Microscopic Evaluation of Concrete Samples from Manholes Exposed on Hydrogen Sulphide

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ABSTRACT

The field test of the sewer system in a rural area was made. The results from two different pressure-gravity systems localized in two settlements were compared. The investigated sewer system operates in serial connection; the sewage from one settlement is pumped to the expansion well in the next one. In both systems, the high concentration of hydrogen sulfide, exceeding 200 ppm, and visible concrete wells corrosion effects were recorded. The samples of corroded concrete from the internal walls of the chosen wells were collected. The results of an electron microscope with the EDS attachment (Energy dispersive X-ray Spectroscopy) analysis showed a significant sulfur content in a concrete surface layer from 11.2% to 64.2% for the first system and from 7.53% to 42.9% for the second one. The exposure of concrete to high concentrations of hydrogen sulfide and relatively high content of sulfur on the surface of concrete might be a reason for hydrogen sulfide corrosion of concrete in the investigated systems.

Keywords: hydrogen sulphide corrosion, biocorrosion, pressure sewage system, hydrogen sulphide

INTRODUCTION

There are several mechanisms of corrosion in sewage systems. In the municipal systems, the concrete elements, i.e. pipelines and manholes, are especially exposed to the hydrogen sulfide corrosion. Retention time in the sewage pump station, given by German design code DIN EN 1671 is 4 hours. Detention time in the whole pressure sewage system (from source to wastewater treatment plant), given by Polish design code PN-EN 1671 (PN-EN 1671:2001. Zewnętrzne Systemy Kanalizacji Ciśnieniowej' 2001) should be less than 8 hours. As the field test shows (Worona 2012; Stachowiak, et al.; Głowacka and Bogusławski 2018), these values are exceeded and wastewater is detained in the system for even several dozen or more hours. Under such conditions, microorganisms use up dissolved oxygen and then conditions are changed into anaerobic. While there

is no dissolved oxygen, bacteria use nitrates and subsequently sulfates (Dąbrowski 2013). Ayoub G. et al. (Ayoub et al. 2004) claim that the sulfate to sulfide reduction does not happen if the concentration of dissolved oxygen is greater than 0.5 mg/ dm^3, Hewdaye, et al. (2006) claim the minimum value as 0.1 mg/dm^3, and Norsker, et al. (1995) – 1 mg/dm^3. The sulfate-reducing bacteria living in the biofilm reduce sulfur from +6 degree to -2. Under anaerobic conditions, divalent sulfur permeated from biofilm to wastewater and forms hydrogen sulphide.

Hydrogen sulfide gas might be a cause of corrosion of the upper elements of manholes, which does not have contact with wastewater. In the lower parts of manhole and pump stations, degradation may also be caused by mechanical corrosion or chemical reactions. On the upper parts, apart from gases, there also might be moisture deposition which favors the microorganism growth.

Gases dissolve in moisture and become substrates for microorganisms. The sulfuric acid, which reacts with the components of concrete causing its degradation, constitutes a metabolism product of the sulfur-oxidizing bacteria. The literature says that *Thiobacillus* bacteria would colonize the surface of concrete only if the pH decreases to 9 (Roberts et al. 2002). The widely assumed theory is that lowering of pH (which initially is between 11–13) is caused by the carbonation process (Wells, et al. 2009; Bowker, et al. 1985). However, Yamanaka et al. (2002) suggest that the sulfur-oxidizing bacteria will grow in the layer even if the pH of the concrete itself ranges from 11–13. In their research, Tazawa EI. et al. (Tazawa, et al. 1994) observed that initially corrosion was caused by carbonic acid and organic acids which are produced by bacteria as well as fungi (Mori et al. 1992). Further pH lowering from 8 to 4 is also caused by bacteria and fungi (Mori et al. 1992). In many samples of corrosion, researchers found a microorganism whose influence on these processes is not well understood (US EPA 1991; Guangming et al. 2015).

The factors contributing to corrosion were outlined in many publications [10, 12, 16, 18]:
- BOD levels
- High sulfate and dissolved sulfide concentration
- High temperatures
- High H_2S concentration
- High turbulence and long detention times
- Low dissolved oxygen levels
- Low water velocity
- Low wastewater pH

MATERIALS AND METHODS

The town covered by the research is located in the West Pomerania province. It is characterized by scattered housing. The tests in the system I were carried out in the period April-June 2018.

In the system II, first series of test were carried out in February 2019, the next one in July 2019. In both systems, the hydrogen sulfide and ammonia concentrations were measured in the manholes. The samples of corroded concrete were taken from the internal walls of wells to measure pH and for a microscope analysis. The hydrogen sulfide concentrations in wells were measured with a Draeger X-am 5000 multi-gas detector equipped with EC-Sensor XXS H2S with a measurement range up to 200.00 ppm. The measurements were performed using an external automatic gas suction pump from different depths of the well. In addition, the ammonia concentration (DraegerSensor XXS NH3, measuring range up to 300.00 ppm) was measured. The pH was measured in a water solution of the concrete samples using a Hach HQ40d pH meter with PHC 301 electrode. A Hitachi TM 3000 scanning electron microscope equipped with EDS unit was used in order to observe the elemental composition spectrum and determine the elemental composition of the analyzed concrete samples.

Sewage system I

This system is a gravity-pressure serial network. Wastewater flows in series of six settlements from S6 to S5 and so on to S1 and wastewater treatment plant. The tests were carried out in expansion wells, where the sewage from the previous settlement expands and further flows gravitationally to the pump station, which pumps it then to the next settlement. Manholes were marked corresponding to the number of towns in which sewage expands, i.e. EW3, EW2, and EW1. The settlements were labelled S1-S6. Figure 1 shows a scheme of the system I. Characteristics of sections from pump stations to studied expansion wells are shown in Table 1.

The estimated retention time in pipelines is from 6 to 27.5 hours. It means that sewage
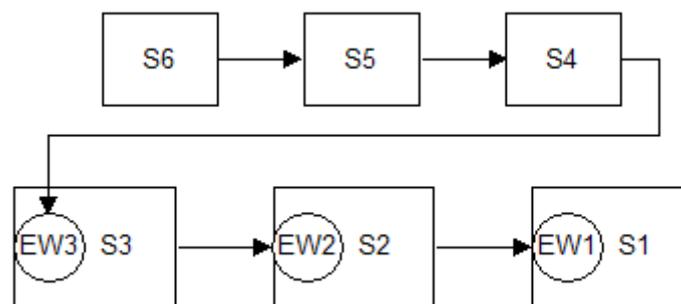

Fig. 1. Scheme of sewage system I.

Table 1. Data about pipelines and estimated sewage detention time in network I

Manhole designation	Pressure pipe length	Diameter	Pipeline capacity	Estimated detention time in pipeline
	[m]	[mm]	[m³]	[h]
I EW3	2715	125	25.9	18.5
I EW2	1671	125	15.9	6
I EW1	3445	125/160	49.3	27.5

is detained for even more than a day (I EW1) in the closed pipe without an air supply, which is much more than design codes recommend (DIN EN 1671; PN-EN 1671:2001). Manholes are made of C35/45 concrete.

Sewage system II

The system includes 9 settlements, which are connected by the pressure-gravity network in the semi-parallel system. Figure 2 shows the scheme of the network. Towns 1 to 5 are marked figuratively as S1–5 because tests were not carried out at these settlements. The measurements were conducted in manholes marked as EW1, EW2 and pump stations – P2, P3.

The characteristics of the studied sections are shown in Table 2. The estimated retention time in pipelines is from 5.4 to 183.7 hours. In the worst case, sewage stays in the pipeline for more than a week (II P2 – II EW2). Such a long retention time results in dissolved oxygen depletion and, anaerobic conditions, anaerobic bacteria growth and consequently fermentation and hydrogen sulfide generation. In the case of the II EW2 expansion well, wastewater runs from two pressure pipelines. In one of them, the retention time is relatively short (5.4 h) but in the second, the retention time is much longer (183.7 h), for this reason, the manhole is endangered by hydrogen sulfide generated in the section with longer detention time. The II P2 and II P1 pump stations are made of polymer concrete. Other manholes and II P3 are made of concrete C35/45. Figure 3 shows the corroded II EW 2 manhole.

RESULTS AND DISCUSSION

Concentration of gases

Table 3 shows measurements of the concentration of hydrogen sulfide and ammonia in the air space of manholes in the network I.

The average concentration of hydrogen sulfide observed was from 67.6 to 82.8 ppm, but in every well, 0 ppm of gas and also concentrations over the measurement range were observed. The observed ammonia concentrations ranged from 121.4 to 134.5 ppm. Similarly as in the case of hydrogen sulfide, very low values (5 to 8 ppm) and the values over the measurement range were observed. In the case of hydrogen sulfide, 7% of all measurements (I EW1) and 21% (I EW3) were over 200 ppm. The ammonia concentrations over 300 ppm were from 13% (I EW1) to 21% (I EW3) of all measurements.

Table 4 shows average the results pertaining to the concentrations of hydrogen sulfide, ammonia and methane in air space of manholes in network II.

The average observed hydrogen sulfide concentrations ranged from 32.5 to over 200 ppm. The concentration of ammonia was from 121 to
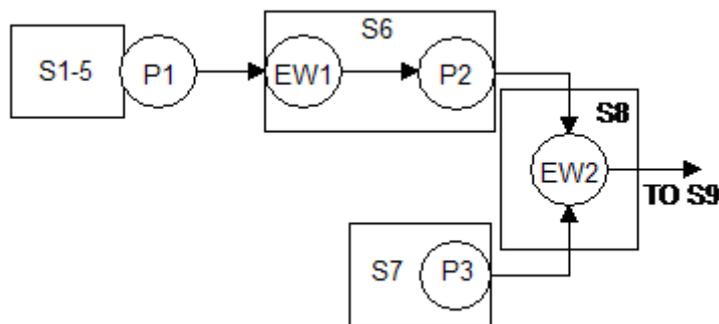

Fig. 2. Scheme of sewage system II.

Table 2. Data about pipelines and estimated sewage detention time in network II

Manhole designation	Section	Diameter [mm]	Length [m]	Pipeline capacity [m³]	Estimated detention time [h]
II P2	P2-EW2	176.2	2139	52.1	183.7
II EW2					
II P3	P3-EW2	110.2	1557	14.8	5.4
II EW2					
II P1	P1-EW1	141	3796	59.2	156.1
II EW1					

Fig. 3. Corroded manhole II EW2.

over 300 ppm. In the II P2 pump station and expansion well EW2 methane were observed. The measurements of gases concentration confirm the odor problem in the network and indicate hydrogen sulfide mechanism of corrosion.

PH of concrete

The pH of the water extract of concrete samples from I EW1 was 3.73. For comparison, a reference concrete was made in the laboratory. The pH of its sample was 10.76 (in literature, fresh concrete has pH 11–13 (O'Connell et al. 2010)). The conductivity of sample from I EW1 was 2.64 mS/cm and laboratory sample 0.61 mS/cm.

Table 5 shows the pH and conductivity measurements in network II.

Low wastewater pH from 2.18 to 3.75 indicates the presence of acids in the water solution. The pH of laboratory concrete was 10.76. In comparison to the laboratory value, a decreasing of pH by 7.01 up to 8.58 was observed. It means intensive processes of corrosion are going on in both systems.

Table 3. The average concentration of gases in the manholes in network I

Manhole designation	H_2S [ppm]					NH_3 [ppm]				
	average	standard deviation	min	max	median	average	standard deviation	min	max	median
I EW3	82.8	88.2	0	>200*	55.0	150.6	133.7	8	>300*	156.0
I EW2	67.6	77.9	0	>200*	31.0	134.1	134.5	6	>300*	40.0
I EW1	69.5	76.7	0	>200*	31.0	126.0	121.4	5	>300*	71.0

* Above the measurement range, which was 200 ppm for hydrogen sulfide and 300 ppm for ammonia.

Table 4. The average concentration of gases in the manholes in network II

Manhole designation	H$_2$S	NH$_3$	CH$_4$
	[ppm]	[ppm]	[%]
II P2	170	290	0.05
II EW1	32.5	129.5	0
II P3**	55	121	0
II EW2	>200*	>300*	0,8

* Above the measurement range, which was 200 ppm for hydrogen sulfide and 300 ppm for ammonia.
** Ferrox was dosed to II P3 pump station.

Microscope analysis

Figures 4, 5, 6 show the EDS microscopic analysis for a sample from network I, manhole I EW3. Table 6 presents the results of the elemental composition analysis of the tested samples from system I. Table 7 presents the results of sample analysis in system II. This data was collected by Bogusławski B. et al. [2019] and here it is presented for comparison with system I. Table 8 presents the elemental composition of a new manhole sample.

System I

Table 6 presents the elemental composition analysis of the tested samples taken from the internal walls of wells in the system I.

The EDS analysis showed that in the system I, the main component in the tested concrete sample is oxygen, constituting from 34.4% to 49.63%. A high share of sulfur from 29.25% to 35.43% was observed, which strongly suggests the occurrence of the a reaction between sulfuric acid and concrete components. Calcium (from 2.85% to 13.50%) and silicon (from 6.3% to 7.65%) were also found in the samples. Carbon was identified only in a sample from well I EW1 – 14.35%.

System II

Table 7 presents the elemental composition analysis of tested samples taken from the internal walls of wells in system II.

In system II, oxygen is also the main component (from 28.1% to 51.42%). Sulfur has high share ranging from 7.53% to 42.9%, which includes hydrogen sulfide corrosion mechanism. Calcium (from 0% to 23.58%) and silicon (0.4%

Table 5. The pH measured in a water solution of concrete from the manholes in network II

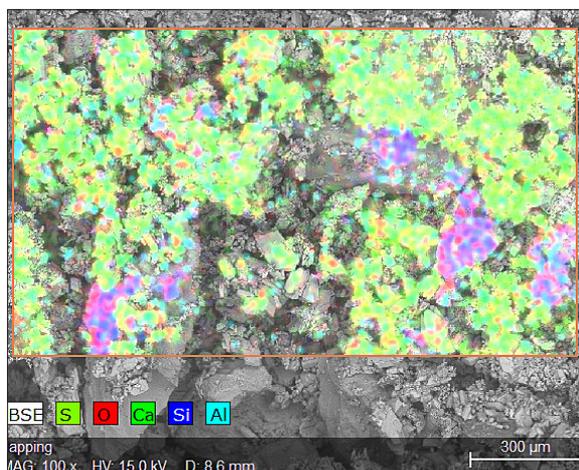| Manhole designation	pH		Average conductivity [mS/cm]
	min	max	
II EW1	2.18	3.52	3.55 ± 1,35
II P3	2.77	3.50	2.65 ± 0,25
II EW2	3.16	3.75	2.7 ± 0,18

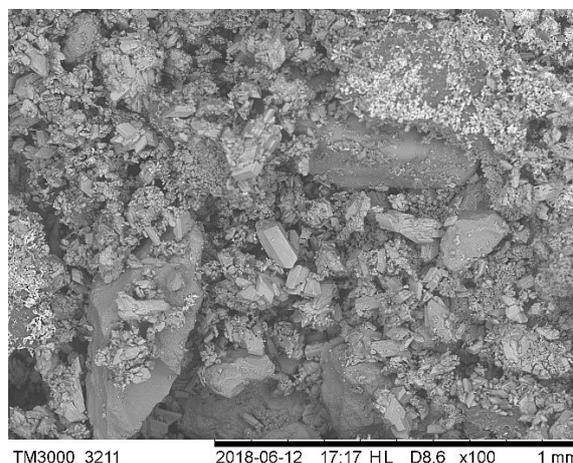**Fig. 4.** Map of identified elements

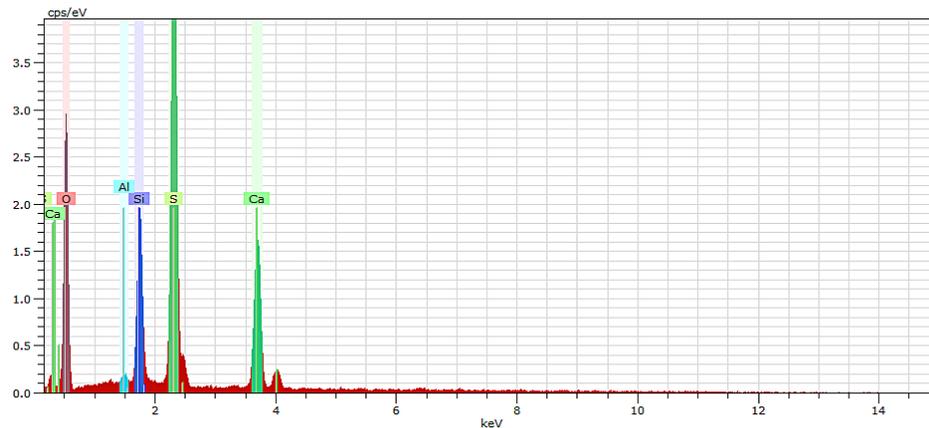**Fig. 5.** SEM image of the external layer of the concrete, mag ×100

Fig. 6. Energy spectrum of elements identified on sample

Table 6. The average percentage participation of elements on the surface of samples [%]

Manhole designation	Elements [%]				
	S	O	Ca	Si	C
I EW3	29,25 ± 23,85	49,63 ± 14,17	13,50 ± 6,94	7,65 ± 7,55	-
I EW2	35,0 ± 21,86	47,92 ± 12,49	10,8 ± 5,05	6,3 ± 5,01	-
I EW1	35,43 ± 12,21	34,4 ± 6,78	2,85 ± 1,80	6,40 ± 6,34	14,35 ± 1,75

Table 7. Average percentage participation of elements on the surface of samples (Bogusławski, et al. 2019)

Manhole designation	Elements [%]				
	S	O	Ca	Si	C
II EW1	14,2 ± 3,25	50,47 ± 1,25	11,93 ± 9,17	2,83 ± 2,31	20,57 ± 15,43
II P2	42,9	28,1	-	0,4	28,7
II P3	7,53 ± 4,17	51,42 ± 7,16	10,17 ± 6,98	9,58 ± 12,16	20,43 ± 18,91
II EW2	20,25 ± 1,18	49,35 ± 1,69	23,58 ± 3,27	4,75 ± 1,91	2,10 ± 2,40

Table 8. The average percentage participation of elements on the surface of the sample from a new manhole (Bogusławski, et al. 2019)

Sample	Elements [%]				
	S	O	Ca	Si	C
New manhole	0	50.43 ± 1.00	19.07 ± 7.93	14.7 ± 5.65	10.27 ± 1.67

to 9.58%) were also observed. An important share of carbon was identified (2.1% to 28.7%).

The sample taken from new manhole contains mostly oxygen (50.43%) and calcium (19.07%). Importantly, no sulfur was found, which indicates a high share of sulfur in the samples from network I and II due to the reactions between wastewater, gases, and components of concrete.

Single concentrations of sulfur were much more varied in network I (standard deviation 12.21–23.85%) than in network II (standard deviation 1.18–4.17%), but the average sulfur share from many photos of the same sample was much more varied in system II than in system I.

CONCLUSIONS

The studied systems have similar characteristic; hence, no significant differences in the results of gases concentrations, pH and elemental composition were observed. The retention times in pipelines are more significant in network II but in both are much higher than recommended in the literature. The oxygen from sewage is used up after several hours, consequently, in the studied systems, most of the time sewage is under anaerobic conditions. During expansion in the expansion well, hydrogen sulphide is released and causes odor and corrosion problems.

High concentrations of hydrogen sulphide were observed, often exceeding 200 ppm. Low pH of water solution of concrete taken from internal walls of manholes (compared to the control sample) from 2.18 to 3.75 indicates the presence of acids, which reacts with concrete components. The EDS analysis showed a high share of sulfur in the surface layer of concrete. In system I, the share was between 29.25–35.43%, wherein the highest observed was even 64.2%. In system II, the share was from 7.53% to 42.9%. It indicates the occurrence of reactions between sulfuric acid and compositions of concrete.

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