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Corrosive effects of H₂S and NH₃ on natural gas piping systems manufactured of carbon steel

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Abstract

The main difference of biomethane in comparison to natural gas is its higher concentration of compounds conducive to corrosion and a higher risk of corrosion to steel piping.

During the last decade, high-volume injection of biomethane into a transmission network through a steel piping for natural gas has become more actual in the EU, meaning the focus on related problems is fairly recent. In general, the approach to the biomethane injection has been limited to an assumption that when mixed with natural gas, the amount of corrosion inducing compounds stays below the risk level. The objective of the current article is to systematise prior scientific research regarding the corrosive effects of H₂S and NH₃ on natural gas piping systems manufactured of carbon steel. A simplified methodology will be developed for the verification of information and based on that, the corrosion-sensitivity to H₂S and NH₃ found in biomethane of the main steel brand used in Estonian gas piping will be checked.

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1. Introduction

1.1. Basic information and goals

Biomethane is a purified biogas with a methane content of 96–99 %, and it is equipotent to natural gas, as it is usable everywhere where natural gas is used; accordingly a lot of research on further production and application of biomethane and biogas is performed in countries, where infrastructure of natural gas is well developed (for example, in Latvia) [1–6]. The main constituents of biogases are methane (CH_4) and carbon dioxide (CO_2) but they also contain significant quantities of undesirable compounds (contaminants), such as hydrogen sulfide (H_2S), ammonia (NH_3), and siloxanes.

Biogas can be retrieved from bogs, swamps, landfills as a result of natural processes and, by the means of special digesters, from manure, sewage, herbaceous biomass and other biodegradable waste. The calorific value of retrieved biogas generally remains between 5–7 kWh/m³, depending on the methane content of biogas that in turn depends on the source material, its nutrient content, moisture and other factors.

In order to transfer biomethane into the natural gas piping system, the manufacturer must follow the requirements established by companies providing the natural gas transfer service. In Estonia, such company is Elering AS. When establishing their requirements, Elering has followed the requirements of several EN and ISO standards, including injection technologies and requirements for measurement systems of injected gas [7].

The objective of the current article is to systematise prior scientific research about the corrosive effects of H_2S (theoretically highest corrosive effect) and NH_3 (no concentration requirements due to absence in natural gas used in Estonia) on natural gas piping systems manufactured of carbon steel.

A simplified methodology will be developed for the verification of information, and on the basis of that, the corrosion-sensitivity to H_2S and NH_3 found in biomethane of the main steel brand used in Estonian gas piping will be checked.

1.2. Current requirements

Harmful compounds found in biomethane and their concentration affect both the corrosion of transfer piping and gas consumers (negative effect on equipment and processes). Hereby, it should be mentioned that the formation of corrosive effects of harmful components is often connected to reaching the dew point in a gaseous environment (condensed water is a key factor to the formation of acidic solutions).

Requirements to the general quality of gas and components discussed in the study effective in Estonia are:

- Content of $\text{H}_2\text{S} + \text{COS} \leq 0.007 \text{ g/m}^3$;
- The temperature of biomethane must stay from 0 °C up to 40 °C;
- Water and hydrocarbons content is not allowed;
- No restrictions to NH_3 concentration.

Other member states of the European Union have established somewhat different requirements for the injection of non-traditional gaseous fuels into the network in comparison to Estonia [7–10].

1.3. Defining corrosion conditions

For the verification of theoretical corrosion factors and performance of corrosion tests, it is reasonable to follow conditions that are most conducive to and likely to cause chemical corrosion. In the current study, we have used conditions effective and distinctive to Estonia.

Gas temperature. Theoretically, chemical corrosion taking place in a gaseous environment can be described by using the Arrhenius equation, i.e. corrosion rate increases as temperature increases. Respective to the quality requirements to piped gas, the maximum allowed injection temperature to the gas piping system is 40 °C, this also being the basis for the planning of tests.

By using the test method, it is in principle possible to determine correlation between reaction speed and temperature in accordance with the Arrhenius equation. Such correlation would theoretically allow us to calculate corrosive effects resulting from an increase in temperature, the occurrence of which would have taken longer at the defined (40 °C) temperature. However, using higher temperatures is not justified in this case, as in practice the oxidation kinetics of

metal corrosive process change in parallel with the temperature.

If a solid oxide layer is formed on the surface of the metal, an important stage in further corrosion is the diffusion of an oxidant and metal through the protective oxide layer. If the oxide layer is solid and strong, the temperature increase will not cause a remarkable acceleration of corrosion and received results could be interpreted erroneously.

Pressure. According to Dalton's law of partial pressures, total pressure exerted in a mixture of gases is the sum of partial pressure of each individual gas. In the ideal gas mixtures, the ratio of partial pressures equals the ratio of the number of molecules, i.e. partial pressures of gases present in a mixture are proportional to their concentrations.

In current work, the results are based on biomethane pressure of 50 bars (respective to Estonian conditions). The choice is based on the fact that the oldest part of the network, Tallinn – Narva gas pipeline, was built for a maximum operating pressure (MOP) of 38 bars and other piping system parts were projected to work at MOP of 55 bars but are currently used at an operating pressure of up to 50 bars [11].

Recalculation is required as, considering the specific characteristics of the testing device, tests cannot be performed at a pressure of 50 bars (see chapter 3.3). If necessary, results can be recalculated for other pressures. During recalculation we apply the Ideal Gas Rules (compressibility factors are not taken into account).

Gas moisture. Dry water vapour does not constitute an aggressive environment when discussing chemical corrosion. The negative effect isn't directly related to water vapour but to its liquid or solid phase that could occur due to cooling or compression of gas. In the presence of a liquid phase of water vapour, electrochemical corrosion mechanisms will be activated that have a much stronger effect on corrosion than chemical corrosion. This being the reason why the content of liquid particles is not allowed by the quality requirements of piped gas. When planning our tests we assume it to be a dry gas (with no liquid phase).

Gas speed has a strong effect in the early formation stage of the oxide layer. When speeds get very high, especially when solid particles (dust) are present in the gas, there is the danger of the destruction of oxidized protective layers (erosion) that could in turn remarkably speed up the corrosive process. Generally, natural gas/biomethane does not contain solid particles. Therefore, we will not consider gas speed hereafter.

2. Corrosion properties

Below, chemical corrosion properties of components to be studied under established conditions have been listed. Above all, when determining such properties information from various corrosion tables has been used [12–15]. In research articles, there is practically no information regarding studies of gaseous corrosion (a subcategory of chemical corrosion) caused by biomethane (also natural gas) to be found. The predominant test subject is electrochemical corrosion in the presence of liquid particles [16, 17].

An article [18] listing the description of test methods is worth mentioning separately. The specimen used during the test was inserted into a specially built container, in order to assess the effect of corrosion on steel that contains small amounts of sulfur, oxygen and moisture. The test period was 120 hours at low temperatures (5–40 °C). The main research outcome was the finding that corrosion is stronger when the temperature is below the dew point of water. Oxygen had a remarkable effect on corrosion intensity. However, the research provided no conclusions regarding the effect of corrosion on the lifespan of a piping system.

Another point of interest is a study carried out in 2015 by Force Technology, researching options for the injection of biomethane into a natural gas piping system [19]. In the study, the corrosion mechanism and speed were modelled at different concentrations of harmful components. Main attention was aimed towards components that are likely to be found in higher concentrations in biogas than in natural gas, those being H₂O, CO₂, H₂S and O₂. Research results were used to establish requirements for the injection of biomethane into the natural gas piping system in Denmark. H₂S and CO₂ concentrations used in calculations were fixed respective to requirements effective during the process of carrying out the works, respectively 5 mg/Nm³ and 3 %mol. Main results of the study show that the presence of liquid H₂O particles has the highest effect on the development of corrosion, remarkably increasing the amount of corrosion. Therefore, the gas piping system must be dry. The importance of the dryness of gas has been stressed repeatedly. The main biomethane parameter pointed out was the dew point of water, being –8 °C at 70 bars. Under such conditions, the concentrations of H₂S and CO₂ would be respectively 5 mg/nm³ and 3 % (in correlation with values effective in Denmark) and the concentration of O₂ up to 0.5 %, without the development of additional corrosion (same value that is currently effective in Estonia in regard to injection of biomethane).

2.1. Hydrogen sulfide

H₂S can affect steel indirectly by the means of sulfuric acid created as a result of contact between H₂S and moisture as well as directly in the process of a chemical reaction with gaseous H₂S.

The combined effect of H₂S with carbon dioxide (CO₂) has been discussed separately in different researches [20, 21]. Said topic is not relevant in the context of current study as the combined effect has been identified/described only for the liquid phase. In such case, both the ratio of H₂S and CO₂ concentrations (partial pressures) and the pH of the solution play an important role.

The corrosion caused by H₂S when coming in contact with carbon steel at a temperature of 20 °C is 0.1–1 mm/per year. Same results have been listed in Sandvik corrosion tables (dry gas, with the temperature of up to 100 °C, the corrosion rate is 0.1–1 mm/per year) [22]. In case of alloyed steels (e.g. X13), the corrosion rate at temperatures between 20–100 °C is below 0.1 mm/per year.

An increase in temperature also increases the corrosion rate and at a temperature of 200 °C, the corrosion rate exceeds 1 mm/per year, meaning that carbon steel is not suitable for use under such conditions.

The combination of H₂S and water could produce sulfuric acid that has a corrosive effect on carbon steels. In case of moist hydrogen sulfide, the corrosive effect increases rapidly. At a temperature of 20 °C, the corrosion rate stays between 1–3 mm/per year, and at a temperature of 100 °C it exceeds 10 mm/per year. This means that the presence of H₂S in moist conditions causes significant corrosion of carbon steel and therefore it is not a viable material under current circumstances.

H₂S has a corrosion inducing effect in flue gases produced in burning processes, especially in equipment functioning on condensation. Therefore, H₂S must be removed from biogas in order to protect compressors, tanks and engines.

H₂S is a principal compound that reacts with most metals and its chemical activity increases in conjunction with an increase in pressure and concentration, in the presence of water and on higher temperatures [23].

2.2. Ammonia

High concentration of NH₃ is a problem for gas engines and its allowable concentration is generally limited by manufacturers. An average allowed concentration is 100 mg/nm³. As a result of burning NH₃ forms nitric oxides.

NH₃ without moisture does not cause corrosion to most materials. The corrosion rate of carbon steels within a temperature range of 16–20 °C is <0.001 mm/per year, at a temperature of 300 °C 0.1 mm/per year and 500–600 °C 0.12–0.28 mm/per year.

In the presence of water, it has been determined that NH₃ could induce stress corrosion cracking in carbon steels. Several studies have been carried out, in order to determine the links between material qualities and causes for stress corrosion cracking. Stress corrosion cracking is intensified by cold treatment, welding and use of stronger steels. It is also induced by the presence of air and water concentration higher than 790 mg/m³ [24].

3. Testing methodology for the corrosion process

A theoretical analysis of the abovementioned corrosion processes shows that the effect of NH₃ and H₂S on the risk of chemical corrosion in a steel gas piping system is fractional. In order to verify the theoretical part, we will assess the corrosion process experimentally. For that, a specimen must come in contact with an aggressive environment under specific temperature and pressure. This means that equipment used for studying corrosion processes must allow the formation of an aggressive gaseous environment that could, in turn, be used to affect the specimen. Suitable test methodologies and measures have been established below.

3.1. Test object and its preparation

The test object of tests regarding corrosion risks caused to a steel gas piping system by compounds found in biomethane is a metal specimen that has been cut out from a steel pipe characteristic to the Estonian natural gas transmission network, meeting the material requirements of gas piping system class L290 NB [25]. It is reduced

(deoxidized) steel that, due to its balanced structure and reduced porousness (porousness that is created by gases getting stuck in metals during their solidification), has the highest resistance to hydrogen-induced damage.

Below, there is a schematic showing basic dimensions and surface areas of produced specimens. The designations specified on the schematic (Figure 1) have been used in calculations of corrosion product's limit value (Table 1).

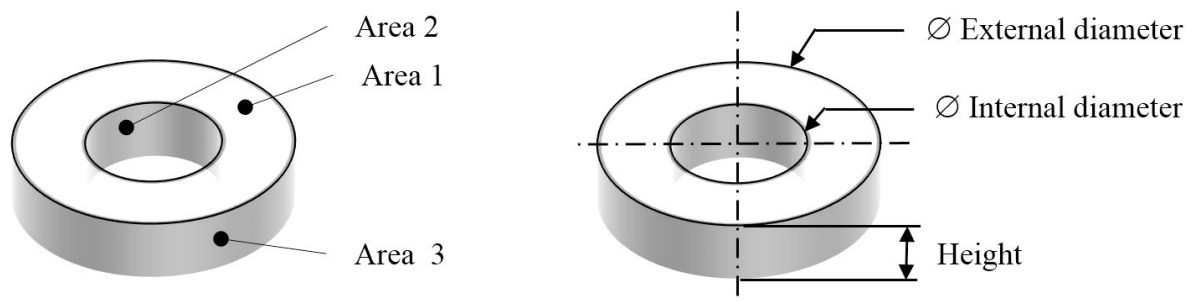


Fig. 1. Basic dimensions of the specimens and designations of surface areas used in the calculations.

3.2. The test device, test process and analysis of results

In order to study the effects of H_2S and NH_3 , a test device that applies tubular furnace as one of its main components will be used. In the beginning of the test, specimens will be placed in a graphite pipe/holder and then into a quartz pipe. The purpose of using graphite is to even up the heating and the allocation of temperature in the specimen. Exiting gases will be neutralised in suitable columns (see Fig. 2).

To assure safety in the event of leaks, the main parts of equipment will be placed in a fume hood. The test device does not allow continuous observation of mass change in time. In order to reduce inaccuracies during a test, two specimens will be analysed simultaneously. The duration of one test at a fixed temperature of $40\text{ }^{\circ}\text{C}$ will be up to 99 hours (due to the specific functioning of the equipment). It must be added that 99 hours was the time that the test device was exposed to gas at a fixed temperature of $40\text{ }^{\circ}\text{C}$. The time required to increase the temperature of specimen has not been included in 99 test hours.

The test was planned as follows. Corrosive gas will be directed into a quartz pipe that passes through a furnace. Corrosive effect tests will be carried out at a pressure of 2 bars. For the assessment of H_2S effects of the gas mixture, a 5 % H_2S gas (rest being N_2) will be used, for NH_3 effects it will be 100 % NH_3 . Respective to prerequisites established in chapter 1.3, H_2S and NH_3 concentration values of gases that will be used correspond to an equivalent pressure of 50 bars, respectively 0.2 %mol and 5 %mol upon recalculation.

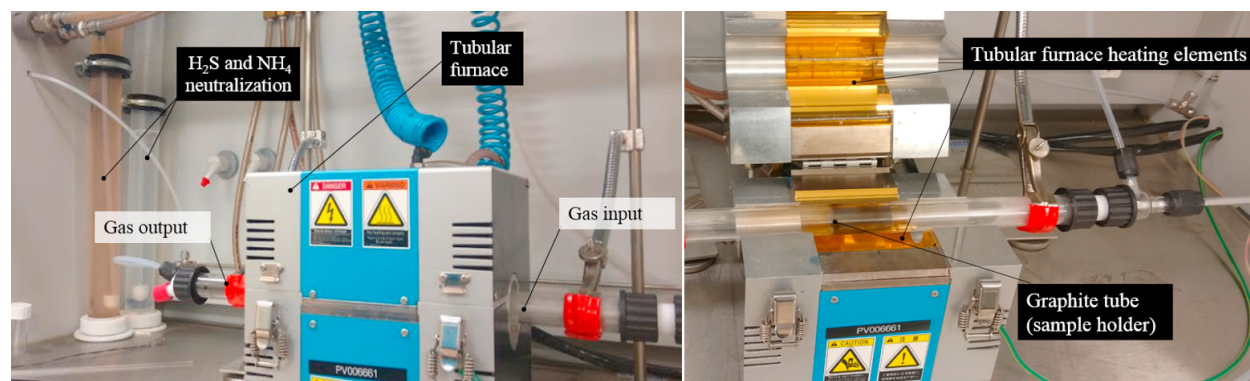


Fig. 2. The test device and its basic elements.

Information regarding the duration of specific tests and the mass change of the test device will be recorded. Certified and calibrated scales *Precisa 404a*, with a measurement accuracy of 0.1 mg, were used for measuring the mass change. The underlying indicator of the corrosion analysis results is the mass change of the studied specimen. Based on the composition of the products of corrosion, the mass of steel that participated in the formation of rust can be calculated. Mass can be recalculated as the corrosion depth indicator on the grounds of the surface area and metal density of the specimen and the composition of the products of corrosion. By establishing the limit value for corrosion depth (generally below 0.1 mm/per year), the limit mass for product of corrosion formation that will not pose a threat of corrosion when not exceeded can be calculated. Table 1 shows the calculation process for finding the limit mass of a corrosion product in an H_2S environment for one specimen. The difference in the dimensions of used specimens is small and will not be established separately.

In regards to the specific specimens it can be concluded that the material is very resistant to corrosion if the mass increase resulting from corrosion does not exceed 2.32 mg. Calculations and tests were carried out conservatively and selections take into account the corrosion product with the highest mass change per mole of iron.

Table 1. Calculation of the change in the limit value of corrosion product (on the example of H_2S).

No.	Name	Equation	Value	Unit
1	External diameter	(1)	13.5	mm
2	Internal diameter	(2)	6.5	mm
3	Height	(3)	4	mm
4	External circumference	(4) = $\pi \cdot (1)$	42.39	mm
5	Internal circumference	(5) = $\pi \cdot (2)$	20.41	mm
6	Area, external diameter	(6) = $\pi \cdot (1)^2/4$	143.1	mm ²
7	Area, internal diameter	(7) = $\pi \cdot (2)^2/4$	33.2	mm ²
8	Area 1	(8) = (6) – (7)	109.9	mm ²
9	Area 2	(9) = (3) · (5)	81.6	mm ²
10	Area 3	(10) = (3) · (4)	169.6	mm ²
11	Total area	(11) = 2 · (8) + (9) + (10)	471	mm ²
12	Volume	(12) = (3) · (8)	439.6	mm ³
13	Volume	(13) = (12) / 1000	0.4396	cm ³
14	Weight	(14) = (12) · (01)	3.45	g
15	Corrosion limit after test	(15) = (03) · (04)	0.00110	mm
16	Corrosion limit after test	(16) = (11) · (15)	0.5162	mm ³
17	Corrosion limit after test	(17) = (16) · 0,001	0.0005162	cm ³
18	Corrosion limit after test	(18) = (01) · (17)	0.00405	g
19	FeS molar mass	(19)	88	g/mol
20	Fe molar mass	(20)	56	g/mol
21	Molar mass difference	(21) = (19) – (20)	32	g/mol
22	Ration	(22) = (21) / (20)	0.57	
23	Mass increase limit	(23) = (18) · (22)	0.00232	g
24	Mass increase limit	(24) = (23) · 1000	2.32	mg
25	Mass increase limit	(25) = (24) · 1000	2315	µg

4. Results and discussion

H_2S . The first test series was carried out in an H_2S environment; its results can be seen in Table 2. In order to increase the competence of information and offer parallel and more long-term results, it was decided that two tests will be carried out using the same specimens. Mass changes listed in Table 2 are minimal (maximum registered change

0.3 mg) and close to a measurement error. When assuming that the corrosion product of the test is FeS and the duration of the test 99 hours (only considering the time when the specimen was at a temperature of 40 °C), the change in the limit mass value would be 2 mg.

Table 2. The duration of tests carried out in an H_2S environment and the mass change of the specimens.

Test	Specimen	Duration, h	Mass before experiment, g	Mass after experiment, g	Mass change, mg
1	1	99	3.5080	3.5080	0.0
	2	99	4.3207	4.3210	−0.3
2	1	99	-	3.5079	0.1
	2	99	-	4.3207	0.0

NH_3 . No mass changes in either specimen were identified when carrying out tests in an NH_3 environment (mass change is not higher than 0.1 mg). In order to reduce the risks related to the implementation of the results of current research, the performance of repeated long-term tests should be considered.

5. Conclusions

High-volume injection of biomethane into a natural gas transmission network has become more actual in the EU, meaning the focus on related problems is fairly recent. One of them is a limitation of corrosion inducing compounds below the risk level. In this article scientific research regarding the corrosive effects of H_2S and NH_3 on natural gas piping systems manufactured of carbon steel is systematized. Simplified methodology for the verification of corrosion risks is proposed and the corrosion-sensitivity tests of the main steel brand used in Estonian gas piping to H_2S and NH_3 is checked.

The results of other studies and tests analysed in this article show that liquid H_2O particles have the highest corrosion inducing effect. Gas in transmission network must be dry as water and liquid hydrocarbon content is not allowed. Therefore, the only type of corrosion caused by piped gas can be chemical gaseous corrosion. The condition of metal gas piping is mainly affected by external surface corrosion (in case of underground pipelines). Countermeasures required to reduce the risk of corrosion are mainly directed towards protecting the pipe from external corrosion. The formation of corrosive effects of harmful components is quite often related to reaching the dew point in a gaseous environment (condensed water is the main factor for the formation of acidic solutions).

Corrosion resistance tables of metals show that at temperatures below 40 °C, carbon is extremely resistant in an NH_3 environment (corrosion speed below 0.1 mm/per year), presuming that the gas is dry (with no liquid particles). An exception is H_2S , against which carbon steels are resistant (corrosion below 1 mm per year) according to corrosion resistance tables of metals.

Based on test results, we cannot differentiate the effect of higher concentrations of corrosion-inducing compounds studied (H_2S and NH_3) in dry gases to the corrosion of carbon steel in comparison to limit concentrations allowed for natural gas. The tested material (carbon steel L290 NB) is very resistant to NH_3 and H_2S at low temperatures (up to 40 °C).

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