



## Swelling and plasticization of the polymer membrane under the influence of contaminants containing hydrogen sulfide

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### ABSTRACT

The article presents the effect of sulfur-containing gaseous pollutants on the operation of a polymer membrane. Preliminary experimental results of the separation process of a nitrogen-hydrogen sulfide mixture simulating the impurities are presented. A nitrogen gas mixture with 100 ppm H<sub>2</sub>S was used. UBE's UMS-A5 membrane module was used for the study. The obtained results of the separation process illustrate the effect of the action of a specific pollutant on the permeation properties of the tested membrane. Changes in the concentration of hydrogen sulfide in the retentate stream were determined in relation to the time of long-term studies. The research was carried out in several stages. After the measurement process of hydrogen sulfide separation was completed, a long-term process of rinsing the membrane was carried out until it was completely cleaned of sulfur compound contamination. The results of the conducted research suggest a negative effect of sulfur compounds on the transport properties of the polymer membrane. The authors intend to continue research in this area to expand the information on the above-mentioned phenomenon to protect polymer membranes and their transport properties. The results obtained may be helpful for the development of H<sub>2</sub>S fouling management strategies that will later protect and improve the membrane's durability. This may include using special protective coatings or adding special additives to the material to increase its resistance to H<sub>2</sub>S. In this way, it can be ensured that the gas separation process will be reliable and efficient, even under H<sub>2</sub>S contamination conditions.

*Keywords:* Swelling; Plasticization; Polymer membrane; Hydrogen sulfide

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### 1. Introduction

Hydrogen sulfide is a colorless, highly toxic gas with a characteristic odor. In the environment, it is found in volcanic gases, swamps, and some mineral waters and accompanies oil and natural gas deposits. It is also a product produced by bacteria in the process of rotting animal and plant remains. For this reason, H<sub>2</sub>S is often found in biogas in toxic amounts as a byproduct. The strongly corrosive as well as toxic properties of hydrogen sulfide make it essential

to remove it early in any industrial process where there is a risk of its presence. Its presence in wastewater causes corrosion of pipes, which can progress at a rate of up to 10 mm/y. The emission of hydrogen sulfide into the atmosphere also leads to environmental pollution and promotes the phenomenon of acid rain.

Hydrogen sulfide is well sensed by the olfactory organ at very low concentrations. The threshold for sensing hydrogen sulfide in the air is 0.0007–0.2 mg/m<sup>3</sup>. Concentrations of hydrogen sulfide in excess of 7 mg/m<sup>3</sup> (5 ppm) are

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considered hazardous to health, and its toxic effects manifest themselves through paralysis of the respiratory system. The high toxicity and intense and unpleasant odor of hydrogen sulfide are the reasons by which its emissions and permissible air concentrations are regulated by legal acts such as Directive 2008/50/EC of the European Parliament and of the Council of May 21, 2008, on air quality and cleaner air for Europe [1] or Directive 29 2010/75/EU of the European Parliament and of the Council of November 24, 2010, on industrial emissions [2].

On the other side, sulfide compounds derived from hydrogen sulfide are used in many industrial processes, such as the production of paper, dyes, man-made fibers, explosives, and fertilizers. In addition, hydrogen sulfide has found applications both in analytical chemistry and in the petrochemical or nuclear industries, such as a separator during heavy water production. Recently, an innovative way to convert  $H_2S$  into pure hydrogen has been developed. The hitherto expensive method of, “disposing” of hydrogen sulfide (as a waste product in oil or natural gas refining) involves heating it to a temperature of about  $800^{\circ}C$ – $1,100^{\circ}C$  and then passing it through a series of condensers, heaters, and catalytic reactors to convert it into sulfur and water, in the so-called Claus process (gas desulfurization process). The sulfur thus obtained can be sold on, but the high temperatures make the process energy-intensive and therefore expensive. Now, researchers at Rice University say [3] they have found an efficient and inexpensive way to process hydrogen sulfide while recovering the sulfur and capturing useful hydrogen gas. The new method [3] uses a specially designed silicon dioxide powder nano-catalyst, each grain of which is coated with gold nanoparticles just a billionth of a meter wide [3]. These gold particles react strongly to a specific wavelength of visible light, shooting out short-lived electrons known as “hot carriers”. They carry with them enough energy to effectively separate hydrogen sulfide molecules into hydrogen and sulfur atoms, which can then be separately captured (for example, by membrane separation methods) [3]. This process can be powered entirely by sunlight, so it is almost free in terms of operating costs where sunlight is available. What’s more, according to Rice University researchers [3], the process will be just as effective when artificial light, such as LED lighting, is used.

The world’s energy industry is grappling with a number of issues stemming from restrictions on harmful greenhouse gas emissions and thus related to climate and environmental protection. Energy storage methods are becoming increasingly important. Hydrogen, one of the most promising future energy carriers, is mainly produced by natural gas reforming or coal gasification, where mixtures containing hydrogen, carbon dioxide and impurities such as carbon monoxide and hydrogen sulfide are obtained. Recently, there has also been increasing talk of producing so-called green hydrogen from biogas, which is also contaminated with hydrogen sulfide. The gas mixtures obtained by the above-mentioned processes need to be separated, for example, using increasingly popular membrane methods. However, hydrogen sulfide can be a problem in membrane separation processes, as contact of this gas with the polymer membrane can lead to swelling or plasticization of the or speed up its aging [4–7]. Therefore, the main challenges

posed to membranes fabricated from glassy polymers and used in gas separation processes under aggressive feed conditions are to minimize the plasticization and swelling effects of the membrane. For this purpose, crosslinking, heat treatment, or mixed matrix membranes [4,8–17].

Commercial membrane modules dedicated to biogas, for example, are  $H_2S$  resistant (up to a certain concentration, for example, 3% by volume). Many companies offer such modules, but they are designed for high flow rates (this is semi-technical and/or larger scale) disqualifying its use in a laboratory installation. Furthermore, companies offering biogas purification plants (for biomethane) recommend that the raw biogas should be pre-treated beforehand, that is, subjected to  $H_2S$  removal and dehydrated [18]. Therefore, as a first step of the study, it was decided to check how the separation properties of the module would possibly be affected by  $H_2S$  - if this hydrogen sulfide would nevertheless leak uncontrolled - into the pretreated biogas, as can happen under real conditions.

Due to the lack of available low-flow membrane modules, one could be tempted to prepare a self-developed membrane that is also resistant to  $H_2S$ . However, the path from the development of a new membrane material to its practical application and commercialization is very long. Despite the synthesis and evaluation of hundreds, if not thousands, of new materials, more than 90% of current commercial membranes are made from less than 10 membrane materials, most of which have been in use for decades. Freshly made thin composite membranes often lose 25% of their permeability within a few days and another 25% within the next week or two. Even the best of today’s membranes demonstrate a decrease in permeability of 30% or more within three or four years of life, with most of the decrease occurring in the first six months of service [19]. Therefore, due to the lack of availability of a low-flow module on the market (dedicated to laboratory research), the authors decided to choose a module dedicated to air separation (for low flows), which is not  $H_2S$ -protected.

The purpose of the study was to determine the effects of hydrogen sulfide on a polymer membrane that was not intended to come into contact with this contaminant. A UBE UMS-A5 polyimide membrane designed for air separation was used for the study. The membrane’s transport properties were compared before and after the separation of a mixture containing 100 ppm hydrogen sulfide in nitrogen. On this basis, the effect of hydrogen sulfide on the permeance of nitrogen was tentatively estimated. The effect of hydrogen sulfide on the coefficients of other gases will be studied further. The  $H_2S/N_2$  gas mixture was chosen for the study for the following reasons: firstly,  $N_2$  is an inert, perfect gas; in this case, we will not have competitive sorption with respect to  $H_2S$ ; secondly, for the UBE UMS-A5 module, the permeance of  $N_2$  and  $CH_4$  is comparable ( $Q_{CH_4} = 12$  GPU,  $Q_{N_2} = 26$  GPU) [20].

## 2. Methodology and scope of the research

Permeation testing during exposure of UBE’s UMS-A5 polymer membrane to  $H_2S$  was carried out in a test installation, a schematic diagram of which is shown in Fig. 1. Because hydrogen sulfide is a highly toxic gas (the maximum

allowable concentration is  $7 \text{ mg/m}^3$  [21], or 5 ppm), an existing stationary membrane installation was converted to a mobile installation to ensure safety and the ability to quickly ventilate the test space. This gained the ability to conduct research with direct access to open space.

The main component of the system was a UBE UMS-A5 module with a membrane made of modified polyimide. The gas (100 ppm  $\text{H}_2\text{S}$  in  $\text{N}_2$ ) was introduced through the inlet port into the fibers of the membrane module, where it partially dissolved in the membrane material and then diffused into the inter-fiber space and further outside the module (permeate). The rest was collected at the module outlet as retentate. The module, mainly designed for air separation, used a polyimide membrane. The parameters used in the experiments were within the pressure and temperature ranges recommended by the manufacturers. The suppliers did not disclose data on membrane area and thickness. The technical parameters of the module are shown in Table 1 [22]. However, the suppliers of the module have not disclosed data on its surface area or membrane thickness. For this reason, these data are missing from Table 1.

During the permeation research, the flow rate and pressure in the feed stream, retentate and permeate were measured and controlled. The temperature was also measured in the feed stream, and the amount of hydrogen sulfide concentration in the retentate stream was determined every 5 min. Measurements were made with a Nanosens DP-28 portable analyzer (Poland), which has a measuring range of 5,000 ppm and an accuracy of  $\pm 50$  ppm, the feed gas flow

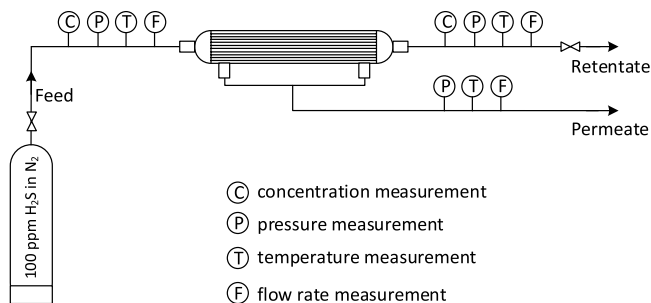


Fig. 1. Schematic of the experimental membrane installation.

Table 1  
Technical parameters of the module [22]

Module type	UMS-A5
Manufacturer	UBE
Housing material	Stainless steel
Membrane material	Modified polyimide
Length, mm	680
Length of the working part of the module, mm	465
Diameter of the wider part of the module/diameter of the working part, mm/mm	47/29
Weight, kg	2.2
Maximum inlet temperature, °C	40
Maximum inlet pressure, bar(g)	9.9
Maximum particle size in the feed gas, $\mu\text{m}$	0.01
Maximum oil content in the feed gas, ppm	0.001

rate was  $300 \text{ cm}^3/\text{min}$ , and the feed pressure was varied in the range of 2.8–6.2 bar (a). The upper limit of the feed gas pressure in this case was determined by both the limitations of the pressure and flow meters used. Aalborg's DFM27 (Aalborg Instruments & Controls, Inc., - USA) (0–500 mL/min) and GFM17 (0–200 mL/min) flow meters with an accuracy of  $\pm 1\%$  of the measuring range were used to measure the flow rate of the feed gas, retentate and permeate. The pressure was measured using pressure transducers (Cole-Parmer P-series, USA) with an accuracy of 0.1 psi. The temperature was measured using a Cole-Parmer Digi-Sense transducer (USA), which provided an accuracy of  $0.1^\circ\text{C}$ .

Each day, the system was flushed with pure nitrogen after testing.  $300 \text{ cm}^3/\text{min}$  of nitrogen was supplied to the membrane module at a pressure of 4.4 bar (a). The flushing was carried out for about 90 min.

### 3. Experimental results and their analysis

The results of research into the permeation process of a mixture containing 100 ppm of hydrogen sulfide in nitrogen in UBE's UMS-A5 module are shown graphically in Fig. 2. The graph shows that for the first 40 min of plant operation, pure nitrogen is obtained on the retentate side, with no

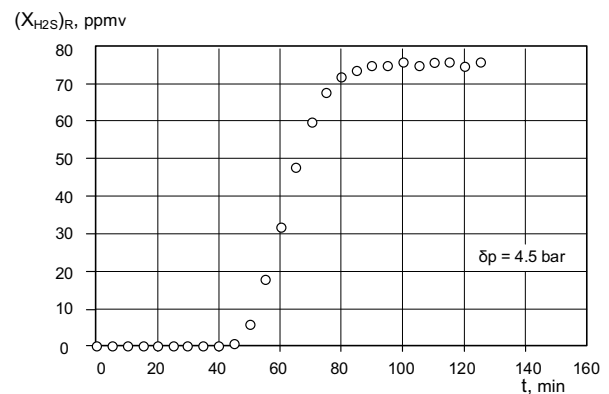


Fig. 2. Hydrogen sulfide separation - change in hydrogen sulfide concentration in the retentate over time for a pressure ratio of 4.5 ( $\delta p = \text{supply pressure/permeate pressure}$ ).

admixture of hydrogen sulfide. Only after this time does the concentration of hydrogen sulfide monotonically increase until a constant value of 75 ppm is obtained. This value is reached after 90 min of plant operation. The concentration of hydrogen sulfide was measured only on the retentate side. The lack of such measurements on the permeate side was due to the limitations of the meter used to analyze the  $H_2S$  concentration - the permeate flow rate was about 56 mL/min, and the nominal flow rate of the analyzed gas should be about 300 mL/min.

As mentioned earlier, the plant was flushed with pure nitrogen after each series of tests. Fig. 3 shows how the concentration of hydrogen sulfide in the retentate stream changes during the flushing of the plant. It can be seen that for the first 30 min of flushing, there was a constant level of hydrogen sulfide in the retentate at 78–79 ppm, which is slightly higher than the hydrogen sulfide concentration level obtained during the tests. Then, for about 40 min, the level of hydrogen sulfide concentration dropped rapidly to reach zero after about 90 min.

Some compounds, such as carbon dioxide or hydrocarbons, can cause increased flexibility of the polymer chain by lowering the glass transition temperature of the polymer, thus leading to the plasticization of the membrane. Diffusion in the plasticized polymer occurs faster, but the membrane is no longer selective [23–28], and the dependence of the permeation coefficient of the pure component on the feed pressure takes on a parabolic shape [28]. However, plasticization mainly occurs at high pressures of condensing gases.

Membrane swelling, which is the increase in volume of a polymer due to contact with a liquid, vapor or gas caused by the penetration of their molecules deep into the polymer matrix, occurs when the strength of the interactions between the penetrant and polymer molecules is greater than that between the macromolecules themselves [4,8,9,27]. Swelling takes place in three stages. In the first stage, the solvent or swelling agent is absorbed on the polymer surface. In the second stage, the solution penetrates into the polymer to occupy the free volume. In the third stage, the solution penetrates into the polymer chains. The swelling of dense polymers increases the free volume, allowing more fluid to flow through. This, therefore, affects both the

permeability and selectivity of the membrane. As a result, membrane selectivity decreases due to swelling [4,5,7].

Diffusion in polymeric materials can result in swelling and/or chemical reactions with the polymer molecules. This often leads to a deterioration of the mechanical and physical properties of the membrane material. In our case, we are most likely dealing with non-Fickian diffusion. In this case, the course of diffusion is complicated by molecular relaxation, delayed segmental mobility, functional interaction between penetrant and macromolecules, crystallization, and others [29,30]. Non-Fickian diffusion often occurs when the polymer is in a glassy state, and the UBE UMS A5 membrane under study is a glassy polymer. Diffusion rates are higher in amorphous areas than in crystalline areas; the structure of the amorphous material is more 'open'. This diffusion mechanism can be considered analogous to interstitial diffusion in metals - that is, in polymers, diffusion movements occur through small voids between polymer chains from one open amorphous region to an adjacent open. The study shows that hydrogen sulfide was retained in the polymer matrix, so the membrane was swollen or plasticized under the influence of hydrogen sulfide.

The transport properties of polymer membranes can change under the influence of certain factors or simply over time. UBE's website provides information on the resistance of their membrane modules to such contaminants as hydrogen sulfide (up to 3% by volume). However, this information appears with the modules used for  $CO_2$  separation [31], and the UMS-A5 module used in the study was designed for air separation. Therefore, it was decided to see how the hydrogen sulfide content affected the transport properties of the polymer membrane. For this purpose, pure nitrogen permeation tests were to be carried out. Gas from a cylinder (pure  $N_2$ ) was drawn through a control valve and fed into the membrane module. The flow rate, pressure, and temperature of the feed gas, permeate and retentate were measured and controlled during the research. The tests were to be conducted for a constant feed gas flow rate of 300 mL/min at a constant temperature of about 22°C and for a variable feed pressure in the range of 1.3–7.2 bar (a). During the experiments, it was noted that the amount of permeate flow obtained varied under constant process conditions. This was indicative of the unstable transport properties of the membrane, probably related to the previous permeation of the mixture containing hydrogen sulfide through it. Therefore, it was decided to flush the membrane with carbon dioxide. After each series of permeation through the membrane with pure  $CO_2$ , the membrane was flushed with pure nitrogen. This cycle was repeated until a stable amount of permeate flux was obtained. After about 2 months, nitrogen permeation tests could be carried out. The results of these tests are presented graphically in Figs. 4 and 5. Also included in the graphs, for comparison purposes, are the results of tests that were carried out before the membrane was in contact with hydrogen sulfide. Then, the dependence of the flow rate on the transmembrane pressure difference was also determined for different values of feed gas pressure changed in the range from 1.3 to 7.2 bar (a), at a constant feed gas flow rate of 300 mL/min and at a constant temperature of 22.5°C. As can be seen, the permeate flow rate increases linearly as the transmembrane pressure difference increases, and the

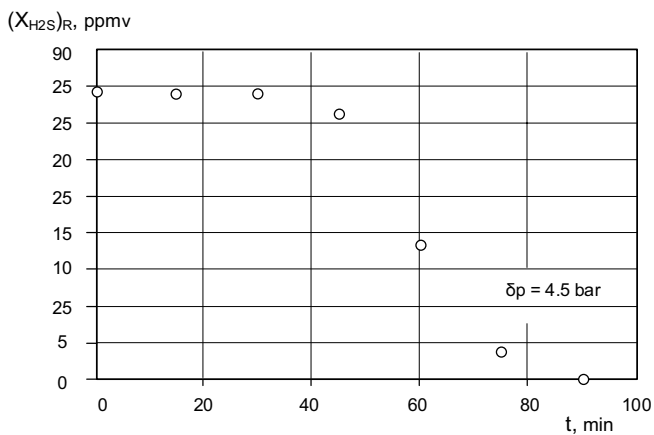


Fig. 3. Membrane flushing - change in hydrogen sulfide concentration in the retentate over time for a pressure ratio of 4.5.

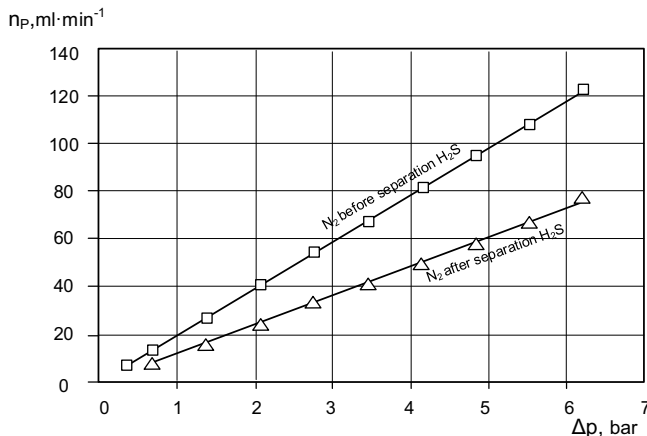


Fig. 4. Dependence of permeate flow rate on transmembrane differential pressure in UBE's UMS-A5 module.

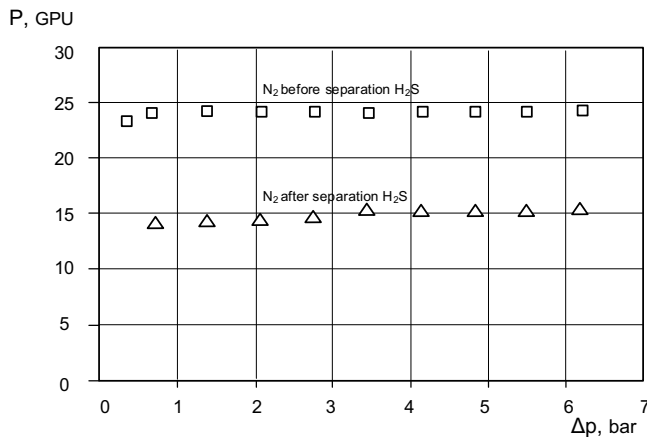


Fig. 5. Dependence of permeance on transmembrane pressure difference in UBE's UMS-A5 module.

graph passes through the origin of the coordinate system, which proves the correctness of the measurements.

It can be seen from the graph shown (Fig. 4) that the transport properties of the polymer membrane under test have changed. In the tests conducted before the membrane was exposed to hydrogen sulfide, the permeate flow rate was 67 mL/min, while in the tests conducted after the membrane was exposed to H<sub>2</sub>S it was only 42 mL/min for the same transmembrane pressure difference of 3.5 bar. The nitrogen permeance determined from the experiments is shown in Fig. 5. It can be seen here that the experimental points align very well along a straight line parallel to the abscissa axis. This means that the nitrogen permeance was constant at a given temperature and independent of pressure. Fig. 5 uses GPU, which is a commonly used unit in membrane technologies when the thickness of the active membrane layer is unknown. For clarity of the article, the conversion factor is given: GPU = 1 × 10<sup>-6</sup> cm<sup>3</sup>(STP)/cm<sup>2</sup>/s/cm·Hg. It is worth mentioning that a 1 μm-thick membrane having a permeability of 1 barrer has a permeance of 1 GPU [32].

It can also be noted that the nitrogen permeance obtained now is 1.6 times lower than the nitrogen permeance that

was determined before the membrane was in contact with hydrogen sulfide. Thus, it can be concluded that the separation of hydrogen sulfide (100 ppm H<sub>2</sub>S in N<sub>2</sub>) caused a permanent change in the transport properties of the tested membrane, that is, the polyimide membrane has plasticized. It is noteworthy that, despite the negative effect of hydrogen sulfide on the transport properties of the tested membrane, it did not affect the linear dependence of nitrogen permeability on the transmembrane pressure difference. In order to confirm this thesis, further research will be carried out.

#### 4. Conclusions

The aim of this study was to determine the effect of hydrogen sulfide-containing contaminants (entering the membrane in an uncontrolled manner) on the separation capabilities of a membrane module dedicated to air separation. It was found that the polymer membrane can be an adsorbent for H<sub>2</sub>S. Therefore, it is necessary to flush the hydrogen sulfide out of the membrane and to determine its new transport properties.

In summary, in the experiments, it was noticed that under constant process conditions, the size of the resulting permeate flow changed, suggesting unstable transport properties of the membrane, perhaps related to the previous permeation of the H<sub>2</sub>S-containing mixture through the membrane. Only after the membrane was flushed with pure CO<sub>2</sub> for many hours, was a stable permeate flow obtained under stable process conditions. Then the permeation experiments with pure nitrogen were repeated and the results are shown in Figs. 4 and 5. It was found that hydrogen sulfide caused a reduction in the permeance of nitrogen from 24.2 to 15.3 GPU. It is most likely that the tested membrane has plasticized and therefore its transport properties have changed. In addition, the results of these research studies confirm the fact that each membrane is dedicated to a specific process. The use of a membrane with a different purpose in aggressive conditions (e.g., in the presence of acid gases) may be associated with a change in the transport properties of the membrane used. Further studies will be carried out to confirm this thesis. Furthermore, the results of these studies confirm the fact that each membrane is dedicated to a specific process. The use of a membrane with a different purpose in aggressive conditions (e.g., in the presence of acid gases) may involve a change in the transport properties of the membrane used.

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