

cencji. W przypadku dużych instalacji zwykle konieczne jest stosowanie procesów absorpcyjnych; jeśli zachodzi konieczność selektywnego wydzielenia H_2S absorpcja fizyczna jest szeroko stosowana. Natomiast, jeśli oczyszczany gaz zawiera duże ilości siarkowodoru i ditlenku węgla, absorpcja chemiczna z wykorzystaniem węglanów lub amin stosunkowo korzystnie ekonomicznie spełnia to zadanie. Należy przy tym pamiętać, że węglany nie mogą być używane do oczyszczania gazów z H_2S , jeśli nie zawierają także CO_2 , ponieważ ditlenek węgla jest wykorzystywany do ich regeneracji. Zastosowanie amin zwykle pozwala osiągnąć satysfakcjonujący stopień oczyszczenia przy stosunkowo niskiej cenie. Poza wspomnianymi kryteriami, na wybór technologii oczyszczania, wpływ mają wymagania zleceńodawcy, normy ochrony środowiska na danym obszarze oraz doświadczenie projektantów i konstruktorów instalacji.

Literatura

1. <http://www.eia.gov/cfapps/ipdbproject/IEDIndex3.cfm?tid=3&pid=26&aid=2> 30.01.2014.
2. Raport roczny PGNiG 2012.
3. *Ullmann's Encyclopedia of Industrial Chemistry*. Wiley-VCH 2001.
4. <http://www.odolanow.pgnig.pl/odolanow/produkty/ghe> 30.01.2014.
5. <http://www.lupkipolskie.pl/strefa-wiedzy/rodzaje-gazu-i-jego-wykorzystanie#2> 30.01.2014.
6. Darin L., Bowles G., Bowles E.B.: *Shale gas measurement and associated issues*. Pipeline & Gas Journal 2011, **238**, 7.
7. Praca zbiorowa pod redakcją, Taniowski M.: *Technologia chemiczna – surowce*. Wydawnictwo Politechniki Śląskiej 2010.
8. Kohl A.L., Nielsen R.: *Gas Purification*. Gulf Professional Publishing 1997.
9. Molenda J.: *Gaz ziemny*. WNT 1996.
10. <http://www.engineering-solutions.airliquide.com/en/about-us-global-engineering-and-construction-solutions/technologies-air-liquide-lurgi-cryo-zimmer/acid-gas-cleaning-and-co2-recovery.html> 30.01.2014.
11. <http://www.uop.com/?document=uop-selexol-technology-for-acid-gas-removal&download=1> 30.01.2014.
12. <http://www.jacobs.com/products.aspx?id=6290> 30.01.2014.
13. Baker R.W., Lokhandwala K.: *Natural Gas Processing with Membranes: An Overview*. Industrial & Engineering Chemistry 2008, **47**, 7, 2109–2121.
14. Patent Nr 4923493, USA, *Method and apparatus for cryogenic separation of carbon dioxide and other acid gases from methane*.
15. Mokhatab S., Poe W.A.: *Handbook of natural gas transmission and processing*. Gulf Professional Publishing 2012.

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Methods for sweetening natural and shale gas

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Natural gas is the most important fossil fuel next to coal and oil. World proven natural gas reserves locate it in the second position after coal and before crude oil. The largest conventional natural gas sources are typically located in countries with large crude oil resources. Large proven gas reserves are in Russia, the USA, the Middle East, Venezuela and Nigeria. Countries with the largest mining this material are the U.S. and Russia, and in Europe, Norway and Netherlands. According to data provided by the EIA [1] world gas consumption in 2011 amounted to 3.36 trillion m^3 , in Europe during this period were used 0.54 trillion m^3 . According to data contained in the annual report prepared by PGNiG [2] in Poland in 2012 were used 14.9 billion m^3 of which 4.3 billion m^3 came from domestic production; 2.3 billion m^3 of gas was used by nitrogen plants; 1.5 billion m^3 by power plants

and heating plants; 1.6 billion m^3 were used in the trade and services sector; 3.9 billion m^3 used individual customers; 5.6 billion m^3 falls on other industrial customers.

Natural gas consists mainly of methane and a small addition of higher hydrocarbons. In addition to the organic components of natural gas deposits accompany the inorganic gases. The most important non-hydrocarbon components are nitrogen, carbon dioxide, hydrogen sulfide, and helium. The presence of helium or other noble gases are extremely desirable because of the versatility of this gas and its high market value.

A typical gas composition is shown in Table 1 [3].

The gas composition is a characteristic for the bed from which it is derived. Gases with relatively high carbon dioxide content are located in Wyoming, USA. Some natural gases contain above 1% vol of helium. A few deposits such as in Canada Bearberry are used only for the production of sulfur due to the high content of H_2S (90% vol).

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Currently, the only economically viable source of helium is natural gas deposits with an average content of about 0.1%. Natural gas deposits rich in helium are in the United States – mainly in the central states and the Rocky Mountain region. In addition, cost-effective resources of helium are present in Algeria, Russia and Poland [4].

Table 1

Typical natural gas composition

Compound	Molar fraction
Hydrocarbons	
Methane	0.75 – 0.99
Ethane	0.01 – 0.15
Propane	0.01 – 0.10
<i>n</i> -Butane	0.00 – 0.02
Isobutene	0.00 – 0.01
<i>n</i> -Pentane	0.00 – 0.01
Isopentane	0.00 – 0.01
Hexane	0.00 – 0.01
Heptane plus higher hydrocarbons	0.00 – 0.001
Nonhydrocarbons	
Nitrogen	0.00 – 0.15
Carbon dioxide	0.00 – 0.30
Hydrogen sulfide	0.00 – 0.30
Helium	0.00 – 0.05

In addition to the proven conventional natural gas reserves in the world, there are huge deposits of methane trapped in clathrates (methane hydrates) located at the bottom of the oceans. In contrast, of particular importance for the Polish economy are layers of shale gas and the possible recovery of methane from coal mines (currently 80% of coal production comes from deposits rich in methane). Shale gas is formed in shale rocks that contain a lot of organic matter. Its composition is similar to the composition of the natural gas derived from conventional deposits. Typical shale gas contains methane (75–95%) and nitrogen, and sometimes traces amounts of ethane, propane, noble gases, oxygen, and carbon monoxide. Shale gas does not contain harmful hydrogen sulfide [5]. Averaged composition of shale gas extracted in the US is shown in Table 2 [6].

Table 2

Shale gas composition in the USA

Compound	vol %
Hydrocarbons	
Methane	94.3
Ethane	2.7
Propane	0.6
Butane	0.2
Pentane	0.2
Nonhydrocarbons	
Nitrogen	1.5
Carbon dioxide	0.5

Before extracted gas will go to the public, it must be subjected to a purification process to meet the requirements of the standards. Methods of treatment depend on the composition of the gas produced. Removal of sulfur compounds and carbon dioxide is one of the most important stages of the purification of natural gas [3, 7, 8, 9]. Removal of hydrogen sulfide and carbon dioxide is necessary because of their corrosive effects in presence of humidity on steel from which the pipelines are made. In addition, H₂S is a highly toxic gas with a very unpleasant odor of rotten eggs. Gas desulphurisation is also necessary due to the requirements of environmental protection. H₂S is an activator compound for solid hydrates of hydrocarbons. Forming hydrates in pellets of transmitting gas installations may even lead to obstruction of the pipeline. Very deep removal of sulfur from the gas is required in chemical plants, where natural gas is a raw material for chemical synthesis, due to the poisoning of catalysts by sulfur compounds. Carbon dioxide as well as nitrogen is usually a burden

during the gas transport over long distances. For example, the Yamal-Europe gas pipeline has a length of nearly 4200 km and by Poland in a day passes approximately 50 million m³ of gas. Separation of methane from other components contributes to significant savings in the transport of raw materials over long distances.

The basic and most frequently used method of removing acidic components includes the processes of absorption. In this process H₂S and CO₂ are absorbed in the physical solvent. The most commonly used absorption processes for removing H₂S and CO₂ are:

1. Purisol process developed by Lurgi AG, now licensed by Air Liquide [10]. This process used as a solvent N-methylpyrrolidone (NMP) which is a high boiling liquid and characterized by well solubility of H₂S. The solubility of CO₂ is almost nine times smaller than hydrogen sulfide. Due to the large differences in solubility, this process may be used to selectively remove H₂S in the presence of CO₂. Treated gas contains, less than 0.1 vol % of CO₂, and a few ppm H₂S.
2. Selexol process developed by Allied Chemical Corporation, now a license is issued by UOP LLC [11]. Initially it was developed for the removal of CO₂ in plants producing ammonia, but very quickly found use in natural gas purification systems. It is currently one of the most popular methods for removing H₂S and CO₂ from natural gas. If the installation of gas purification is located near the oil field, obtained a relatively pure stream of carbon dioxide can be re-injected into an oil well to enhanced oil recovery. As the solvent used is a mixture of homologues of the dimethylether of polyethylene glycol. This process provides a very good cleaning gas of CO₂ when there is not hydrogen sulfide.
3. Sepsolv MPE process developed by BASF, is not currently licensed. As the solvent used is a mixture of polyethylene glycol methyl isopropyl ethers with an average molecular weight of approximately 316. This process is similar to the Selexol process, both regard to the characteristics of the solvent and the manner of carrying out the process.
4. Fluor process using, as a solvent propylene carbonate. This is usually the first step in the purification of CO₂-rich gas. Desorption can be carried out using only the pressure reduction without heating the solution. This technology is applicable in the case of gases containing up to 50 vol % CO₂, after leaving the absorber the gas contain approximately 1–2 vol % CO₂.
5. Rectisol process initially developed by Lurgi and then developed jointly with Linde. This process uses as the solvent methanol. The process is conducted at a temperature between -10 to -30°C. Despite such a low temperature, viscosity of the methanol is low, and there is no problem with the dissolution of H₂S and CO₂. After purification the gas contains about 0.1 ppm H₂S and some CO₂. The absorption can be carried out in one column, where H₂S and CO₂ are absorbed simultaneously or in two columns, then it is possible to do it selectively.

Physical absorption process is not subjected to gases containing higher hydrocarbons, due to their relatively high solubility in used solvents. Mostly obtained by the desorption gas rich in hydrogen sulphide is passed to a Claus unit for the separation of elemental sulfur.

In addition to the physical absorption processes for purifying the gas, from the 30's of the twentieth century chemical absorption is widely applied using, as solvents hydroxyamines. The most commonly used are aqueous solutions of monoethanolamine (MEA), diethanolamine (DEA), diisopropylamine (DIPA), diglycolamine (DGA), and N-methyldiethanolamine (MDEA). Chemical absorption due to lower capital expenditures is used especially for smaller streams treated gas.

For gases with a carbon dioxide content greater than 10 vol % as a solvent in absorption process is normally used a hot 25–35% solution of potassium carbonate further typically activated by various substances.

There exist also processes in which are both the physical and chemical absorption applied. In the process of Sulfinol [12] for the absorption of H_2S , CO_2 , COS, and mercaptans is used a mixture of sulfolane and DIPA or MDEA with water. Pollution absorbing solution composition depends on the type and concentration of the purified gas. This process is widely used especially in the USA and Canada and more often for the purification of gases having high contents of impurities such as the compounds of H_2S , CO_2 , COS, and mercaptans. Other processes, which fall into this category include Selexfining, Flexsorb PS and Amisol.

In the case of small gas flows with a low content of hydrogen sulfide liquid oxidation processes are applicable. In this category, the methods of treatment can be divided into the following steps:

1. The absorption of H_2S in the basic solution.
2. Oxidation of dissolved H_2S to elemental sulfur with simultaneous reduction of the oxygen carrier or microorganisms.
3. Reoxidation of the active ingredients with the oxygen from the air, and in some processes using bacteria.
4. Separation of sulfur in the process of filtration, centrifugation, flotation or sedimentation. Sometimes it is necessary to further purify the product.

Examples of processes in this group include Unisulf processes and Hyperion.

Unisulf process uses vanadium compounds for the oxidation of absorbed H_2S . For the reoxidation uses organic oxygen carriers. Hyperion process uses for example chelates to oxidize H_2S , in this case, it is possible to avoid adverse effects of vanadium compounds on the environment.

Adsorption processes are used in particular in the case where the gas contains small amounts of impurities. It is also used to deep remove from gas water and carbon dioxide prior to liquefaction. As the adsorbents are used zeolites, molecular sieves and activated carbon.

In recent years, more frequently at all stages of the purification are applicable membrane processes. Membranes are readily used to remove nitrogen, carbon dioxide in offshore installations and higher hydrocarbons. One important application is their use for the purification of the gas directed to the gas turbine [13].

Cryogenic processes are used in all cases helium secretion. Distillation of liquefied natural gas allows accurate separation into individual fractions. The disadvantage of this method is primarily the high cost of the process. One of the most interesting and economic ways of cryogenic separation was proposed by ExxonMobil Upstream Research Company [14]. In this method, one stage is removed at the same time H_2S and CO_2 , by controlling the solidification and melting of CO_2 .

The choice of treatment of natural gas from carbon dioxide and hydrogen sulfide is a difficult and complex and require consideration of many issues [15]. The main problems to be considered when selecting a treatment technology are: the gas flow rate, composition, pressure and temperature, the desired degree of purity of the gas, its purpose and whether the pollutants are to be segregated in a selective manner. In addition, cannot be avoided the financial issues associated with the construction of a new installation or an attempt to adapt existing solutions and the cost of the license. In the case of large installations, it is usually necessary to use the processes of absorption, if selective physical separation of H_2S is necessary, the absorption is widely used. In contrast, if the purified gas contains large amounts of hydrogen sulphide and carbon dioxide, a chemical absorption in carbonates or amines, relatively economically fulfills this task. It should be remembered that the carbonates cannot be used for waste gas from the H_2S , if they do not also contain CO_2 , since carbon dioxide is used to regenerate them. The use of amines usually gives a satisfactory degree of purification at a relatively low price. In addition to these criteria influence the choice of treatment technology to the customer requirements, environmental standards in the area and experienced designers and installation.

References

1. <http://www.eia.gov/cfapps/ipdbproject/IEDIndex3.cfm?tid=3&pid=26&aid=2> 30.01.2014
2. Raport roczny PGNiG 2012.
3. Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH 2001.
4. <http://www.odolanow.pgnig.pl/odolanow/produkty/ghe> 30.01.2014
5. <http://www.lupkipolskie.pl/strefa-wiedzy/rodzaje-gazu-i-jego-wykorzystanie#2> 30.01.2014
6. Darin L., Bowles G., Bowles E.B.: Shale gas measurement and associated issues. Pipeline & Gas Journal 2011, 238, 7.
7. Praca zbiorowa pod redakcją, Taniewski M.: Technologia chemiczna – surowce. Wydawnictwo Politechniki Śląskiej 2010.
8. Kohl A.L., Nielsen R.: Gas Purification. Gulf Professional Publishing 1997.
9. Molenda J.: Gaz ziemny. WNT 1996.
10. <http://www.engineering-solutions.airliquide.com/en/about-us-global-engineering-and-construction-solutions/technologies-air-liquide-lurgi-cryo-zimmer/acid-gas-cleaning-and-co2-recovery.html> 30.01.2014
11. <http://www.uop.com/?document=uop-selexol-technology-for-acid-gas-removal&download=1> 30.01.2014
12. <http://www.jacobs.com/products.aspx?id=6290> 30.01.2014
13. Baker R.W., Lokhandwala K.: Natural Gas Processing with Membranes: An Overview. Industrial & Engineering Chemistry 2008, 47, 7, 2109–2121.
14. Patent Nr 4923493, USA, Method and apparatus for cryogenic separation of carbon dioxide and other acid gases from methane
15. Mokhatab S., Poe W.A.: Handbook of natural gas transmission and processing. Gulf Professional Publishing 2012.

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