Engineering Ltd. is today one of the largest global suppliers of neon, krypton and xenon. Other Ukrainian noble gas producers supplying the global market are Ingas AE (Mariupol) and UMG RT Gas (Kiev).

Ingas AE obtains its noble gases from the PJSC Magnitogorsk Iron and Steel Works smelting combine and the Krywyj Rih metallurgical combine (owner: ArcelorMittal Kryviy Rih PJSC), whereby in addition to up to 1000 t O_2, 7400 t N_2 and 80 t Ar daily, all other noble gases are also produced.

UMG RT Gas is supplied by the metallurgical combines in Zaporizhia (PJSC "Zaporizhstal") and Mariupol (PJSC Azovstal Iron & Steel Works and PJSC Ilyich Iron & Steel Works). The air separation units associated with the Ilyich metallurgical complex in Mariupol were built and opened by the French Air Liquide SA in 2007. In addition to 60,000 m^3 O_2/h, they produce N_2, Ar, and Kr-Xeand Ne-He gas mixtures. Air separation plants are also associated with the Azovstal metal combine in Mariupol, which also produce an Ne-He gas mixture and an Kr-Xe crude gas mixture, in addition to gaseous and liquid O_2, N_2 and Ar.

The chemicals combine PJSC *Severodonetsk Azot Association* operates air separation units in Severodonetsk in which, the company claims, a *Xe-*N_2 *mixture* is produced, in addition to O_2, N_2 and Ar.

Crude krypton/crude xenon purification plants are operated by Ingas AE in Mariupol, as well as crude neon (and presumably helium), and crude krypton/crude xenon plants in Odessa, operated by Cryoin Engineering Ltd.

United States of America

Helium

Helium has been commercially produced in the USA for a century; the USA has dominated the world helium market during this period. The USA was the only helium producer worldwide for many decades. It has only been during the last decade that US influence has begun to decline and is likely to continue to decline significantly in the coming years.

The first US natural gas well with elevated helium content was drilled in the spring of 1903 by a small company in Dexter, Kansas. A natural gas deposit, which yielded 250,000 m^3 natural gas/d, was encountered at a depth of only around 120 m. However, the gas did not burn, in contrast to other natural gases. Later analyses by the University of Kansas identified a composition of 71.89% N_2, 15.02% CH_4, 0.80% H_2, 0.20% O_2 and 12.09% *inert gases*, among them 1.84% He.

Another 44 natural gas deposits in Kansas and Missouri were analysed for their helium content by 1906. In all of them, helium was identified at elevated levels, with geological structures becoming apparent in the subsurface and a connection between high nitrogen levels and increased helium content becoming clear. Because there was no use for helium at that time, nothing was made of these initial observations.

In 1914, the chemist Dr. Géza-Victor Austerweil draws attention in his book “Applied Chemistry in Aviation” to the fact that non-combustible helium would be better suited than hydrogen for balloon filling. Unfortunately, there just was not enough of it.

After entering the war on April 6, 1917, interest in using helium for reconnaissance airships grew in the USA (cf. Canada). In particular, the fully developed Petrolia natural gas field near Wichita Falls, Texas, attracted the government’s attention, because it was well-known that nitrogen-rich natural gas with 1% He had been produced there since 1907. In July 1917, it was decided to instruct the US Bureau of Mines (USBM), founded in 1910, to secure the future US strategic helium supply. Various companies then built three smaller helium pilot plants under the code name “Argon Plant” and using a part of the Petrolia natural gas:

- Argon Plant No. 1 in Fort Worth by Linde Air Products (note: legal predecessor of what later became Praxair, Inc.), commissioned in 1918, throughput capacity 140 m^3 natural gas/d, production of helium gas with 70% He, after purification with 92% He, decommissioned in January 1919.
- Argon Plant No. 2 in Fort Worth by Air Reduction Company, commissioned 01/05/1918, throughput capacity 140 m^3 natural gas/d, production of helium gas with 70% He, decommissioned in April 1919 and later converted to a helium purification plant.
- Argon Plant No. 3 in Fort Worth by Jeffries-Norton Company, commissioned 01/10/1918, throughput capacity 830 m^3 natural gas/d, production of helium gas with 20% He, decommissioned and scrapped in June 1919.

The Linde Air Products company prevailed on the limited helium plant supplier market and on 22/10/1918 – 20 days before the end of the war – was commissioned to build a commercial plant with a capacity of 830 m^3 of helium/d. In April 1921, this plant went into production and produced 7200 m^3 of helium within the first four months. By the time the plant was finally shut down in January 1929 due to the depletion of the Petrolia natural gas field, it had produced 1.3 Mm^3 of helium, a volume previously thought impossible.

After the First World War, the USA also planned to commission three large airships, each of which would require between 28,000 and 56,000 m^3 of helium for their initial filling. On March 3, 1925, the “*Helium Conservation Act of 1925*” was enacted, in which all activities related to the commodity helium were transferred to the responsibility of the US Bureau of Mines. As of March 3, 1927, the use of helium by non-state-owned companies and the export of helium were also banned in a first amendment to the “*Helium Conservation*

Act". Following the abolishment of USBM at the end of 1995, responsibility for helium was transferred to the US Bureau of Land Management (USBLM) in 1998.

In 1925, the possibility of using helium for diving purposes was discovered. In 1926, treatment of asthma using helium was added.

USBM had already set up a large helium exploration programme in 1919 and discovered two large natural gas deposits with elevated helium levels on national land:

- No. 1: Woodside Dome in Emery County, Utah, decreed as Helium Reserve No. 1 on 21/03/1924.
- No. 2: Harley Dome in Grand County, Utah, decreed as Helium Reserve No. 2 on 26/06/1933.

In 1927, the privately-owned Girdler Corporation of Louisville, Kentucky, erected two helium plants in Dexter, Kansas (see above) and Thatcher, Colorado. In Thatcher, natural gas had been drilled in March 1927, which contained more than 7% He in addition to 81% N_2. Between October 1927 and February 1930, these two privately-owned helium plants together produced around 220,000 m^3 of helium. After the second amendment to the "*Helium Conservation Act*" in 1937 (see below) came into force, the government entered into negotiations with the owner and was finally able to acquire the two plants on 03/11/1938, but then dismantled them in 1944.

By 1924, the Cliffside natural gas deposit had been discovered in Potter County, Texas, containing about 1.75% He. Once USBM had concluded a purchase agreement with the owners of the field in 1927, detailed exploration for helium began in February 1928. Beginning in August 1928, a new helium plant was built west of Amarillo, Texas and, after its completion on May 6, 1929, the first 5500 m^3 of helium were sent by train to the Air Force in Langley, Virginia. In the 1930s, the helium plant at Amarillo was supplied with 830,000 m^3 of natural gas daily from four wells in the Cliffside natural gas field, from which 12,500 m^3 of helium were separated daily. In 1933 and 1935, however, two United States airships were lost in accidents, which clearly lowered the government's interest in helium. To be able to continue operating the Amarillo plant at all, helium was allowed to be "leased" from 1936 to the Goodyear Zeppelin Corporation and also sold to the US Public Health Service to treat asthma. When the German airship Hindenburg caught fire on the approach to Lakehurst, New Jersey on 06/05/1937 and went up in flames because it was filled with hydrogen instead of helium, a second amendment to the "*Helium Conservation Act*" came into effect on 01/09/1937 and the sales and export ban on helium lifted again. In 1938, 3250 m^3 of helium were sold to private customers, mainly hospitals. By mid-1939 the private use of helium in the USA had grown to 28,000 m^3. However, the request of the German Reich to acquire 500,000 m^3 helium was not fulfilled.

At the beginning of World War II and the subsequent entry of the USA into the war as of December 8, 1941, the military demand for helium once again increased significantly. Non-governmental needs, especially for the newly developed magnesium welding of aircraft parts under a helium atmosphere, also required large volumes of the noble gas. In 1941, 75,000 m^3 of helium were already in demand by companies in the USA. The Amarillo plant was able to produce only 1 Mm^3 helium/a, so that an additional plant (Exell Plant) near Masterson, Texas, was designed with a capacity of 665,000 m^3 and went into production on 13/03/1943. It utilised natural gas from the south-western section of the Panhandle natural gas field (Channing area in Moore, Potter, Oldham and Hartley Counties, Texas), which contained about 1% helium.

In 1924, oil was first discovered in the Rattlesnake oil and gas field near Shiprock, New Mexico, and natural gas with 73% N_2 and 7.6% He was discovered at a depth of 2100 m in a deeper well in June 1942. This new and significant helium deposit was developed until May 1943 and then taken over by USBM at the symbolic price of US$1.

Although the Amarillo and Exell plants actually exceeded their maximum capacities at full capacity, military demand continued to significantly outstrip helium supply. As early as the spring of 1943, therefore, construction of additional helium plants had begun in Otis and Cunningham, both Kansas, and near Shiprock, New Mexico. The Otis began operating in October 1943, the Cunningham plant in January 1944 and the Navajo plant near Shiprock in March 1944. However, after only 18 days of production time, the Navajo plant was put into standby mode due to surplus capacity. In the fiscal year 1944 (01/07/1944–30/06/1945) USBM was able to produce 3.8 Mm^3 of helium with four of the five plants in production.

Similar to after the First World War, the demand for helium collapsed again quickly following the end of the Second World War. The Cunningham plant was dismantled in July 1945, because the supplying natural gas field was experiencing production problems. The Otis plant was temporarily shut down a month later. Reinjection of previously separated helium into the Bush Dome horizon (a self-contained dolomite horizon underlying an impermeable anhydrite stratum) at the Cliffside natural gas field, had already commenced for temporary storage in early 1945. By the end of June 1945, 560,000 m^3 of helium had thus been returned to the natural gas field. By the end of June 1948, this had increased to 1.9 Mm^3 of helium.

In 1949, it was technically possible for the first time to produce high-purity helium (Grade A) with a purity of 99.995% He (today: > 99.997% He). Purity had previously been limited to 98.2%. The Exell plant was converted accordingly and soon supplied the gas, which was demanded by the welding industry in ever larger quantities. In August 1950, the Amarillo plant was reactivated due to the Korean War (finally decommissioned on April 15, 1970), followed by the Otis plant in March 1951 (finally decommissioned in 1968). Finally, in 1953, the Navajo plant at Shiprock followed. In the summer of 1955, however, reservoir water unexpectedly penetrated the supplying Rattlesnake natural gas reservoir, thus preventing its further use. Until that date, only 1.2 Mm^3 of helium had been extracted from a calculated reserve of more than 22 Mm^3 of helium.

The demand for helium, and especially Grade A helium, grew substantially in the mid-1950s. In response, USBM quickly expanded the capacity of the Exell plant from 2.5 Mm^3 of helium/a to 6.7 Mm^3 of helium/a from June 1957. In 1960 additional capacity of 1.7 Mm^3 of helium/a was added and then another 1.1 Mm^3 of helium/a in 1968. The Exell helium plant was finally decommissioned in 1998. To cover demand, 1.9 Mm^3 of helium were also drawn from the Cliffside storage field between 1955 and 1958. Non-governmental inquiries into helium were dealt with at lower priority.

The Keyes natural gas field in Cimarron County, Oklahoma, newly discovered by the Colorado Interstate Gas Company, presented a new, future helium deposit and was already investigated as a priority from August 1954 on. In April 1958, USBM came to an agreement with the gas company on future use and in August 1959, based on this natural gas deposit, the Keyes helium plant began producing. In July 1959, the helium plant at Shiprock was also finally back in operation. The available helium volume then expanded to such a degree that in the following few years between 2.1 and 4.8 Mm^3 of helium were able to be re-injected into the Cliffside storage field.

In 1950, in Apache County, Arizona, several additional natural gas deposits were discovered at Pinta Dome and the three Navajo Springs natural gas fields (Navajo Springs, East Navajo Springs, Tohache Wash). As later investigations demonstrated, they contained n with 89.4–90.6% N_2, 8.0–9.0% He, 0.8–0.9% CO_2 and 0.5–0.7% Ar. The recoverable helium reserves in the Pinta Dome natural gas field were estimated at 16.6 Mm^3 and those of the Navajo Springs natural gas fields at 8.5 Mm^3. On this basis, first Kerr-McGee Oil Industries, Inc. began construction of a privately-owned helium plant, which then produced around 15 Mm^3 of helium between 1961 and early 1976 using the 181 Mm^3 of natural gas taken from the Pinta Dome natural gas field. The Arizona Helium Corporation followed with another plant, which was in production between 1964 and 1976. They refined around 6 Mm^3 of helium from 75 Mm^3 of natural gas from the Navajo Springs natural gas fields. In 1967, the Dineh bi-Keyah natural gas field (with 4.65–5.65% He) was also discovered in Apache County, the recoverable helium resources of which were originally estimated at 36 Mm^3 (currently with proven helium reserves of 53 Mm^3, Pusch et al. 2018), and which did not go into production until 2003. The helium in the Dineh-bi-Keyah natural gas was separated in the helium plant at what was then Newpoint Gas Services, Inc. in Shiprock.

On September 13, 1960, a further amendment to the “*Helium Conservation Act*” of 1925 came into force. With this “*Helium Amendment Act*”, USBM was permitted to buy raw helium from privately-owned helium plants and store it in the Cliffside field for later use by the government. The Department of the Interior was allowed to borrow up to US$47.5 million from the Treasury Department but was obliged to repay it at a later date. To generate sufficient funds for this purpose, the price for Grade A helium for government customers was raised from US$0.68/m^3 to US$1.26/m^3.

14 companies then submitted proposals for privately-owned helium plants, five of which were approved in the second half of 1961:

- Northern Helex Company for a plant in Bushton, Kansas, operational from December 1962. (In 1979 Union Carbide Corporation erected a purification plant in Bushton in order to produce Grade A helium there directly from the pretreated crude helium).
- Cities Service Helex, Inc. for a plant in Ulysses, Kansas, operational from 1963.
- National Helium Corporation with a plant in Liberal, Kansas, with a planned capacity of 160,000 m^3 helium/d, operational from July 1963.
- Phillips Petroleum Company with two plants in Dumas, Texas, operational from April 1963, and Sherman County, Texas, in operation since December 1962.

To connect these helium facilities to the Cliffside storage area, where the crude helium was to be stored in the interim, the plants were connected by a 725 km pipeline network. This network was operational from July 1962.

The US$1.26/m^3 Grade A helium price set by the USBM was high enough to attract the attention of private competitors. In 1964, a helium plant with a capacity of 5 Mm^3 helium/a was built in Otis, Kansas by the Kansas Refined Helium Company, based around the Reichel natural gas deposit (with 1–2% He) in Rush County, Texas. In 1966, a helium plant was added at the Elkhart, Kansas, site by the Alamo Chemical Company and Gardner Cryogenics, based around the Greenwood gas field in south-eastern Colorado/south-western Kansas. In 1967, three privately-owned helium plants, at Navajo Springs, Otis and Elkhart, were in a position to supply both gaseous and liquid helium in Grade A quality and to substantially undercut the price dictated by USBM for government agencies by US$0.50/m^3. All privately-owned companies therefore acquired their helium from these three non-government plants.

In 1966, US helium demand by government agencies peaked at 22.4 Mm^3 of helium as a result of the booming US space programme. This volume has never been exceeded again during the following 50 years. Nevertheless, in 1968, four more non-government helium plants went into production with the ability to produce both crude and grade A helium:

- Cities Service Cryogenics with a crude helium plant in Scott City, Kansas, and a purification plant supplied by a separate pipeline (Jayhawk Plant) (Grade A) in Ulysses, Kansas.
- Arizona Helium Corporation in Navajo, Arizona, decommissioned 1969.
- Air Reduction Company in Teec Nos Pos, Arizona (crude helium), decommissioned 1969, with a purification plant for Grade A helium in Shiprock, New Mexico.
- Linde Air Products in Amarillo, Texas, decommissioned 1969.

Due to the sharply declining government sales of helium, the resulting increase in the Department of the Interior’s enormous deficit and the 790 Mm^3 helium stored in the interim in the Cliffside field since the amendment to the Helium Act in 1960, USBM no longer saw the necessity of acquiring more helium and cancelled the contracts for the four suppliers with effect from 28/03/1971. All of the companies involved filed a lawsuit against this decision; their helium was, however, no longer accepted as from 12/11/1973. In the following two years, around 120 Mm^3 of helium was lost unused, before USBM decided in 1975 to make the government-owned Cliffside storage field available, for a storage fee, for storing crude helium by privately-owned companies. Northern Helex Co. was the first company to accept this option and from September 1975 saved around 17 Mm^3 of helium annually.

In general, the Cliffside storage field was regarded as a *helium flywheel*: in winter, a great deal of natural gas was demanded, and therefore helium produced, but barely used. In summer, the demand for natural gas, and thus helium production, declined. However, enough helium had been stored during winter to supply industry.

As of July 1, 1976, the Department of the Interior's debt to the Treasury as a result of the 1925 Helium Conservation Act and its amendments had increased to US$412 million, accruing an annual interest of US$24 million. This contrasted with a net income of US$1 million from helium sales.

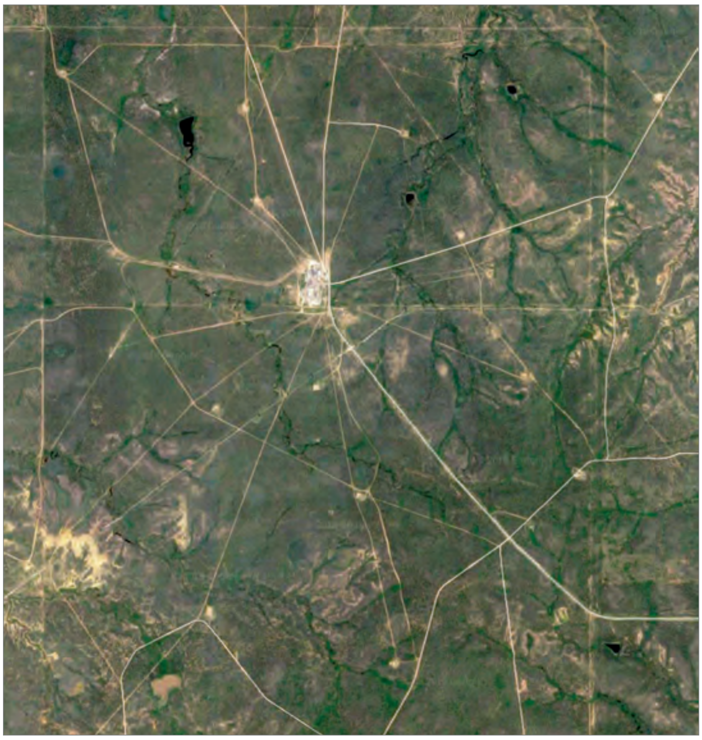

Fig. 53: Satellite image of Cliffside helium storage facility north-west of Amarillo, Texas, USA. The pipelines from/to the production/withdrawal wells are easily visible, photo: Google Earth.

As early as 1962, the largest Tip Top natural gas field was discovered in Sublette County, Wyoming, by Mobil Oil Corporation but was not developed at the time due to the unfavourable composition with 66% CO_2, 21% CH_4, 5% H_2S and 0.6% He. The helium resources amounted to at least 1.25 bn. m^3. The field was finally developed in 1978, with all the undesirable constituents being separated before the methane was utilised. In 1986 an ExxonMobil helium plant went into production at the Shute Creek, Wyoming, site, with an initial capacity of 42,000 m^3 of helium/d and now 110,000 m^3 of helium/d or 40.2 Mm^3 of helium/a. This currently makes it the largest helium plant in the world.

Early in the 1990s, it became apparent that the government's helium storage programme was no longer needed in this format. In addition, BLM's debt to the Treasury Department resulting from the helium programme had grown to more than US$1.3 bn. Therefore, on 09/10/1996, *another amendment to the Helium Conservation Act* came into force and became known as the *Helium Privatization Act* of 1996. It stipulated that the US government:

- cease the production and sale of Grade A helium by 1998 (after which, in March 1998, the last government-owned helium plant, the Exell Plant in Texas, was closed and later sold to a private company).
- should ditch all helium-related assets in 2015 and especially,
- by 01/01/2015 at the latest must sell all its helium from the national strategic helium reserve (except for a remainder of 16.6 Mm^3 reserved for the government), the Cliffside storage field, which held 978 Mm^3 of helium at that time, "*without causing market fluctuations*", in order to pay its debts to the Treasury Department.

The sale price necessary to meet the latter demand was specified at US$1.55/m^3 of crude helium in 2000, while private companies sold crude helium for US$1.15/m^3. The helium market was stable and increased demand by US industry or even the government was not anticipated. However, the robustly growing international demand, which could not be met by the helium facilities in Algeria, Qatar, Poland and Russia at that time, was forgotten. The selling price of the private US producers rose sharply, such that the customers predominantly switched to helium from the Cliffside storage field, the selling price of which was fixed and only increased very hesitantly. US research establishments, in particular, were affected and argued against the strict implementation of the 1996 "*Helium Privatization Act*".

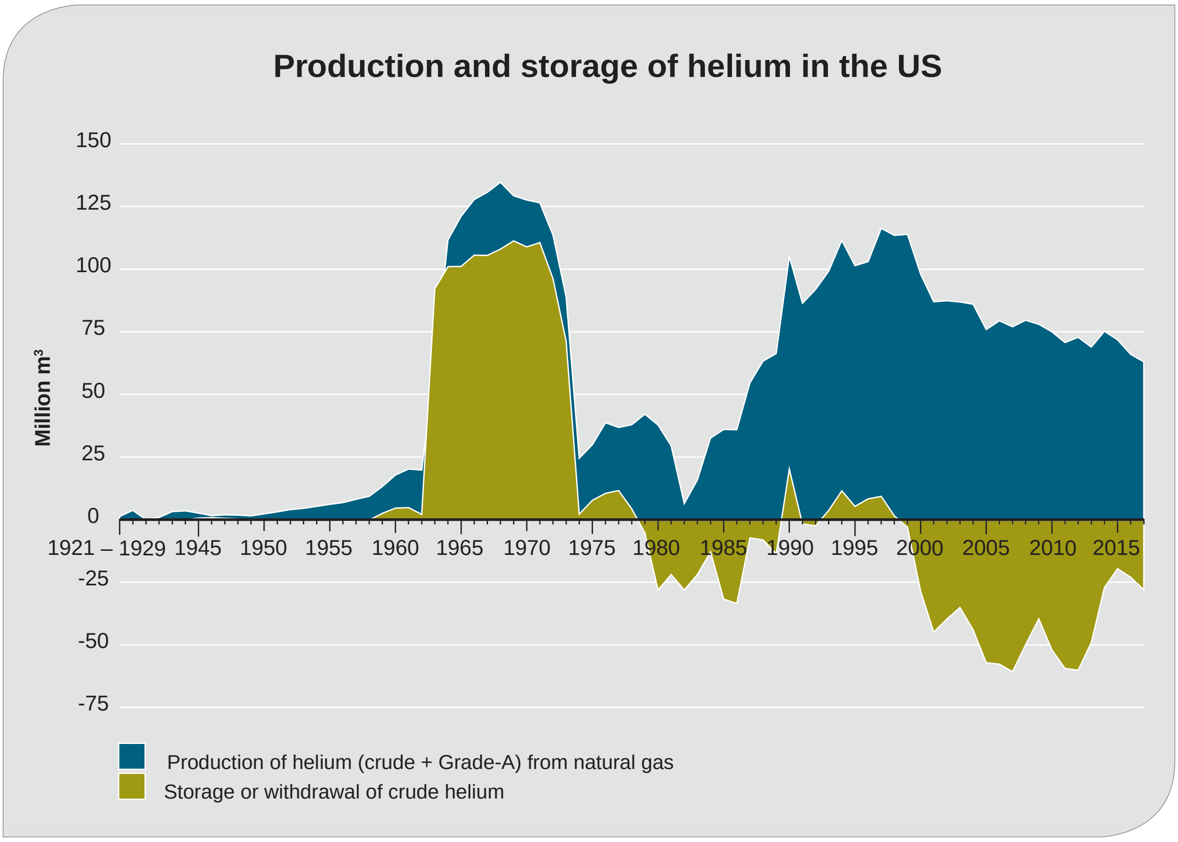

Fig. 54: Production and storage of helium in the USA, according to US Bureau of Mines and US Geological Survey data.

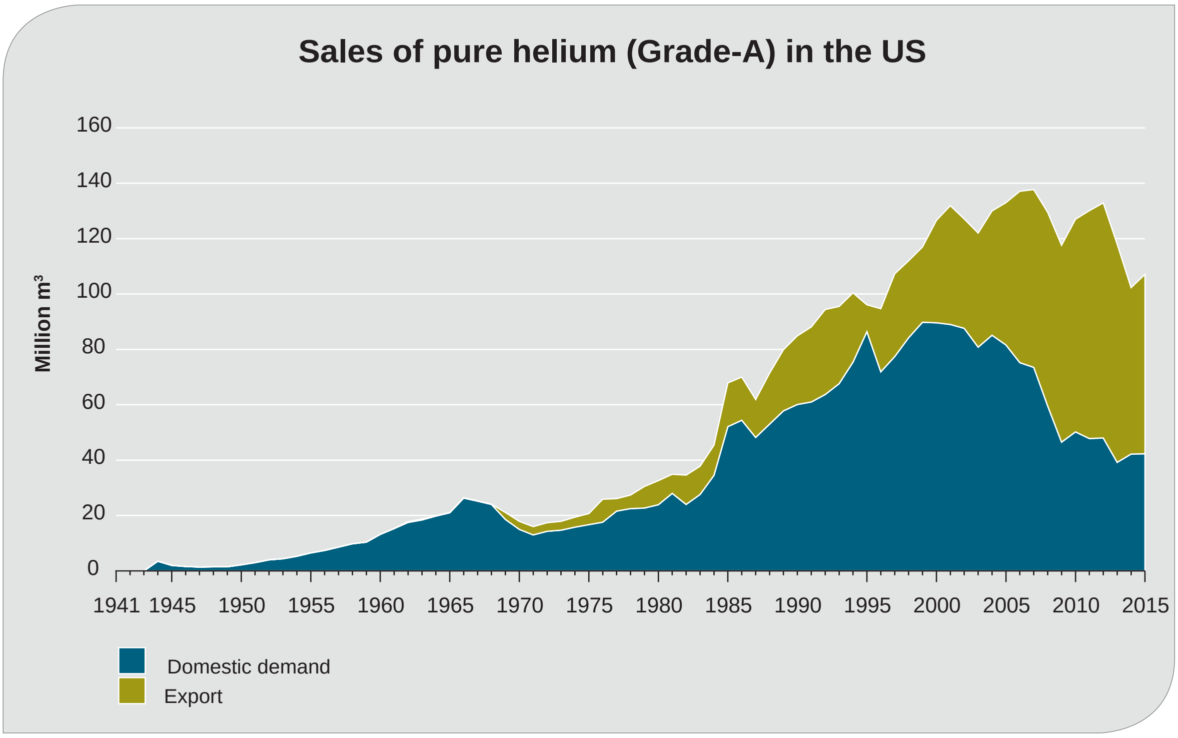

Fig. 55: Evolution of sales of pure helium (Grade A) in the USA, according to US Bureau of Mines and US Geological Survey data.

In 2004, USBLM, in collaboration with three private helium producers and one power company, commissioned a crude helium enrichment plant (CHEU) at the Cliffside field (Fig. 56). It can process up to 600,000 m^2 of untreated gas daily at 29.4% He (average crude helium content) to

- crude helium (with 75–78% He for input and return to the helium pipelines),
- natural gas (for injection into the national natural gas pipeline network) and
- natural gas condensate (for sale to private companies)

With effect from 02/10/2013 the "*Helium Privatization Act*" was revised to form the "*Helium Stewardship Act*". This now stipulates that 83.2 Mm^3 of helium remain in the Cliffside field for government purposes and the remaining helium be publicly auctioned in specified quantities until the remaining quantity given above is achieved. To date, the following helium auctions have been held in the USA at the instigation of USBLM:

- 1st auction on July 30, 2014: auctioned, 2.6 Mm^3 crude helium, average revenue US$5.82/m^3
- 2nd auction on August 26, 2015: auctioned, 7.6 Mm^3 crude helium, average revenue US$3.74/m^3
- 3rd auction on July 20, 2016: auctioned, 11.1 Mm^3 crude helium, average revenue US$3.86/m^3
- 4th auction on July 19, 2017: auctioned, 13.9 Mm^3 crude helium, average revenue US$4.29/m^3
- 5th auction on August 31, 2018: auctioned, 5.8 Mm^3 crude helium, average revenue US$10.09/m^3
- 6th auction in September 2018: auctioned, 2.5 Mm^3 crude helium, average revenue US$6.31/m^3

Fig. 56: The Crude Helium Enrichment Unit (CHEU) on the Cliffside storage facility north-west of Amarillo, Texas, USA, seen from space, photo: Google Earth.

In addition, USBLM must sell all remaining components of the government helium system (e.g. the pipeline network) by 30/09/2021. US Geological Survey was asked to evaluate national helium resources and present an international helium demand study to congress.

In 2016 the "*Helium Rush*" led to a search for new helium sources, primarily in the USA, as a result of the persistently high helium price. New technologies, such as pressure swing adsorption and membrane separation, increasingly allowed helium production from previously uninteresting natural gas deposits. In addition to this, the Cliffside storage field was continuously emptying and there was an accompanying public debate over the future of helium supplies in the USA, as well as the weak oil and gas markets, which were driving hydrocarbon companies to seek alternative sources of revenue.

It is questionable whether the USGS/USBLM helium production data for the USA are even comprehensive as a result of the numerous private activities. For example, the president of American Gas Products (AGP), the largest seller of balloon gas in the USA, with headquarters in Everett, Massachusetts, reports that their helium supply is completely independent of all major natural gas producers and the BLM natural gas storage facility, and that they buy their helium from five independent wells (Garvey 2017b). According to AGP's homepage, the company "owns" four of its own helium wells in Utah, Colorado, Oklahoma and Kansas. However, they may actually be the IACX Energy production facilities (see Table 28).

As of 31/12/2017 the following 19 helium plants were in operation in the USA, as far as is known:

Table 28: List of active, deferred and planned helium facilities in the USA, as far as known.

State	Plant/Location	Company	Capacity (mill. m^3 Helium/a)	Start	Origin	Helium product
Arizona	Dineh-Bi-Keyah	IACX Energy[3]	1.8[1]	2014	Helium rich (N_2-) natural gases	95 – 98 % He
Arizona	St. John	IACX Energy	0.2	planned	CO_2-rich natural gases with 0.009 – 0.134 % He	95 – 98 % He
Arizona	Pinta Dome	IACX Energy	0.4	planned	Helium rich (N_2-) natural gases	95 – 98 % He
Colorado	Ladder Creek/ Cheyenne Wells	DCP Midstream, LLC	14.0[6]	(1986), 1998	from natural gas fields in eastern Colorado and from Dineh-Bi-Keyah natural gas field, AZ	95 – 98 % He
Colorado	Badger Wash	IACX Energy	0.2	2015	from denitrification of natural gas	95 – 98 % He
Colorado	Doe Canyon	Air Products Corp., Inc.	6.4[4]	2015	CO_2-rich natural gas with 73.3 % CO_2, 19.7 % N_2, 3.94 % CH_4, 0.5 % He	Grade-A[5]
Kansas	Jayhawk/Ulysses	Linn Energy, LLC	16.9	1962	Hugoton natural gas field	Crude helium
Kansas	Jayhawk/Ulysses	Praxair, Inc.	26.4	(1968), 1998	from the Jayhawk/Kansas plant of Linn Energy, LLC, which treats He-rich natural gas from the Hugoton natural gas field and from the Dineh-Bi-Keyah natural gas field in AZ	Grade-A
Kansas	Bushton*	Praxair, Inc.	18.7	1962	Crude helium from the BLM pipeline system	Grade-A
Kansas	Otis	IACX Energy	0.3	2009 2016	from denitrification of natural gas Crude helium from the BLM pipeline system	95 – 98 % He Grade-A
Kansas	Otis	Linde Global Helium, Inc.	30.5	(1965), 2009	Otis-Albert natural gas field	Grade-A
Kansas	Liberal/National	DCP Midstream, LLC	29.2	1963	from various natural gas fields in Oklahoma	Crude helium

Table 28 (continued).

State	Plant/Location	Company	Capacity (mill. m^3 Helium/a)	Start	Origin	Helium product
Kansas	Liberal	Air Products Corp., Inc.	27.8	(1966), 1991	from the Liberal/Kansas plant of DCP Midstream, LLC, which treats He-rich natural gases from various fields in Oklahoma	Grade-A
Kansas	Hodgeman	IACX Energy	0.9	2013	from denitrification of natural gas	95 – 98 % He
Oklahoma	Keyes	Badger Midstream Energy, LP	11.6	(1959), 1996	Keyes natural gas field and others	Grade-A
Oklahoma	Paden	IACX Energy	0.2	2015	from denitrification of natural gas	95 – 98 % He
Texas	Fain	Pioneer Natural Resources Co.	3.9	1965	Panhandle-West natural gas field	Crude helium
Texas	Borger/Rock Creek	DCP Midstream, LLC	4.0	2001	Panhandle West natural gas field	Crude helium
Texas	Sunray	Eagle Rock Energy Partners, LP	3.5	1993	Panhandle-West- & Hugoton natural gas fields	Crude helium
Texas	Sher-Han	DCP Midstream, LLC	12.5	1962	Hugoton natural gas field	Crude helium
Texas	Gruver/Panhandle*	Air Products Corp., Inc.	3.1	1982	from the Sher-Han/Texas plant of DCP Midstream, LLC, which treats He-rich natural gases from various fields in northern Texas	Grade-A
Utah	Harley Dome	IACX Energy	2.8	2013	Helium rich (N_2) natural gas field	95 – 98 % He
Utah	Woodside Dome	IACX Energy	1.7	planned	Helium rich (N_2) natural gas field	95 – 98 % He
Wyoming	Shute Creek	ExxonMobil Gas Marketing	40.2$^{2)}$	(1966), 1986	LaBarge natural gas field	Grade-A
Wyoming	Dry Piney Creek	QEP Resources	19.4	Q3 2019	LaBarge natural gas field	n. a.

** deferred, 1) Doubling of capacity planned, 2) Production 2013: 36.1 Mm^3, 2014: 38.8 Mm^3, 2015: 37.4 Mm^3, 2016: 35.8 Mm^3, 3) field owner: 75% NASCO Energie & Rohstoff AG, 25% Nacogdoches Oil & Gas, Inc, 4) Assumed production 3.8 Mm^3/a due to low CO$_2$ demand (Forbes 2017), 5) In the form of liquid helium, 6) According to Gubler et al. (2016): Production* approx. 2 Mm^3/a due to low natural gas supply

Fig. 57: Generalised map of important helium-bearing natural gas fields and current helium production, transport and storage facilities in the USA, map: Marcel Radke (BGR), after USGS Minerals Yearbook.

Other companies are also planning to produce helium in the USA, including Highlands Natural Resources, Inc. from helium-bearing natural gas in Montana, American Helium Inc. from the Four Corners region in the south-west of the USA, and Gulf Energy Corporation from a crude oil and natural gas field in New Mexico (Garvey 2017a).

Currently, 104 natural gas fields with greatly elevated helium levels are known from eleven states in the USA (cf. Table 29). Six of these fields: Hugoton, Panoma, Keyes, Panhandle West, the Riley Ridge region

Table 29: Overview of the most important US natural gas fields with elevated helium levels, according to various individual sources and internet data. The helium levels frequently vary within what are sometimes very large fields.

State	Field name	Orginal natural gas content (billion m^3)	Grade He (%)	Orginal helium content (billion m^3)
Kansas/Oklahoma/ Texas	Hugoton	2300 3)	0.2 – 1.9 (Ø 0.6)	13.8
Texas	Panhandle	850	0.1 – 2.2 (Ø 0.5)	4
Arizona/New Mexico	St. Johns	445 1)	0.1 – 0.8	1.8
Wyoming	LaBarge	11.1 4)	0.0 – 0.6 (Ø 0.6)	0.4
Oklahoma	Keyes	28	0.3 – 2.7 (Ø 2.2)	n. a.
Kansas	Greenwood	28	0.4 – 0.7	n. a.
Texas	Cliffside	n. a.	1.7 – 1.8	Helium storasge
Kansas	Panoma	n. a.	0.4 – 0.6	n. a.
Kansas	Otis-Albert	4.8	1.2 – 2.3 (Ø 1.3)	0.07
Arizona	Dineh-bi-Keyah	1.4	4.7 – 5.7	0.05
Arizona	Pinta Dome	n. a.	5.4 – 9.8 (Ø 8.0)	0.017
Colorado	Model Dome	0.09	6.7 – 8.3 (Ø 8.0)	0.007
New Mexico	Rattlesnake	0.07	7.3 – 8.0 (Ø 7.6)	0.005
New Mexico	Hogback	n. a.	1.4 – 8.0 (Ø 7) 2)	n. a.
New Mexico	Ute Dome	n. a.	0.1 – 0.6	n. a.
New Mexico	Table Mesa	n. a.	5.4 – 5.7	n. a.
New Mexico	Beautiful Mountain	n. a.	4.0 – 7.1	n. a.
Utah	Lisbon	n. a.	0.3 – 1.1	n. a.
Utah	Harley Dome	n. a.	0.2 – 8.0 (Ø 7.0)	n. a.
Utah	Woodside Dome	n. a.	0.7 – 1.5	n. a.
Wyoming	Tip Top	n. a.	0.4 – 0.8	n. a.
Montana	Cabin Creek	n. a.	0.4	n. a.
Kansas	Reichel	n. a.	1.5 – 2.0	n. a.
Kansas	Cunningham	n. a. 2)	0.5 – 1.2	n. a.

n.a. = not available, 1) of which approx. 140 bn. m^3 recoverable, 2) exhausted, 3) of which approx. 1120 bn. m^3 recoverable, remaining reserves approx. 100 bn. m^3 (as of 2017), production (2016): 2.7 bn. m^3, decreasing annually by 6–7% (Forbes 2017), 4) According to Illichmann (2018), the remaining gas reserves of the He-rich Riley Ridge region within the LaBarge natural gas field in 2016 amounted to 860 Mm^3.

of the LaBarge field and the Cliffside field, which is used as a helium storage facility, contain around 97% of all helium reserves identified in the USA.

As of December 31, 2006 (more recent data are not available) helium reserves in the USA amounted to 20.6 bn. m^3 of helium, including 4.25 bn. m^3 of *measured reserves* (including 670 Mm^3 in the Cliffside storage field) 5.33 bn. m^3 of *probable resources*, 5.93 bn. m^3 of *possible resources* and 5.11 bn. m^3 of *speculative resources*. The large natural gas fields Hugoton, Panhandle West, Panoma, Riley Ridge and Cliffside together contained an estimated 3.9 bn. m^3 of helium.

Phetteplace (2014) calculated the total geological natural gas content (12.037 bn. m^3) and the total geological helium content, which is around 6.98 bn. m^3 at helium levels between 0.415 and 0.0014%, from 29 unconventional natural gas deposits (shale gas) in the USA. However, because only around 10% of the shale gas is technically recoverable, the technically recoverable helium volume also drops to around 700 Mm^3, distributed across 29 individual reservoirs.

Gubler et al. (2016) agree with other experts who believe that shale is generally too porous to effectively retain the small helium atoms. In addition, the helium levels in the US shale gas deposits are not high enough to allow economical separation of the helium. Increased shale gas production in the USA would therefore not lead to increased helium production.

Neon

Linde AG operates more than 35 air separation units worldwide and increased their crude neon capacity in 2016 with a new plant in La Porte, Texas, by 40 million l/a. However, as part of the planned merger of Linde Group with the US company Praxair, Inc., it is planned to sell the majority of the US Linde Group activities to the newly established joint venture MG-Industries, a consortium of Messer Group and CVC Capital Partners Fund VII. According to Spiritus & Betzendahl (2018), air separation units with crude neon production are operating at six other locations in the USA (see Section 5.2).

Argon

Table 30: Argon production capacities in the USA, by company, February 2016 (Suresh et al. 2016).

Company	Number of locations[1] of air separation units with argon capacities	Total argon capacity (short tons/d)
Airgas Merchant Gases[3]	18	65
Air Liquide America L.P.	60	1.825
Air Products and Chemicals, Inc.	32[4]	287
Linde Group	41	280
Matheson Tri-Gas, Inc.	17	96
Praxair, Inc.	50	695
Procal (Air Products/Air Liquide)	3	n.v.
Dakota Gasification Company	1	n.v.
total	**222**	**~3.250**[2]

1) Some with several individual plants in one location, 2) Corresponding to approx. 2950 t, 3) Taken over in 2016 by Air Liquide America l.P., 4) According to Internet data in summer 2018: 34 sites

According to Suresh et al. (2016), argon production capacities in the USA amounted to approximately 2950 t/d in February 2016 (see Table 30), corresponding to just around 1.1 Mt/a or 645 Mm^3/a.

However, according to Garvey (2017c), argon production capacity in the USA in 2016 was significantly higher at 5200 short tons (st)/d (= 4700 t/d), corresponding to an annual production in excess of 1.7 Mt/a or 1.03 bn. m^3/a. These percentage capacities were distributed among the following companies: Praxair, Inc (30%), Air Liquide America L.P. (34%), Air Products and Chemicals, Inc. (16%), Linde Group (13%), Matheson Tri-Gas, Inc. (6%) and other companies (1%). By 2019, argon capacity is expected to reach 5600 st/d, i.e. a growth rate of + 2.8%/a. The percentage company distribution is forecast by Garvey (2017d) as follows: Praxair, Inc (32%), Air Liquide America L.P. (31%), Air Products and Chemicals, Inc. (15%), Linde Group (13%), Matheson Tri-Gas, Inc. (8%) and other companies (1%).

As a result of the high domestic production of approximately 645 Mm^3 Ar/a (according to Suresh et al., 2016) and 1.03 bn. m^3 Ar/a (according to Garvey 2017c), the USA's domestic demand (according to Suresh et al. (2016) amounting to 810 Mm^3 in 2016) can be met completely. In 2017, the USA imported only around 30.4 Mm^3 of argon, almost exclusively from Canada, and exported 35.7 Mm^3 of argon, predominantly to various countries in Central America.

For some years, all new major air separation units in the USA have been equipped with argon columns as standard to meet the high demand.

Krypton, xenon

According to Spiritus & Betzendahl (2018), air separation units produce crude krypton/crude xenon at 13 sites in the USA (cf. Section 5.4). Linde AG operates one purification plant at the Alpha, New Jersey site (see above) and Praxair, Inc. operates another in Burns Harbor, Indiana. Also noteworthy is the fact that Electronic Fluorocarbons LLC also produce numerous speciality gases in their plant in Ivyland, Pennsylvania, among them neon, krypton and xenon in purities up to 7.0.

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