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The influence of the internal microbiome on the materials used for construction of the transmission natural gas pipelines in the Lodz Province

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Abstract. This paper presents investigation results of the influence of gas microbes on the biocorrosion rate of the materials used for gas pipelines construction in the Lodz Province. Samples of two types of carbon steel and cast iron were stored in the laboratory pipeline model reflecting the real conditions of working natural gas pipelines were. In the next step the influence of cathodic protection with parameters recommended for protection of underground structures was tested. Analyses of biological corrosion products generated on the test surface were carried out using a scanning electron microscope with an X-ray analyzer. The level of ATP was measured to confirm presence of the adsorbed microorganisms on the observed structures. Corrosion rates were determined by gravimetric methods. In the course of the study it was revealed that the rate of biocorrosion of steel is lower than that for cast iron. Our results also proved that the weight corrosion rate depends on the number of adhered microorganisms. In addition, it has been found that application of the carbon steel cathodic protection decreases its weight corrosion rate. The information obtained will help to increase the knowledge on the rate of biological corrosion causing losses/pits inside gas pipline.

1 Introduction

As a result of technological progress, rise in the living standards and broadly understood economic development, increasing usage of the electric energy is observed. Moreover, some of newer regulations, e.g. in the EU concerning the climate, require decrease of the usage of the fossil fuels for the electricity production. This promotes an increase in usage of the natural gas, which stands out among others conventional fuels due to its low greenhouse gas emissions (see Table 1) and high calorific value. In 2014, share of the natural gas in the electricity market was 2.06%, but it is expected to increase even up to 10% [1] by year 2030. Presently, the domestic natural gas reserves cover only 30% of total demand, so it is necessary to cover the deficit through import [2].

Gas pipelines are the most common way of natural gas transportation because it is relatively inexpensive, safe and environmentally friendly [3]. In Poland According to General Statistic Office data for 2013, the distribution and transmission network of natural gas pipelines length was over 140 000 km [4]. In the Lodz Province the length of gas pipeline system was only 4 158.9 km [5]. The existing gas connections allow to reach over 6.6 million individual, industrial and wholesale customers in total. Even with ongoing investments in the construction of new gas lines, they are not able to compensate the aging transmission grid. This results in the fact that about 60% of the operating gas pipelines are 30 years old [6].

Table 1. Comparison of greenhouse emissions generated by different types of fuel during production of energy [7].

Fuel	**CO_2**	**CO**	**NO_x**	**SO_2**	**Dust**
	kg/GJ				
Coal	120	1.096	0.177	0.840	1.003
Fuel oil	82	0.034	0.110	0.132	0.005
Natural gas	63	0.015	0.054	0.000	0.009

By now, steel remains the basic construction material of the pipes in the gas transmission lines [8]. Currently in use are both alloyed and unalloyed steel pipes. Their composition is strictly regulated by both Polish and European standards, which determine the contend of alloying elements (such as chromium, nickel, manganese, tungsten, copper, molybdenum, titanium). However, production processes result in presence of unwanted impurities, such as nitrogen, phosphorus,

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sulfur and sulfur oxides.

Steel composition, together with aggressive factors of soil on the underground gas pipelines at large depths makes possible an accelerated external corrosion. Moreover, the humidity, constant temperature and composition of the flowing gas, create a convenient place for the development of microorganisms and, consequently, the biodeterioration of internal surface of the gas pipelines.

In practice, gas systems are protected from outside mainly by coatings (i.e. polyethylene and bitumen) or by cathodic protection in accordance with Regulation of the Minister of Economy of July 30, 2001 on technical conditions of the gas networks [9]. However, those methods do not eliminate the problem of corrosion which is induced by microorganisms on the internal surfaces of pipelines [10].

It is commonly known that microorganisms are able to colonize nearly all habitats. Into the gas networks they can be introduced during replacement or repairs of pipelines as well as during construction of new sections of the network. At that time microorganisms inhabiting ecosystems such as soil, water and air, environmentally non-specific natural gas such as *Bacillus, Clostridium, Pseudomonas* can colonize gas pipielines. These microorganisms may origin also from natural gas deposits or storage areas, where microbes are transported along with the tonnage of fuel.

Microbiological studies of natural gas wells indicate a wide variety of microbial communities, especially in unconventional gas resources [11-13]. Identification of the microorganisms found in the underground gas storage (UGS) indicates the biological origin of natural gas. In consequence they are also be present in the transported gas [14,15]. Some of microorganisms inhabiting the drilling mud or fracturing fluids, belonging to the phylum *Acidobacteria, Actinobacteria, Cyanobacteria, Proteobacteria, Verrucomicrobia* can grow up in the natural gas environment [16].

Lack of direct access to the natural gas transmission lines hinders their maintenance and revision. Changes resulting from the development of microorganisms inside gas pipelines cause disturbances in the correct operation of the gas system. In addition, they reduce the mechanical properties of the materials and even cause their biodeterioration [17].

Changes caused by the presence of microorganisms may lead in extreme to rupture of the pipeline and rapid gas leak, which generates both danger for gas users and the great losses in the industries using gas as the basic raw material.

The physico-chemical conditions, combined with the properties of the microorganisms themselves, their adaptive and defensive capabilities promotes the development of microbial corrosion in an anoxic environment [18-20]. Metabolic activity of microorganisms can start and/or increase speed of the chemical and electrochemical processes in material resulting in corrosion. This phenomenon is called Microorganisms Inducted Corrosion (MIC) or biodeterioration. Deposits loosely bonded with the surface of the metal, growths, pitting and loss of material are typical symptoms of the MIC occurring inside of the pipelines for natural gas transmission [21].

Depending on the type of microorganisms the corrosion deposits may be of different color and odor. For example presence of the iron bacteria results in reddish brown deposits, whereas “black powder”, often accompanied by the smell of hydrogen sulphide, it is indicate the sulphate-reducing bacteria involvement [22, 23]. This deposit (sediment) primarily consists of oxides and hydroxides of iron, siderite ($FeCO_3$) and impurities such as elemental sulfur, hydrocarbons, metal debris, sand and dust. It yields the problems for gas pipeline operators in the dry and wet form, as it accelerates erosion of the gas pipelines materials. In addition, the accumulation of "black powder" leads also to clogging and reduction in pipeline throughput.

The losses generated in the gas supply sector due to the growth and properties of microorganisms are not easy to estimate. It has been estimated that about 40% of all corrosion in the industry is biological-origin corrosion [19,20]. Estimated damage caused by biological corrosion accounts for up to 20-30% of the total cost of corrosion of gas pipelines [24].

In addition, indirect costs associated with interruptions in installations and/or equipment operation increase the volume of corrosion damage.

The aim of the study was to provide the knowledge about the biological corrosion of the internal surface of natural gas pipelines. Investigations of the influence of commonly applied cathodic protection on the microbial growth in the natural gas pipelines can lead to new solutions for more effective protection against the corrosion. It should significantly decrease the costs generated by biocorrosion. This paper presents the influence of the microorganisms on materials constructing gas pipelines in the Lodz Province. The susceptibility of the selected materials to biocorrosion was investigated in the laboratory pipeline model reproducing conditions of the real gas pipeline. In addition, the influence of cathodic protection on the adhesion and growth of microorganisms in the environment of gas pipelines has been tested.

2 Materials and Methods

For this study it was possible to collect samples from the real pipelines during their dismantling (Z) or maintenance (S1 and S2) works carried out by the operator. Sampling sites were selected in agreement with an operator of the gas pipelines in the Lodz Province.

Samples were collected from two carbon steel pipelines (S1 and S2) in the Lodz province, what allowed to use in this study microbes naturally inhabiting a gas pipelines of this region.

The samples were cut out from two carbon steel (S1 and S2) and one cast iron (Z) pipelines. Characteristic of two type of carbon steel and one of type cast iron are presented in Table 2.

Preparation of the samples consisted of cutting material into rectangular plates with the active (adhesive) surface of about 1.5 cm^2. They were clean of existing corrosion.

Table 2. Chemical composition of the Z, S1 and S2 materials.

Mate-rial	C	Mn	Si	P	S	Cu	Fe
	Weight percentage of the elements [%]						
Z	3.59	0.48	3.15	0.92	0.082	-	91.778
S1	0.11	0.46	0.19	0.060	0.041	0.097	99.042
S2	0.10	0.48	0.10	0.012	0.013	-	99.295

They were clean of the existing corrosion. The entire surface of the cut pieces was purified in a digestion solution (PN-78 / H-04610), and additionally, the grinding surface was standardized by sanding on ASTM scale 180, 350, 600 grinding papers. Finally, the samples were degreased, sterilized, dried and weighed with accuracy of 10^{-4} g.

Corrosion resistance studies were carried out in a laboratory gas pipeline model for 4 months. Character of the corrosion process required long time of incubation of the samples, therefore the time interval between controls was 1-month long (28 days).

The laboratory set used in this experiment has been projected and constructed by authors. It was consisted of two parallel, cathodically protected and unprotected tubes of length 1 m and diameter 0.1 m each with an external power source (see Fig. 1).

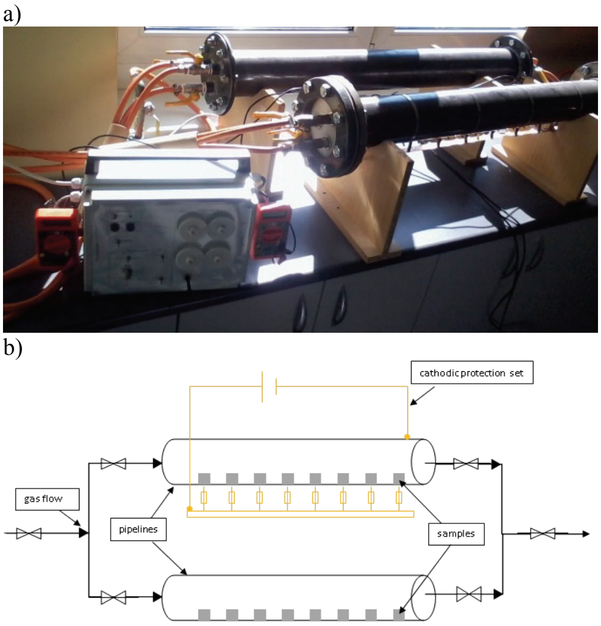

Fig. 1. Laboratory set used for experiment to conduct parallel research on corrosion with and without cathodic protection. (a) photo, (b) scheme.

The model was powered by natural gas without a microbiological filter, what allowed for free migration of the microbes in the system. Assumed parameters of the cathodic protection are in accordance with current cathodic protection criteria for underground construction without or with highly damaged surface protection. In this case the suggested maximal current density was 50 mA/m^2.

For observation and illustration of the changes in active surfaces of materials and bacterial cell adhesion to steel surfaces investigation the Scanning Electron Microscope S-3400N (Hitachi) was used.

In order to confirm the number of living cells in the sample the biochemical method using Portable luminometer type HY-LITE (Merck) was applied. The bioluminescent measurement of ATP (adenosine triphosphate) facilitated estimation the number of molecules of ATP produced during cellular metabolism. It should be noted that at the moment of the cells death, synthesis of ATP is inhibited and all already existing molecules are degraded by intracellular enzymes, ATPase and phosphatase.

Calculation of the corrosion rate of the sample was made by gravimetric method. The corrosion rate was determined directly from the loss of mass depending on the time of microbial activity per sample. Measurements were done with accuracy up to 0.1 mg using an analytical balance of AS 220/X (Radwag). The weight corrosion rate $\mathcal{V}$ [g/(m^2day)] was calculated according to formula (1).

$$\mathcal{V} = \frac{m_0 - m_1}{S*t} \qquad (1)$$

where: m_0 - initial mass of sample [g], m_1 - mass of sample after exposure [g], S-surface of sample [m^2], t-time of exposure [day].

3 Results and discussion

Samples used in this study differed in the content of alloying elements: C, Si, P and S, resulting in their the mechanical properties, including corrosion resistance. Nevertheless, macroscopic observation for both sets of samples (with and without applied cathodic protection) showed delicate black sediment on all active surfaces. After 4 months differences between corrosions occurring in steel (S1 and S2) and cast iron (Z) materials were observed. For S1 and S2 pits and deposits differing in their color from black to brown depending of time of exposure to corrosive conditions were visible, while for Z material corrosion products remained in the form of uniform black coating. However, the apparent differences between samples of the same material with and without presence the cathodic protection were impossible to observe in macroscopic scale.

Given that it was necessary to prove presence of the living microbes to confirm participation of the microorganisms in the occurring degradation processes. For this reason the ATP measurements were used and the obtained results are presented in Table 3. It should be noted all samples were sterile at the beginning of the experiments. It was assumed that all detected microbes were introduced with the gas. The increasing in time ATP production proved also that detected microbes were able not only to survive, but also to grow and develop in the natural gas environment.

Table 3. Comparison of the ATP measurements results for samples incubated in systems with and without cathodic protection.

Material	**Exposure time [day]**	**ATP [RLU]**	
		with cathodic protection	without cathodic protection
Z	28 56 84 112	24 21 25 32	25 23 35 37
S1	28 56 84 112	25 23 37 46	22 21 31 32
S2	28 56 84 112	21 23 25 35	23 25 31 34

Presence of the microorganism was also confirmed by SEM observations, where visible are structures that can be considered as adhering bacteria (Fig. 2).

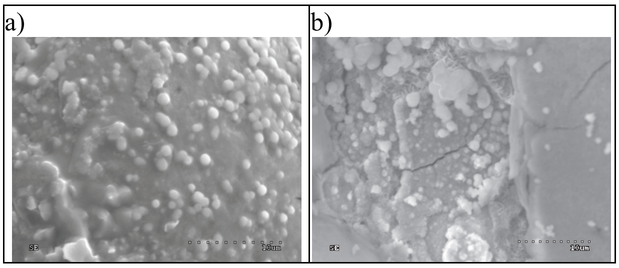
a) b)

Fig. 2. Example of SEM image of adhered microorganisms on the surface of S1 material after 4 month cultivation in natural gas environment with cathodic protection (a) and without cathodic protection (b) (magn. 6000x).

Adhesion of microorganisms to metal surfaces stimulates microbial corrosion, which is a complex multi-stage metal degradation / degradation process. In the course of the ongoing destructive transformations, physical, chemical and biological agents have cumulative effect. Using the gravimetric method, the rate of biocorrosion of the materials tested was determined. Obtained results are presented in Tables 4-6.

According to the obtained results the highest rate of mass loss was observed after the first month of experiment and the lowest in the 4 month, what resulted in the time depending decreasing velocity of gravimetric. For all tested materials determined speed was lower for samples without cathodic protection.

All results obtained during 4 months of the experiment indicated that the highest rate of corrosion was for the cast iron. Calculated gravimetric corrosion velocity for cast iron was approximately 100 times higher than for other investigated materials.

Table 4. Mean values of corrosion rate for iron cast (Z) obtained during 4-month incubation of samples.

Material		t **[day]**	m_0 **[g]**	m_1 **[g]**	Δm **[g]**	V **[g/(m^{2}day)]**
Z	With protection	28	6.3500	6.0034	0.3466	104.0116
		56	6.8359	6.3466	0.4892	67.7233
		84	6.9567	6.2316	0.7251	60.3674
		112	6.4787	5.7510	0.7276	51.9738
	Without protection	28	7.2636	6.9407	0.3228	80.0678
		56	6.5401	6.0696	0.4705	65.9999
		84	6.9552	6.2883	0.6669	54.0060
		112	7.1906	6.4274	0.7631	44.2447

Table 5. Mean values of corrosion rate for steel S1 obtained during 4-month incubation of samples.

Material		t **[day]**	m_0 **[g]**	m_1 **[g]**	m **[g]**	V **[g/(m^{2}day)]**
S1	With protection	28	5.7660	5.7602	0,0058	1,5033
		56	6.3861	6.3785	0,0076	0,8988
		84	6.7824	6.7705	0,0119	0,8720
		112	7.3371	7.3238	0,0134	0,6594
	Without protection	28	5.9769	5.9712	0,0057	1,3403
		56	6.7482	6.7394	0,0088	0,9524
		84	7.6246	7.6126	0,0120	0,7722
		112	6.6636	6.6497	0,0139	0,7568

Table 6. Mean values of corrosion rate for S2 material obtained during 4-month incubation of samples

Material		t **[day]**	m_0 **[g]**	m_1 **[g]**	m **[g]**	V **[g/(m^{2}day)]**
S2	With protection	28	5.0348	5.0277	0.0071	1.4475
		56	5.7137	5.7073	0.0065	0.5774
		84	5.5244	5.5128	0.0116	0.7030
		112	5.9689	5.9562	0.0127	0.5466
	Without protection	28	4.4904	4.4851	0.0053	1.2134
		56	4.2578	4.2507	0.0071	0.8492
		84	4.5710	4.5611	0.0099	0.7230
		112	4.1325	4.1220	0.0105	0.6398

In the case of the iron, the highest mean gravimetric corrosion velocity V (104.0116 g/(m^{2}day)) was observed after first month of incubation, while the lowest value – 44.2447 g/(m^{2}day) was obtained for the fourth month of incubation for samples without cathodic protection.

The weight corrosion rates for both steel materials were similar with only slightly higher corrosion velocity for material S1. Similarly to the cast iron the highest corrosion velocities for both S1 and S2 materials were observed in the first month of experiment for samples stored with cathodic protection (V=1.5033 g/(m^{2}day) and V=1.4475 g/(m^{2}day) respectively). After 4 months of experiment duration for S1 and S2 the lowest rate V=0.6594 g/(m^{2}day) and V=0.5466 g/(m^{2}day, respectively was obtained.

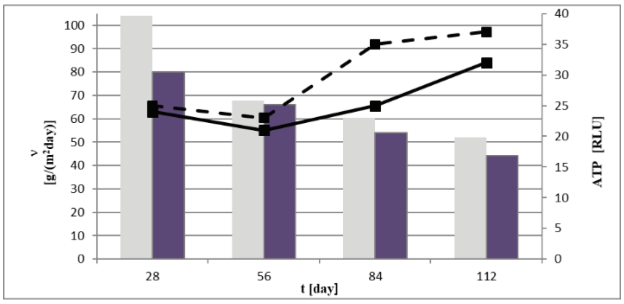

Fig. 3. Correlation between mean values of the gravimetric corrosion rate and ATP measurements for Z material with protection (light bar and continuous line, respectively) and without cathodic protection (dark bar and dashed line, respectively).

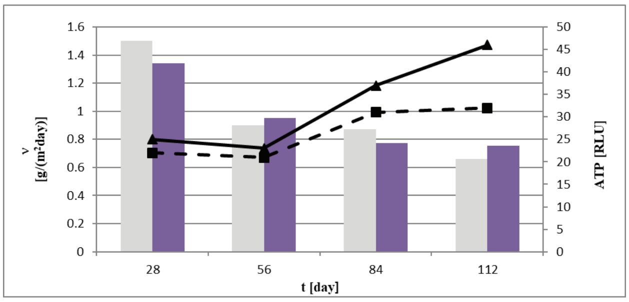

Fig. 4. Correlation between mean values of the gravimetric corrosion rate and ATP measurements for S1 material with protection (light bar and continuous line, respectively) and without cathodic protection (dark bar and dashed line, respectively).

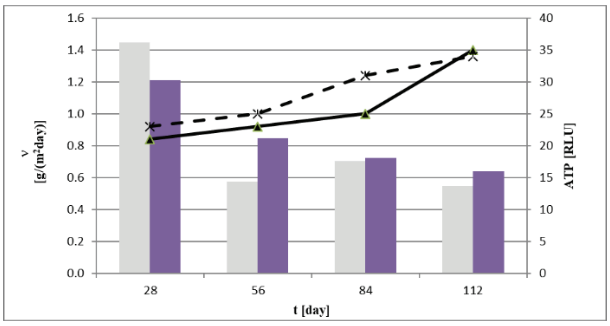

Fig. 5. Correlation between mean values of the gravimetric corrosion rate and ATP measurements for S2 material with protection (light bar and continuous line, respectively) and without cathodic protection (dark bar and dashed line, respectively).

In Figs. 3-5 correlation between corrosion velocity (V) and relative number of microbial cells (ATP) is presented. In all figures the following notation was used: samples with cathodic protection – bright bar for cathodic protection velocity and continuous line for ATP, and for samples without cathodic protection – dark bar and dashed line, respectively.

By comparing the values obtained so far it has been observed that with the development of microorganisms, the weight corrosion rate at which corroded materials are tested is reduced. At the same time, the growth of microorganisms on the studied surfaces was observed in the lag phase.

4 Conclusions

The research results allow for better understanding of the process of biocorrosion in materials used for the construction of gas pipelines in the Lodz Province. Experiments performed revealed that microorganisms involved in biocorrosion of the internal surfaces of the gas lines can migrate with gas flow. Applied ATP measurement and SEM observations for investigation of the bacterial growth rate indicated nearly constant rate of adhesion and growth of microorganisms. It was also noticed that the corrosion rate was decreasing in time. It could be due to the biofilm formation, which in turn could block access to the pipeline surfaces for other corroding agents. The highest gravimetric rate of biocorrosion was observed for cast iron. It is suspected that the observed nearly 100 times higher rate of biocorrosion was caused by much higher content of the carbon in the cast iron. In addition, the results suggest that unsuitable parameters applied for cathodic protection might stimulate the growth of microorganisms and catalyze the biocorrosion.

However, the conclusions based on present research results should not be treated as general concerning all gas pipelines. It is suggested that for better understanding of the biocorrosion processes in the gas lines there should be carried out studies taking into account also different materials and different cathodic protection parameters.

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