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Biomonitoring Studies and Preventing the Formation of Biogenic H_2S in the Wierzchowice Underground Gas Storage Facility

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Abstract: The article discusses the results of biomonitoring research at the Underground Gas Storage (UGS). Hydrogen sulphide, as one of the products of microbiological reaction and transformation, as well as a product of chemical reactions in rocks, is a subject of interest for global petroleum companies. The materials used in this research work were formation waters and stored natural gas. The biomonitoring of reservoir waters and cyclical analyses of the composition of gas stored at UGS Wierzchowice enabled the assessment of the microbiological condition of the reservoir environment and individual storage wells in subsequent years of operation. Investigations of the formation water from individual wells of the UGS Wierzchowice showed the presence of sulphate reducing bacteria bacteria (SRB), such as *Desulfovibrio* and *Desulfotomaculum genera* and bacteria that oxidize sulphur compounds. In the last cycles of UGS Wierzchowice, the content of hydrogen sulphide and sulphides in the reservoir waters ranged from 1.22 to 15.5 mg/dm^3. The monitoring of natural gas received from UGS production wells and observation wells, which was carried out in terms of the determination of hydrogen sulphide and organic sulphur compounds, made it possible to observe changes in their content in natural gas in individual storage cycles. In the last cycles of UGS Wierzchowice, the content of hydrogen sulphide in natural gas from production wells ranged from 0.69 to 2.89 mg/dm^3, and the content of organic sulphur compounds converted to elemental sulphur ranged from 0.055 to 0.130 mg $S_{el.}$/Nm^3. A higher hydrogen sulphide content was recorded in natural gas from observation wells in the range of 2.02–25.15 mg/Nm^3. In order to explain the causes of hydrogen sulphide formation at UGS Wierzchowice, isotopic analyses were performed to determine the isotope composition of $\delta^{34}S_{H_2S}$, $\delta^{34}S_{SO_4}$, $\delta^{18}O_{SO_4}$ in natural gas samples (production and observation wells) and in the deep sample of reservoir water. The results of isotope tests in connection with microbiological tests, chromatographic analyses of sulphur compounds in natural gas collected from UGS Wierzchowice and an analysis of the geological structure of the Wierzchowice deposit allow us to conclude that the dominant processes responsible for the formation of hydrogen sulphide at UGS Wierzchowice are microbiological, consisting of microbial sulphate reduction (MSR). The presented tests allow for the control and maintenance of hydrogen sulphide at a low level in the natural gas received from the Wierzchowice Underground Gas Storage facility.

Keywords: underground gas storage; natural gas; formation waters collected; hydrogen sulphide; organic sulphur compounds; sulphate reducing bacteria

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1. Introduction

The new requirements in the scope of environmental protection, as well as the need to reduce CO_2 emissions in the energy sector, result in an increased natural gas consumption, meaning that it is crucial to ensure regular supplies thereof. Therefore, supply of

natural gas, as the most eco-friendly fuel and the appropriate underground storage facilities (UGS) are a priority and key issue for the national economy. Assurance of energy reserves is also the subject of scientific studies [1,2].

Wierzchowice Underground Gas Storage Facility is the largest natural gas storage facility in Poland, operating since 1995, established in the carbonate deposits of the Zechstein Main Dolomite and Rotliegend, separated by cupro-bearing shales [3].

The presence of sulphur compounds in natural gas can interfere to the quality of gas, especially in UGS. Sulphur compounds, which occur in water extracted in the process of natural gas extraction, get into the aquatic environment in the form of sulphates, sulphides, and hydrogen sulphide. The maximum concentration of hydrogen sulphide depends on the geological structure of the deposit and its hydrogeological properties. The decisive role in these conditions is played by biological sulphate reduction processes with the participation of anaerobic bacteria (SRB), the source of organic matter for bacteria in metabolic reactions is bituminous substance.

One of the main representatives of the bacteria of the SRB group—*Desulfovibrio desulfuricans* has the ability to use organic compounds of various chemical structures, from hydrocarbons, fatty acids, alcohols, and other substrates [4].

These bacteria have the ability to reduce not only sulphates, but also sulphites, various polysulfides, and colloidal sulphur (except for crystalline sulphur). In the sulphate reduction reaction, sulphate sulphur is reduced to sulphides and hydrogen gas is oxidized to water. Carbon from organic substances is oxidized to carbon dioxide. Energy from this process is used for growth, reproduction, and biosynthesis in bacterial cells.

SRB can only oxidize those chemical compounds, the interaction of which with sulphates causes a release of energy. The antagonistic group of microorganisms with oxidative activity often accompanies SRB in a deposit, which is a source of microbial hydrogen sulphide, is often found in many deposits around the world [5]. One of the methods of fighting biogenic contamination is the use of biocide/H_2S scavenger products. In the global oil industry, nitrate-based treatment is also used [6] in order to inhibit reduction reactions in favor of the oxidation processes of reduced sulphur compounds and to activate a group of microorganisms beneficial for a deposit.

The main objective of the research is to assess the current condition of individual wells based on laboratory analyses of formation media, and then, on the basis of the obtained results, to develop effective methods for neutralizing hydrogen sulphide and reducing its content in the natural gas recovered to a value compliant with the applicable EU standards in this regard [1]. As part of the works in question, microbiological tests and chemical analyses of formation waters are performed, along with their interpretation. At the same time, analyses of natural gas collected from all available wells of the Wierzchowice UGS facility are carried out to determine hydrogen sulphide and the other sulphur compounds in individual wells. Conducting research on formation waters and stored gas is extremely important, as it allows to determine to what extent (in individual research cycles and series) parameters such as the content of individual analyzed sulphur compounds, and to what extent microbiological processes of H_2S developing in the formation occur and change.

Processes based on biological transformations of sulphur compounds, including reduction reactions and the accompanying oxidative reactions, constitute one of many types of chemical and biochemical changes taking place in the discussed environment [7,8]. In addition to typical chemical factors, the course and intensity of these reactions are also largely due to specific groups of microorganisms whose action begins in the formation, often even before the gas storage is created. Some of the biogenic processes found in this environment are also the result of the action of microorganisms introduced from the outside into the formation zone, which in many cases may be even more dangerous than the typical autochthonous microorganisms [9–13]. The discussed research makes it possible to identify the intensity and determine qualitatively and quantitatively the microbiologi-

cal and chemical processes in this environment. Maintaining control over biogenic phenomena is currently an important factor in improving the operation of the UGS facility. Also, industrial treatments appropriately planned and carried out in previous years on storage wells allow for reducing the problems caused by the processes of biological hydrogen sulphide formation in the petroleum industry.

As part of biomonitoring tests, the following are performed: (i) microbiological tests (quantitative method, serial dilution method, and sequencing method) of formation waters focused on the presence of SRB (sulphate reducing bacteria), capable of producing H_2S in the reservoir [5,14–19] (ii) microbiological tests (qualitative method and sequencing method) of formation waters for the presence of bacteria which oxidize hydrogen sulphide and reduced sulphur compounds [14,15,20–22], (iii) analyses of the chemical content of hydrogen sulphide and sulphides in formation waters, (iv) research on the effectiveness of biocides [6,23] and hydrogen sulphide scavengers in relation to biogenic hydrogen sulphide and determination of their dosage in UGS conditions based on microbiological and chemical tests of reservoir fluids [6,23–28], (v) analysis of the composition of gas pumped and recovered from UGS, and (vi) analysis of the composition of gas pumped and recovered from UGS.

Works involving biomonitoring studies on the polish Wierzchowice Underground Gas Storage facility are being carried out from the first cycle of operation of the facility until 2020. The research works are carried out annually on all available storage wells, in three sampling series during the operational cycle.

It should be noted that in recent years, a number of studies have been carried out on the elimination and limitation of the activity of unfavorable microorganisms (mainly SRB) [29,30].

2. Materials and Methods

2.1. Formation Waters

For chemicals analyses, to each glass bottle, before collecting the samples of formation water, 5 mL of cadmium acetate solution (which absorbed S^{2-} and generated CdS) were added. More specific descriptions of the research methodology are presented below.

The samples of formation water for microbiological analyses, extracted from the separators of exploitation UGS wells were placed in sterile bottles (full volume). The samples were extracted from the wells: W-28, W-33, W-36, and horizontal wells: WM-A2H, WM-A5H, WM-B2H, WM-B3H, WM-B4H, WM-B5H, WM-B6H, WM-B7H, and seven samples of collective water (from all the exploitation wells). Simultaneously, from the same well separators were taken ca. 50 mL of formation water for chemical analyses, into the 250 mL bottle. Each bottle for contains 5 mL of cadmium acetate solution (concentration: 10% vol. of cadmium acetate in the 5% vol. of acetic acid).

The methodology of SRB isolation includes the quantitative method, based on incubation in the liquid medium, serial dilution method, membrane filtration method, incubation in anaerostats using the agar nutrient medium, and sequencing method.

The methodology of sulphur-oxidizing bacteria isolation includes the qualitative method, based on incubation in the liquid medium, microscopy analysis, and sequencing method. After the immediate delivery to the laboratory each sample (1 mL of formation water) was put into the sterile 50 mL bottles and was fill up by Starkey's liquid medium (full volume). In the case of SRB presence, in the liquid medium appears black coloring and characteristic smell of hydrogen sulphide, after the 30-day incubation in the 30 °C. Simultaneously, each sample (1 mL of formation water) was put into the sterile 100 mL flask and was fill up by liquid medium for the neutrophilic sulphur-oxidizing bacteria and acidophilic sulphur-oxidizing bacteria. After the 45-day incubation, 1 mL of bacterial suspension was put into the fresh medium in 100 mL bottle. When the growth of bacteria appears, samples are sent to CB DNA Center (Poznan, Poland) for the next stage of analyses (16S rRNA sequencing). The same procedure applies to the samples containing SRB.

Hydrogen sulphide in the formation water was determined iodometrically. The method consists in determining the content of S^{2-} sulphide ions in solutions by titration of samples with sodium thiosulphate in the presence of iodine, and then in the presence of starch as an indicator. It is an oxidation-reduction method in which iodine oxidases hydrogen sulphide to sulphur. Prior to the determination, sulphide ions are absorbed from the test solution using an acidified cadmium acetate solution. The content of H_2S and sulphides dissolved in water is determined from the loss of iodine in a specific amount of the standard iodine solution [31].

Sulphide ions were absorbed directly during sampling, and then, after delivery to the laboratory, the samples were titrated with 0.05% sodium thiosulfate ($Na_2S_2O_3$) solution.

Description of the PCR Method

Bacterial suspensions obtained from formation waters were sent to the CB DNA Center (Poznan, Poland) for the next stage of analyses. Extraction of genomic DNA of bacteria was carried out using Genomic Mini Kit (A & A Biotechnology, Poznan, Poland), following the manufacture's instruction. In the amplification of gene fragment 16S rRNA were used universal starters [32,33]. PCR reaction included 40 cycles. For the direct sequencing, we used BigDye terminator v 3.0 Ready Reaction Cycle Sequencing Kid (Amersham Bioscience, UK Ltd., Buckinghamshire, UK), which contained thermostable DNA polymerase (AmpliTag DNA Polymerase). The products of sequencing reactions were purified followed the manufacture's instruction. Purified products were committed using analyzer ABI PrismTM 3100 Genetic Analyzer (Applied Biosystems, Foster City, CA, USA). The obtained results for two complementary strands of a DNA were developed using BioEdit programme ver. 7.1.9. The next stage was to compare obtained results (sequences) to the sequences in NCBI GenBank, using BLAST program (ang. Basic Local Alignment Search Tool).

2.2. Natural Gas

The tested gas came from individual separators of horizontal wells of cluster A (WM-A1bH, WM-A2H, WM-A3H, WM-A4H) and cluster B (WM-B1H, WM-B2H, WM-B3H, WM-B5H, WM-B6H, WM-B7H), as well as from separators of observation wells of the UGS Wierzchowice. Natural gas samples were taken directly into Supelco gas pipettes, which are equipped with a septum that allows direct gas intake for chromatographic analysis. The pipettes are made of chemically inert glass, which does not react with hydrogen sulphide and organic sulfur compounds. Before gas sampling, the pipettes were filled with argon (inert gas) to avoid air in the samples taken. Following the above recommendations allows for obtaining reliable results of chemical analyses of natural gas. Quantitative and qualitative determination of hydrogen sulphide and organic sulphur compounds present in natural gas were performed by gas chromatography using Perkin Elmer Clarus 580 GC chromatograph equipped with parallel detectors: flame photometric detector—FPD (selective for sulphur compounds) and flame ionization detector—FID (selective for hydrocarbons). A PE-Q capillary chromatography column (30 m × 0.53 mm), at a flow rate of 7 mL/min of hydrogen as carrier gas. The following operating conditions of the chromatographic system were applied: photomultiplier voltage = 0.15 mV, temperature of FPD and FID detectors = 290 °C, PPS injector temperature = 260 °C, furnace temperature: 60 °C—isothermal characteristics 1 min, 60–130 °C temperature rise 5 °C/min, 130–250 °C—temperature rise 30 °C/min, 240 °C isothermal trajectory—5 min, sample division between detectors FPD and FID = 3:1.

For the quantitative and qualitative determination of hydrogen sulphide and organic sulphur compounds in natural gas, a set of certified gaseous reference mixtures from Air Products was used. The stability of the chromatographic system was found on the basis of the statistical evaluation of the reproducibility of the results of the analysis of control standard mixtures. It was assumed that if the dispersion of results around the arithmetic

mean is within twice the standard deviation, the chromatographic system is stable and the results of the analyses are repeatable. Standard concentrations of sulphur compounds covered the entire range of their occurrence in the tested natural gas. Calibration curves representing the dependence of the FPD detector signal on the concentration of the determined sulphur compounds were analyzed for individual sulphur compounds. These curves were used to determine individual sulphur compounds in natural gas from UGS Wierzchowice.

2.3. Isotopic Composition of Hydrogen Sulphide

Isotope tests were carried out in the Mass Spectrometry Laboratory of the Institute of Physics at the Maria Curie-Skłodowska University (UMCS) in Lublin. The preparation of samples for isotope studies was performed according to the methodology presented in the US Geological Survey report, recommended for isotope analyses. In order to obtain a sulphur compound from hydrogen sulphide for isotope analysis, the hydrogen sulphide contained in the natural gas was absorbed in a 10% cadmium acetate solution acidified with a few droplets of concentrated acetic acid. The process was carried out in two serially connected bubblers. The obtained CdS precipitate was rinsed with distilled water and then converted to Ag_2S by addition of $AgNO_3$ solution.

Rinsed Ag_2S precipitate was dried in oven at 80 °C and a portion of 10 mg was well mixed in agate mortar with 20 mg of Cu_2O. Subsequently this mixture was loaded into a small copper boat in which the sample was oxidized to SO_2 at 800 °C in a vacuum line with sealed at one end quartz tube reactor [34,35]. The obtained SO_2 gas was purified cryogenically from water and CO_2 according to Kusakabe [36].

2.4. Isotopic Composition of Sulphates

Formation water samples for isotopic sulphate analysis were collected with a depth sampler from the bottom of selected wells. $BaSO_4$ was precipitated by means of an acidified (with HCl) solution of $BaCl_2$. The precipitate was washed by distilled water several times until the disappearance of chloride ions, which were tested in the remaining filtrate using 10% $AgNO_3$ solution. Clean $BaSO_4$ precipitates were dried in small breakers in an oven at 100 °C and then subjected to the procedures for quantitative extraction of sulphur and oxygen for isotope analysis. Under the conditions described no influence of isotope exchange between sulphate ions and water was observed due to low ambient temperatures (18 °C) and the escape of a major fraction of HCl from the beakers to the atmosphere within a few hours.

The isotope ratios ($\delta^{34}S$ and $\delta^{18}O$) were determined by means of a dual inlet and triple collector mass spectrometer on SO_2 and CO_2 gases, respectively. SO_2 was extracted by the method developed in the Lublin laboratory [37–39], whereas CO_2 was prepared by the method described by Mizutani [40] and improved by Halas et al. [41].

We used 5 mg of $BaSO_4$ in each preparation. The reproducibility of both analyses, obtained on the basis of replicated SO_2 extractions, was about 0.16‰. Delta values were normalized to the VCDT and the VSMOW scales by analysis of the NBS-127 standard, for which we accepted $\delta^{34}S = 21.14$‰, after Halas and Szaran [37], and $\delta^{18}O = 8.73$‰ according to the recent calibration performed vs. VSMOW by Halas et al. [41].

The scheme of monitoring studies is presented in Figure S1.

2.5. Biocide Characteristics

The attempt to eliminate microorganisms is connected with application of chemical agents which demonstrate biogenic property, which, apart from the physical method is the most popular and effective technique of elimination of microbiological contamination. The selection of appropriate biocidal agents requires the consideration of factors which have an impact on the process of elimination of contamination in a specific environment. In the oil industry, mainly those agents are needed which show the widest scope of action.

Frequently, triazine derivatives are used in the world industry. Performed laboratory examination covered tests for effectiveness of activity of a biocidal substance. According to available literature [42] sym-triazine is a chemical product which has strong antibacterial properties. It is commonly used as preservative for lubricants and other industrial applications.

The examined antibacterial product, being derivative of triazine, is the result of reaction of formaldehyde with methylamine. The principle of biocidal action of sym-triazine consists in splitting off of a fragment of formaldehyde. Figure 1 shows a chemical structural formula of hexahydro-1,3,5-tris(hydroxyethyl)-s-triazine ($C_9H_{21}N_3O_3$).

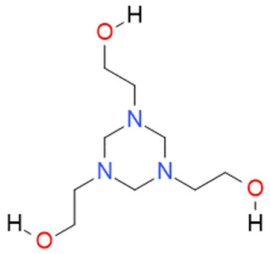

Figure 1. Hexahydro-1,3,5-tris(hydroxyethyl)-s-triazine chemical structural formula.

3. Results

3.1. Microbial Test on Formation Waters

Due to the strategic nature of the facility and other legal restrictions (reservations in contracts), this article presents only selected data obtained as part of the facility's biomonitoring. The results of the tests from the previous operating cycle 2016/2017 and 2019/2020 are presented in the tables below. The article contains two tables with the results of tests on formation waters from cycle XXII (Tables 1 and 2) and comparative tables with the results from 2013 and 2014 (Tables 3 and 4, cycles XIX–XX).

Table 1. The results of microbiological and chemical tests on formation waters collected from Wierzchowice UGS wells—XXII operational cycle (2016/2017).

Exploitation Well	pH of Formation Water	Content of H_2S and Sulphides (mg/L)	Sulphate Reducing Bacteria (CFU/100 mL)	Sulphur Compounds Oxidizing Bacteria	
				Thiobacillus spp. (Growth of Bacteria on Neutrophilic Sulphur-oxidizing Bacteria Medium)	*Acidithiobacillus* spp. (Growth of Bacteria on Acidophilic Sulphur-Oxidizing Bacteria Medium)
WM-B4H	7.01	0.00	-	-	-
WM-B7H	5.22	0.00	-	-	+
W-collective water (from all wells)	5.10	0.48	-	-	-

(+)—bacterial growth was found, (-)—not found.

Table 2. The results of microbiological and chemical tests on formation waters collected from Wierzchowice UGS wells—XXII operational cycle (2016/2017).

Exploitation Well	pH of Formation Water	Content of H_2S and Sulphides (mg/L)	Sulphate Reducing Bacteria (CFU/100 mL)	Sulphur Compounds Oxidizing Bacteria	
				Thiobacillus spp. (Growth of Bacteria on Neutrophilic Sulphur-Oxidizing Bacteria Medium)	*Acidithiobacillus* spp. (Growth of Bacteria on Acidophilic Sulphur-Oxidizing Bacteria Medium)
WM-A5H	4.06	1.49	-	-	-
WM-B4H	6.80	2.15	-	+	-
WM-B5H	5.04	1.97	-	-	-
WM-B7H	5.15	3.08	-	-	-
W-collective water/I (from all wells)	5.18	1.22	-	-	-
W-collective water/II (from all wells)	5.03	3.95	-	-	+
W-collective water/III (from all wells)	5.00	3.20	-	-	+
W-collective water/IV (from all wells)	5.09	2.97	-	-	+

(+)—bacterial growth was found, (-)—not found.

Table 3. The results of microbiological and chemical tests on formation waters collected from Wierzchowice UGS wells—XVIII operational cycle (2013/2014).

Exploitation Well	pH of Formation Water	Content of H_2S and Sulphides (mg/L)	Sulphate Reducing Bacteria (CFU/100 mL)	Sulphur Compounds Oxidizing Bacteria	
				Thiobacillus spp. (Growth of Bacteria on Neutrophilic Sulphur-oxidizing Bacteria Medium)	*Acidithiobacillus* spp. (Growth of Bacteria on Acidophilic Sulphur-Oxidizing Bacteria Medium)
WM-A2H	7.00	15.5	10	+	-
WM-B3H	4.97	0.00	-	-	-
WM-B5H	5.09	0.00	-	-	-
W-33	4.92	2.72	-	-	-
W-collective water (from all wells)	5.16	3.27	-	-	-

(+)—bacterial growth was found, (-)—not found.

Table 4. The results of microbiological and chemical tests on formation waters collected from Wierzchowice UGS wells—XIX operational cycle (2014/2015).

Exploitation Well	pH of Formation Water	Content of H_2S and Sulphides (mg/L)	Sulphate Reducing Bacteria (CFU/100 mL)	Sulphur Compounds Oxidizing Bacteria	
				Thiobacillus spp. (Growth of Bacteria on Neutrophilic Sulphur-Oxidizing Bacteria Medium)	*Acidithiobacillus* spp. (Growth of Bacteria on Acidophilic Sulphur-Oxidizing Bacteria Medium)
W-28	5.24	1.31	-	-	-
W-33	6.10	5.23	-	-	-
W-36	5.30	0.00	-	-	-
WM-A1bH	5.29	1.86	-	-	-
WM-A3H	6.95	14.25	10	+	-
WM-B2H	5.21	0.00	-	-	-
WM-B5H	4.14	0.00	-	-	+
WM-B6H	5.71	5.07	-	-	-
W-collective water (from all wells)	5.02	2.30	-	-	-

(+)—bacterial growth was found, (-)—not found.

The isolated bacterial strains from the studied reservoir waters of UGS Wierzchowice were identified using molecular biology techniques (DNA sequencing method) to the species level with a satisfactory level of sequence identity (Table 5).

Table 5. Species status of microorganism strains.

Strain Designation	Identification by Classical Methods	Identification by Sequencing	% Identity Most Similar Sequence in GenBank
W_1	*Desulfovibrio* sp.	*Desulfovibrio desulfuricans*	99%/DSM 642
W_2	*Desulfovibrio sp*	*Desulfovibrio vulgaris*	98%/DSM 644
W_3	*Desulfotomaculum* sp.	*Desulfotomaculum nigrificans*	99%/DSM 574
W_4	*Desulfotomaculum* sp.	*Desulfohalotomaculum halophilum*	99%/DSM 11559
W_5	*Acidithiobacillus* sp.	*Acidithiobacillus ferrooxidans*	99%/DSM 14882
W_6	*Acidithiobacillus* sp.	*Acidithiobacillus thiooxidans*	97%/DSM 14887
W_7	*Thiobacillus* sp.	*Thiobacillus thioparus*	96%/DSM 505

Among the results from the XVIII and XIX cycles, the presence of sulphate-reducing bacteria in 2 wells out of 14 tested formation water samples was recorded, while in the latest presented biomonitoring analyses (XXII operational cycle) no occurrence of hydrogen sulphide-forming bacteria was recorded. The diagram shows the changes in the content of H_2S in the formation waters in selected storage wells during operational cycles XVIII–XXII (Figure 2).

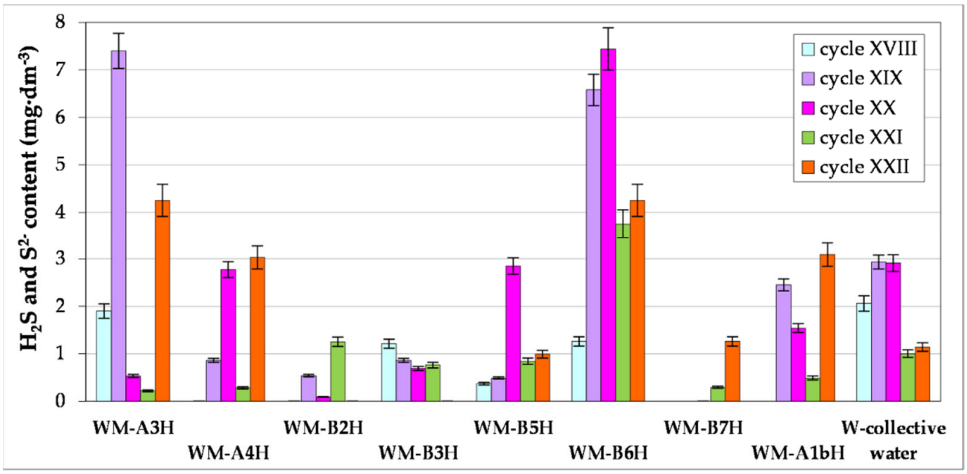

Figure 2. Content of hydrogen sulphide and sulphides in formation waters of selected Wierzchowice UGS wells; cycles XVIII-XXII (average values from three series for every well in subsequent cycles).

In the course of several years of research, it can be noted that the highest levels of hydrogen sulphide are recorded in those wells where previously active anaerobic sulphate reducing bacteria were found.

High levels of hydrogen sulphide in formation fluids are usually accompanied by elevated levels of H_2S in natural gas recovered from exploitation well or from adjacent wells. Moreover, the contamination first appears in the formation water, and then the hydrogen sulphide gradually penetrates into the stored natural gas. The results of the research in the case of waters from the WM-A2H and WM-A3H horizontal wells (Tables 3 and 4) indicate a high level of hydrogen sulphide in the tested waters, which is related to the presence of active sulphate reducing bacteria. Increased levels of hydrogen sulphide (over 10 mg/dm^3 of water), in addition to the previously mentioned wells, were recorded in previous years, i.e., before cycle XVIII, in tests of reservoir fluids from the WM-B6H well (formation water). Currently, as a result of the repeated injection of H_2S scavenger solutions directly into the formation, the value for this well is much lower and amounts to 5.07 mg S^{2-}/dm^3 of formation water (Table 4). The results of the tests on the level of hydrogen sulphide in waters from exploitation wells are characterized by variability in subsequent cycles. On the other hand, the processes of natural oxidation of H_2S were found in the formation water WM-B7H (Table 1), WM-B4H and samples of collective water (Table 2), WM-A2H (Table 3) and in the formation waters WM-A3H and WM-B5H.

3.2. Results of Natural Gas Research

From the XIX cycle of the operation of UGS (2014), systematic monitoring of the composition of gas collected through horizontal wells located in the new Center of UGS wells was introduced: 5 exploitation horizontal wells of cluster A (WM-A1bH, WM-A2H, WM-A3H, WM-A4H, WM-A3H) and 7 exploitation horizontal wells of cluster B (WM-B1H, WM-B2H, WM-B3H, WM-B4H, WM-B5H, WM-B6H, WM-B7H). In individual work cycles of UGS Wierzchowice, the composition of gas from parametric (observation) wells and horizontal clusters A and B was analyzed. The tests were carried out in three series at different levels of gas depletion from the storage: low—series I, medium—series II, and high—series III. The results of the analysis of the hydrogen sulphide content in the gas are presented in Figures 1 and 2. Over research cycles XIX–XXII, the gas from the wells was characterized by the highest hydrogen sulphide content: WM-B6H (2.89–3.03 mg/Nm^3), WM-A1bH (1.08–2.99 mg/Nm^3) and WM-B2H (1.02–2.48 mg/Nm^3). Gas from the remaining wells during the research period contained hydrogen sulphide at a level not exceeding 2 mg/Nm^3. The hydrogen sulphide content in the collective gas was 0.99 mg/Nm^3 (Figure 3).

Chromatographic analyses of natural gas from the selected parametric wells (i.e., W-1, W-3, W-6, W-7, W-25, W-29, W-42 and W-45) performed in cycles XIX–XXII UGS operation showed that the content of hydrogen sulphide was at different levels. The highest content of H_2S was found in the first test series in gas from the W-25 and W-29 wells. The content of hydrogen sulphide in gas from the W-29 well in the XIX cycle was at the level of: 18.73–28.41 mg H_2S/Nm^3, in the XX cycle the content of hydrogen sulphide in the well slightly increased to the value of 22.71–32.24 mg H_2S/Nm^3). However, in cycles XXI–XXII, it dropped to the following range: 15.48–17.78 mg H_2S/Nm^3. The content of organic sulphur compounds in the gas from the W-25 and W-29 wells was 0.257 mg of $S_{el.}/Nm^3$ (W-25) and 0.189 mg $S_{el.}/Nm^3$ (W-29). In the gas from the remaining parametric wells W-1, W-3, W-6, W-7, W-42 and W-45, the hydrogen sulphide content ranged from 1.45 to 2.79 mg/Nm^3, and the total the content of organic sulphur compounds ranged from 0.094 to 0.147 mg $S_{el.}/Nm^3$ (Figure 4).

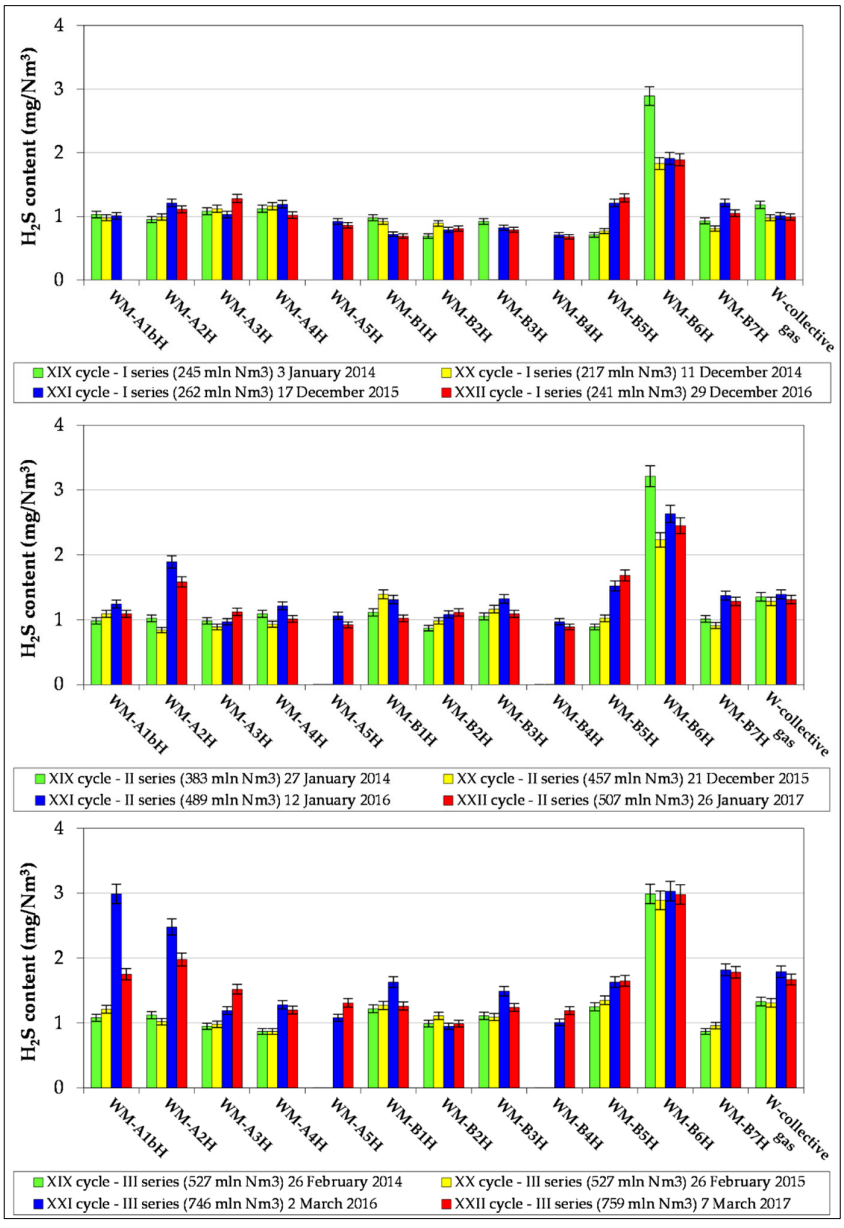

Figure 3. A comparison of hydrogen sulphide content in gas from operational horizontal wells in clusters A and B of the Wierzchowice Underground Gas Storage facility (series I–III).

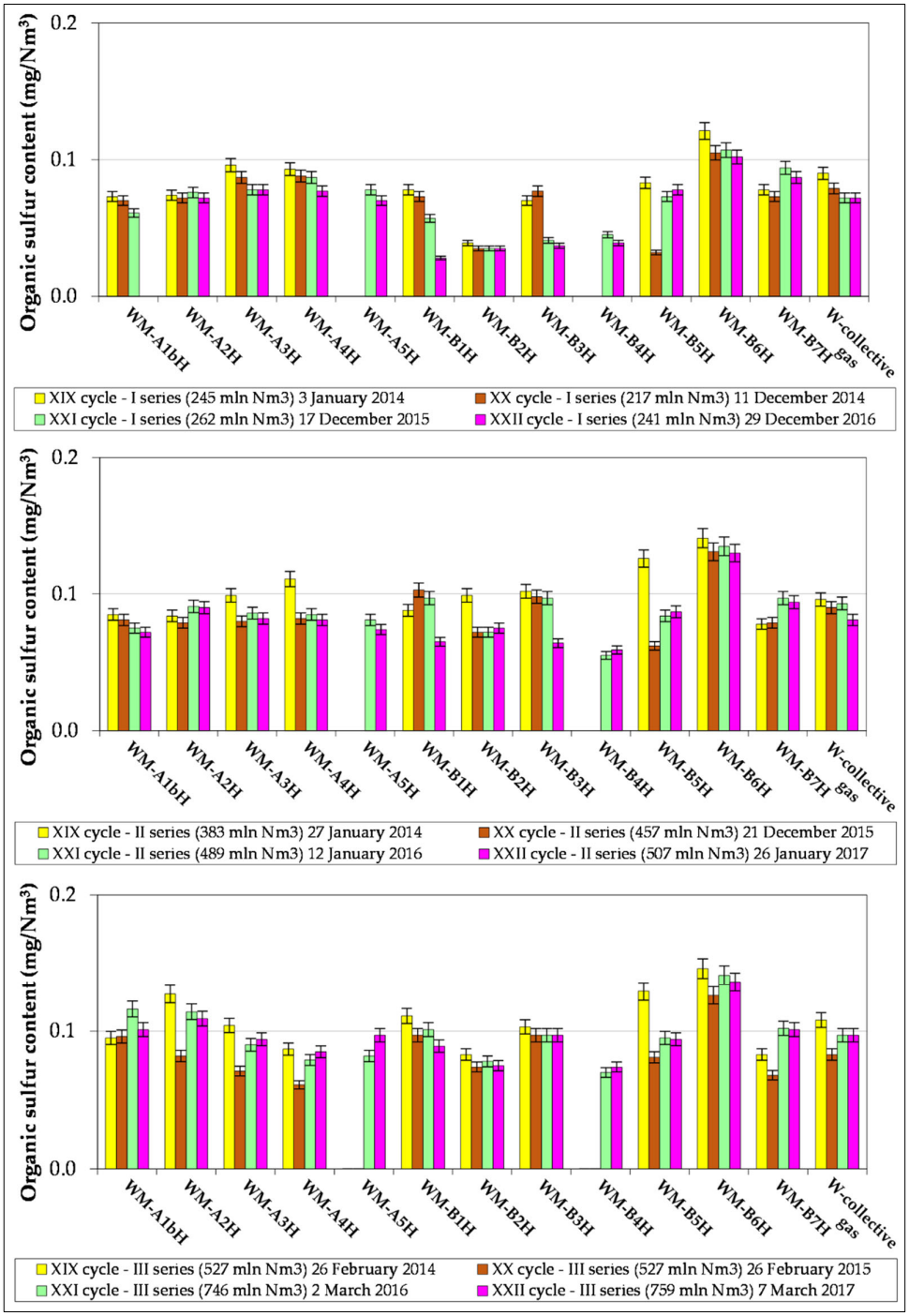

Figure 4. A comparison of the content of organic sulphur compounds in the gas from the exploitation horizontal wells of the A and B clusters of UGS Wierzchowice (series I–III).

In the last tested UGS operating cycle, three series of measurements were carried out in the scope of testing the content of hydrogen sulphide and organic sulphur compounds in the recovered gas. Supplemental Table S1 shows data for 13 gas samples taken from Wierzchowice UGS (I measurement series—initial exploitation phase), and Supplemental Table S2 shows data for 13 gas samples (II measurement series—middle exploitation phase). Supplemental Table S3 presents the data from the chromatographic analyses of 13 gas samples taken from Wierzchowice UGS (III measurement series—final exploitation

phase) (Figure 5). Particular natural gas collections took place with a varying degree of depletion of the underground storage.

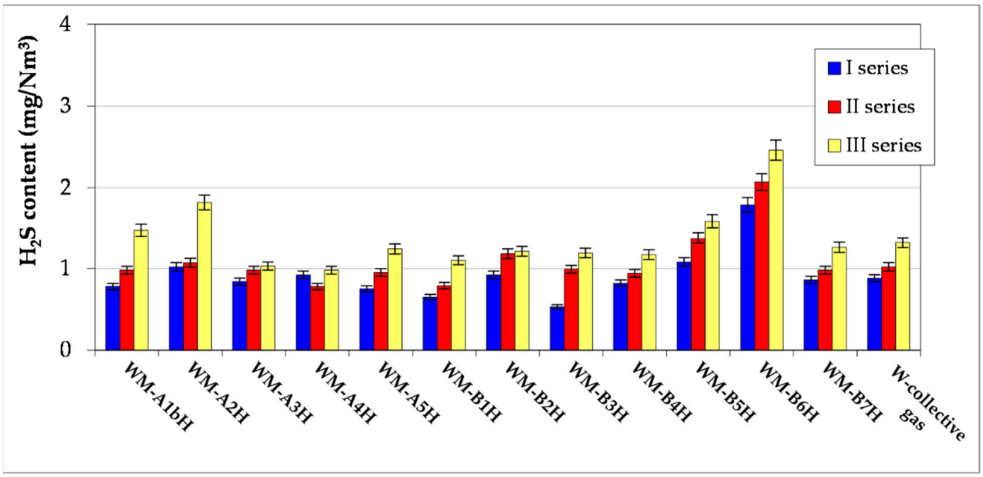

Figure 5. A comparison of H_2S content in natural gas from individual horizontal wells in the XXV exploitation cycle.

The hydrogen sulphide content in the gas from the horizontal wells of Wierzchowice UGS, determined by means of chromatographic analyses, remained at a low level: WM-A1bH (0.78–1.58 mg/Nm^3), WM-A2H (1.02–1.82 mg/Nm^3), WM-A3H (0.84–1.03 mg/Nm^3), WM-A4H (0.78–0.98 mg/Nm^3), WM-A5H (0.75–1.24 mg/Nm^3), WM-B1H (0.65–1.10 mg/Nm^3), WM-B2H (0.92–1.21 mg/Nm^3), WM-B3H (0.53–0.82 mg/Nm^3), WM-B4H (0.82–1.17 mg/Nm^3), WM-B5H (1.08–1.59 mg/Nm^3), WM-B6H (1.79–2.46 mg/Nm^3) and WM-B7H (0.86–1.26 mg/Nm^3). The concentration of hydrogen sulphide was also low in the collective gas, ranging from 0.88 to 1.32 mg/Nm^3.

Only in the gas from the WM-B6H well, a slightly higher content of hydrogen sulphide was recorded during the II and III series of measurements (2.07–2.46 mg/Nm^3). The determined level of hydrogen sulphide contamination of gas from horizontal wells in clusters A and B: WM-A1bH, WM-A2H, WM-A3H, WM-A4H, WM-A5H, WM-B1H, WM-B2H, WM-B3H, WM-B4H, WM-B5H, WM-A6H, and WM-B7H at present poses no threat to the gas quality. However, the increased content of H_2S in the gas from the WM-B6H well during the II and III series of measurements is worrying. The increased content of hydrogen sulphide in the gas from the WM-B6H well was already demonstrated during the monitoring of the gas composition carried out in cycles XII (2006/2007) to XIV (2008/2009) of the operation of Wierzchowice UGS. In the XIV cycle, the content of hydrogen sulphide determined by chromatography during the 1st series was 5.32 mg/Nm^3, and in the II series it slightly increased to the level of 6.38 mg/Nm^3. However, in the III test series, it exceeded the permissible content of H_2S (7 mg H_2S/Nm^3), achieving a level of 7.12 mg/Nm^3. Despite the fact that in the current, XXV (2019/2020) cycle of the Wierzchowice Underground Gas Storage facility, the hydrogen sulphide content in the gas is lower (1.79–2.46 mg H_2S/Nm^3) compared to that determined in the XIV cycle, it is a signal to continuously monitor the degree of contamination with sulphur compounds in the gas from this well in order to take immediate preventive action in the event of a further significant increase in the hydrogen sulphide content.

Chromatographic analyses of gas composition from horizontal wells performed in the XXV cycle of UGS exploitation: WM-A1bH, WM-A2H, WM-A3H, WM-A4H, WM-A5H, WM-B1H, WM-B2H, WM-B3H, WM-B4H, WM-B5H, WM-B6H, and WM-B7H made it possible to identify and determine the quantitative composition of organic sulphur compounds, i.e., methyl mercaptan, ethyl mercaptan, i-propyl mercaptan, n-butyl mercaptan, and dimethyl sulphide. The distribution of the content of organic sulphur compounds is

shown in Figure 6 for gas samples taken during the third series of measurements. The analyzed gas from individual wells contains dimethyl sulphide as well as ethyl, i-propyl and n-butyl mercaptans in comparable amounts. The n-methyl mercaptan in the tested gas occurs in slightly smaller amounts.

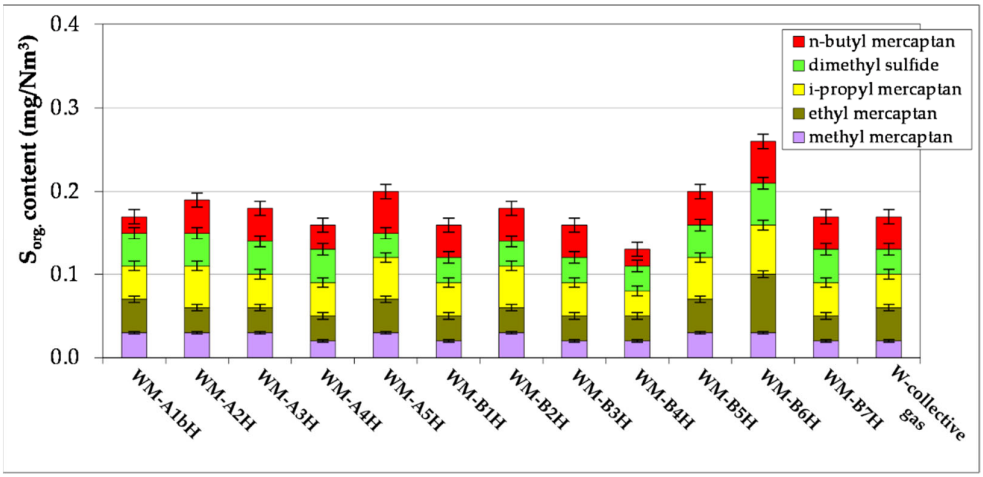

Figure 6. A comparison of the content of organic sulphur compounds in natural gas from individual horizontal wells in clusters A and B of the Wierzchowice Underground Gas Storage facility in the XXV exploitation cycle (III measurement series).

The highest total content of organic sulphur compounds, calculated as elemental sulphur, was recorded in the gas from the WM-B6H well in the amount of 0.125 mg $S_{el.}$/Nm³. In the remaining horizontal wells, it was found that the total content of organic sulphur compounds is at a much lower level: 0.029–0.097 mg $S_{el.}$/Nm³ (Figure 7).

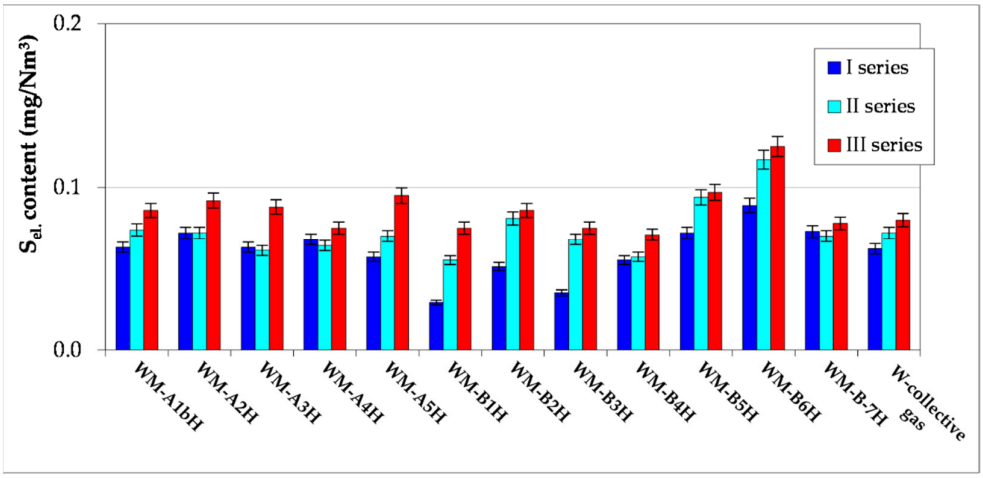

Figure 7. A comparison of the total content of organic sulphur compounds converted to Sel. in natural gas from individual horizontal wells of the Wierzchowice Underground Gas Storage facility in the XXV exploitation cycle.

The composition of natural gas from the horizontal wells in clusters A and B was monitored during the third test series from the XIX cycle of the Wierzchowice Underground Gas Storage facility. In the XIX and XX cycles of UGS Wierzchowice, a chromatographic analysis was carried out of gas from horizontal wells in cluster A (WM-A1bH, WM-A2H, WM-A3H, WM-A4H) and cluster B (WM-B1H, WM-B2H, WM-B3H, WM-B5H, WM-B6H and WM-B7H). On the basis of the obtained results, it can be generally stated that in these test cycles the composition of gas from individual wells is similar. It has been

shown that the content of hydrogen sulphide in gas from the tested wells ranges from 0.87 mg/Nm³ (WM-A4H, WM-B7H) to 1.55 mg/Nm³ (WM-B5H). A higher content of H_2S was recorded for natural gas taken from the WM-B6H well (2.89–2.99 mg/Nm³) (Supplemental Table S4, Figures 8 and 9).

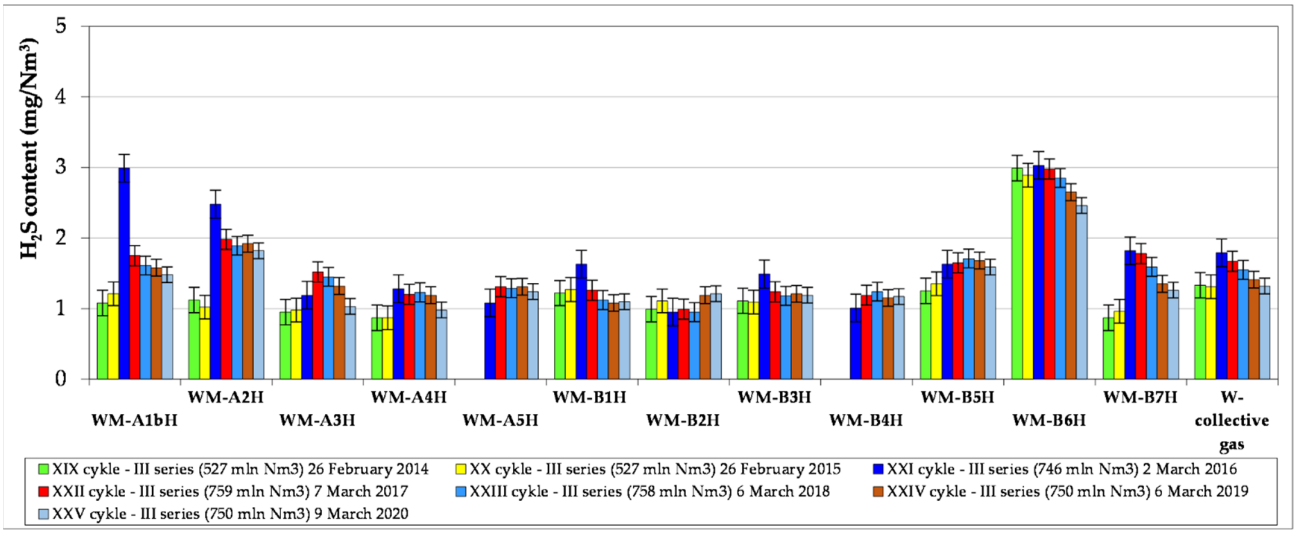

Figure 8. A comparison of the hydrogen sulphide content in the gas from the operational horizontal wells in the A and B clusters of the Wierzchowice Underground Gas Storage facility (series III), cycles XIX–XXIV.

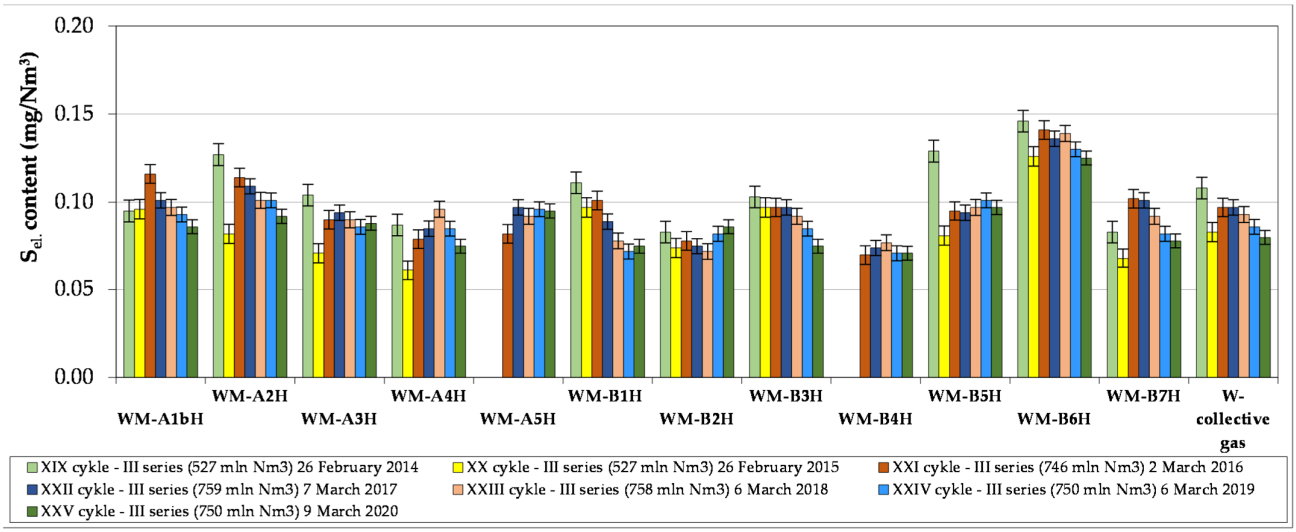

Figure 9. A comparison of the organic sulphur compounds converted to $S_{el.}$ content in the gas from the operational horizontal wells in the A and B clusters of the Wierzchowice Underground Gas Storage facility (series III), cycles XIX–XXIV.

During the third test series of the XXI cycle of the Wierzchowice Underground Gas Storage facility, a sharp increase in the content of hydrogen sulphide in the gas was recorded. It is especially visible in gas from wells: WM-A1bH (from 1.21 to 2.99 mg/Nm³), WM-A2H (from 1.02 to 2.48 mg/Nm³) and WM-B7H (from 0.96 to 1.82 mg/Nm³). The gas from the WM-B6H well in the XXI UGS cycle was at the same high level (3.03 mg/Nm³) as in the XX cycle.

From the XXI to the XXIII cycle of Wierzchowice UGS, the chromatographic analyses carried out to determine the content of sulphur compounds in the gas showed a decrease in its content in almost all horizontal wells in clusters A and B in subsequent cycles of UGS operation. The largest drops were recorded in gas from wells: WM-A1bH (from 2.99 to

1.61 mg/Nm³), WM-A2H (from 2.48 to 1.89 mg/Nm³), WM-B1H (from 1.63 to 1.12 mg/Nm³) and WM-B3H (from 1.49 to 1.18 mg/Nm³). As in the previous research cycles in the current UGS operation cycle, the highest hydrogen sulphide content was determined in the gas from the WM-B6H well (2.85 mg/Nm³), which was similar to the hydrogen sulphide content in the previous Wierzchowice UGS operation cycles.

The third research series of gas composition monitoring carried out in the XXIV and XXV UGS operation cycle showed a continuation of the decrease in the content of hydrogen sulphide in gas from almost all wells in cluster A and B, which had continued since the XXI UGS operation cycle. In the XXIV cycle, slight increases in the content of hydrogen sulphide were recorded only in gas from wells: WM-A2H (from 1.89 to 1.92 mg/Nm³), WM-B2H (from 0.95 to 1.19 mg/Nm³) and WM-B3H (from 1.18 to 1.21 mg/Nm³). However, in the current, XXV UGS operation cycle, slight increases in hydrogen sulphide content were recorded in the gas from the wells: WM-B1H (from 1.08 to 1.10 mg/Nm³), WM-B2H (from 1.19 to 1.21 mg/Nm³) and WM-B4H (from 1.15 to 1.17 mg/Nm³) (Table 5, Figures 6–8).

Figures 10 and 11 show the distribution of hydrogen sulphide content in gas from individual wells of the Wierzchowice Underground Gas Storage facility.

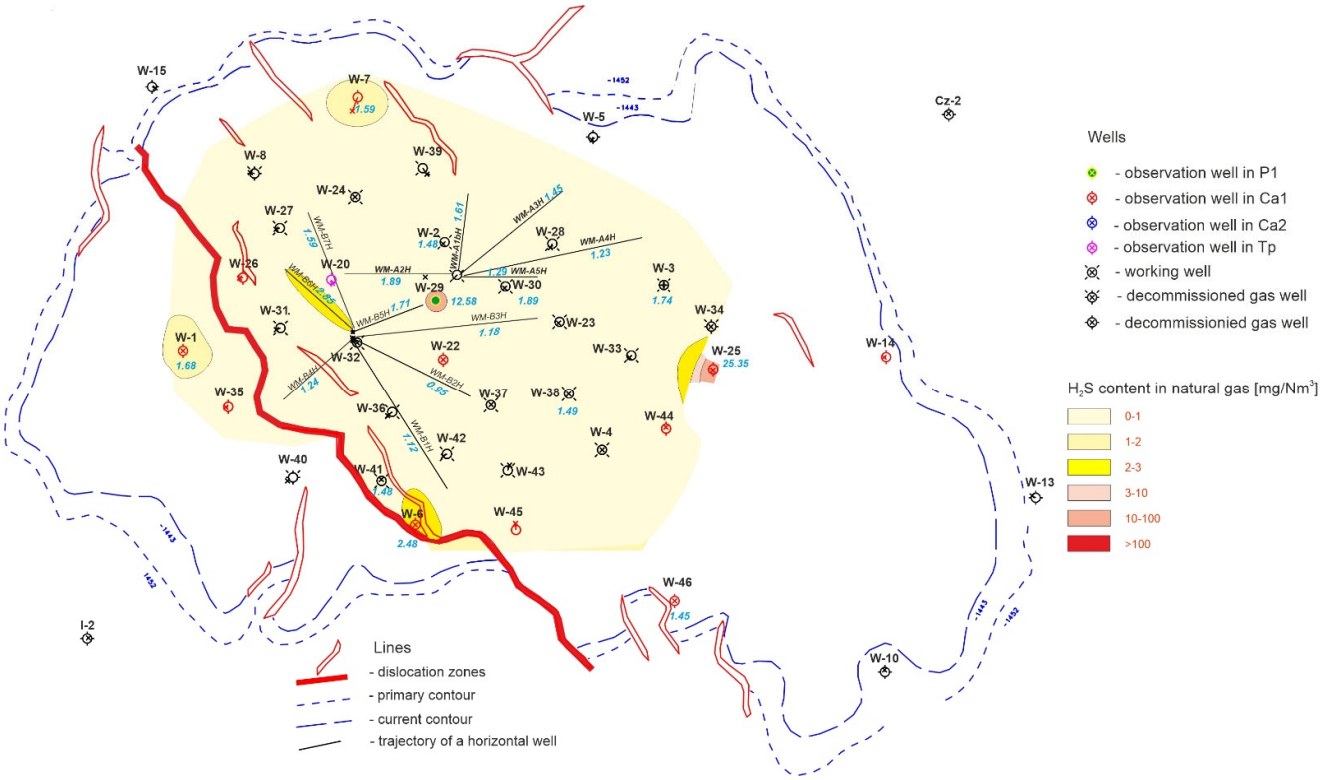

Figure 10. Map of the distribution of hydrogen sulphide content in natural gas from individual wells of the Wierzchowice Underground Gas Storage facility (series III, cycle XXIII).

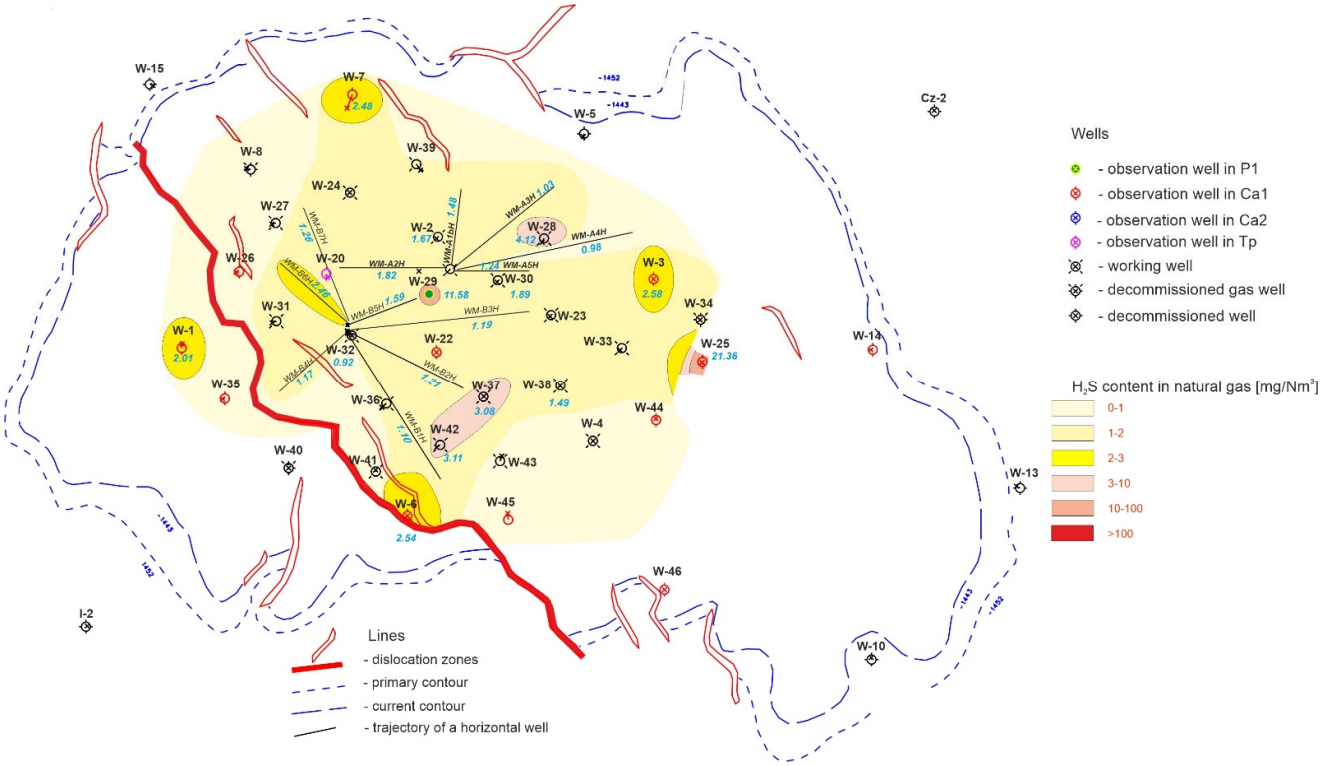

Figure 11. Map of the distribution of hydrogen sulphide content in natural gas from individual wells of the Wierzchowice Underground Gas Storage facility (series III, cycle XXV).

3.3. The Hydrogen Sulphide Biocid and Scavengers Aplication Technologie UGS Wierzchowice

It should be noted that the processes investigated in this study are crucial from the perspective of exploiting natural gas deposits and the issue of underground gas storage. The hydrogen sulphide scavengers are currently used in the petroleum and gas industry together with biocides (which restrict the growth of unwanted microorganisms or completely eliminate the biogenic phenomena). Hydrogen sulphide contaminating the deposit environment significantly hinders the operation of underground gas storage facilities and reduces the quality of the stored material. H_2S penetrates into natural gas via water (or brine) located in the deposit structure, where this chemical compound is generated by a biogenic process, via a microbiological reduction of sulphates. Therefore, it is particularly important to perform effectiveness tests and to select the appropriate, effective preparation. The effectiveness of selected preparations (mainly triazine based scavengers and biocides) in the hydrogen sulphide absorption process was determined, during monitoring studies at Wierzchowice UGS. The laboratory works included quantitative tests, intended to determine the extent to which the tested preparations were capable of neutralizing biogenic H_2S. The best active substance was applied in several exploitation wells of UGS facility in the last years. The concentration of selected scavenger ranged from 1 to 6% of volume.

Biocides based on sym-triazine were used in the Wierzchowice UGS a few times. First, we decided to introduce biocide into all exploitation wells in the solution of 1–2% of volume (in the phase of pumping natural gas into the storage). After this application, in the next cycles we started to pump the solution of biocide in the range of 3–6% of volume. Now, this application is based on H_2S scavenger and biocide solution treatment (active substances are dissolved in methanol). Then these operations are repeated every second or third year, on the selected 4–6 exploitation wells. After all these applications, the content of H_2S in natural gas and formation waters is remained on a stable level, acceptable for further exploitation.

3.4. Results of Isotope Research

Isotope tests are recommended for the identification of sulphate reduction processes in underground gas storage facilities [35,38,39,43–46]. In order to determine the isotopic composition of $\delta^{34}S_{H_2S}$, $\delta^{34}S_{SO_4}$, $\delta^{18}O_{SO_4}$, the tests were carried out with samples of gas collected from the Wierzchowice UGS storage facility both from production wells (WMB-6H, W-33) and observation wells (W-7, W-25, W-29) and a sample well water from the W-46 well (Figures 10 and 11). Isotope analyses of natural gas samples were carried out in two series (1st series, 2005) and (2nd series, 2019). The test results are summarized in Table 6.

Table 6. Results of the isotope analyses $\delta^{34}S_{H_2S}$ for the natural gas samples from the selected UGS Wierzchowice wells and $\delta^{34}S_{SO_4}$ i $\delta^{18}O_{SO_4}$ for the depth water sample from the W-46 well.

Sample	Well	$\delta^{34}S_{H_2S}$	
		1st Series	2nd Series
Ag_2S	W-7	9.97 ± 0.5	12.05 ± 0.3
	W-25	10.54 ± 0.5	12.89 ± 0.2
	W-29	9.85 ± 0.5	12.78 ± 0.3
	W-33	10.68 ± 0.5	12.01 ± 0.2
	WMB-6H	10.99 ± 0.5	12.25 ± 0.3
$BaSO_4$	W-46	$\delta^{34}S_{SO_4}$ = 9.84 ± 0.3 $\delta^{18}O_{SO_4}$ = 11.35 ± 0.3	

The preliminary interpretation of the origin of sulphates on the basis of the isotopic composition of sulphur and oxygen in the SO_4^{2-} ion indicates a connection with Permian evaporators, which is confirmed by the geological structure of the Wierzchowice UGS deposit. In this reservoir, the $\delta^{34}S_{H_2S}$ values are close to or slightly greater than the $\delta^{34}S$ of the sulphate ion precipitated from the water of the W-46 well. These values are within the range characteristic of the Permian period [39]. Large dispersions of the results (1st series) that occurred during the routine analyses of $\delta^{34}S_{H_2S}$ (9.85–10.99%) indicate the presence of organic or inorganic pollutants that occurred during the opening and exploitation of the deposit and the reconstruction of the wells, which indicates that the origin of hydrogen sulphide cannot be excluded from the decomposition of this organic matter. On the other hand, the results of isotope studies (2nd series) are very homogeneous and close to $\delta^{34}S_{SO_4}$ of Permian evaporates sulphates (11%). No distinction is made between the isotopic composition of sulphates and hydrogen sulphide. Such a situation speaks for an almost complete and fast reduction of sulphates available as SO_4^{2-} ion, i.e., an advantage of the reduction rate over the supply of sulphate. Due to the fact that the reduction took place in the aquatic environment, it should be assumed that it was a bacterial reduction without clearly determining whether the biochemical processes responsible for the production of sulphur compounds are of mine or secondary origin, i.e., they were induced naturally or artificially as a result of the access to and exploitation of the Wierzchowice deposit.

4. Discussion

Long-term biomonitoring studies of reservoir waters from individual wells of the Wierzchowice Underground Gas Storage facility showed the presence of SRB bacteria. In addition, the monitoring of natural gas from UGS production and observation wells, which was carried out to determine the content of hydrogen sulphide and organic sulphur compounds, made it possible to observe their changes in natural gas in individual storage cycles. In the last cycles of the Wierzchowice UGS facility, the content of hydrogen sulphide and sulphides in the reservoir waters ranged from 1.22 to 15.5 mg/dm^3, and the content of hydrogen sulphide in natural gas from production wells ranged from 0.69 to 2.99 mg/dm^3 (Tables 1–4, Supplementary Materials Tables S1–S3, Figure 8). A slightly

higher content of hydrogen sulphide was recorded in natural gas from the observation wells, in the range of 2.02–25.15 mg/Nm^3 (Figures 10 and 11).

The conducted research shows that both the content of hydrogen sulphide and organic sulphur compounds in natural gas from production wells and in the formation waters of the Wierzchowice UGS facility in the studied cycles of its operation are much lower compared to other storage facilities, which have been used for over 40 years [26]. An example is the UGS facility in Swarzów (in southern Poland), where treatments with biocides/H_2S scavengers have not been performed for about 20 years. The current results of the natural gas analyses from two wells of the Swarzów UGS showed the presence of H_2S in the range of 24–46 mg/Nm^3. On the other hand, the results of the water analyses from these wells showed the presence of sulphides at the level of 78–102 mg/dm^3. Several years ago, another gas storage facility in the central part of Poland, located in salt strata, was tested [47]. Tests of gas extracted from the most contaminated Z-8 of the CUGS Mogilno (Mogilno cavern underground gas storage) showed the content of hydrogen sulphide in the gas at the level of ca. 35–45 mg/Nm^3.

Based on literature data [35,46,48–50] and preliminary research, several hypotheses about the basic sources of sulphur compounds generation in the Wierzchowice UGS facility can be considered: (i) thermochemical reduction of anhydrites or dissolved sulphates in reservoir waters by C_1–C_2 light hydrocarbons (TSR); (ii) production of hydrogen sulphide by percolation of copper sulphide contained in copper-bearing shales after increasing the acidity of reservoir waters, (iii) bioreduction of sulphates by SRB (MSR), (iv) migration of hydrogen sulphide from the peripheral reservoir waters towards the gas phase, occurring as a result of lowering the pressure in the reservoir (Figure S2).

In order to confirm the presented hypotheses, tests extended by isotope analyses were performed, which are recommended for the identification of sulphate reduction processes in UGS.

The presence of anhydrites in the reservoir level of the Wierzchowice deposit, under the intense influence of natural gas, may lead to the generation of hydrogen sulphide as a result of the thermochemical reduction of sulphates. However, at the UGS Wierzchowice facility the bed temperature is ~50 °C, therefore, the course of the thermochemical sulphate reduction (TSR) reaction is very slow. In the case of the TSR course, the obtained isotope values ($\delta^{34}S_{H_2S} = \delta^{34}S_{SO_4}$) [33,44,49,50] in the studies carried out for UGS Wierzchowice, indicate discrepancies in these values, which proves that the course of TSR processes is slow.

The monitoring of the deposit waters of the UGS Wierzchowice facility allowed to confirm the presence of sulphate reducing bacteria of the *Desulfovibrio* and *Desulfotomaculum genera* in the wells called WM-A2H and WM-A3H in the operational cycles XVIII–XIX and bacteria oxidizing sulphur compounds (including the accumulated biogenic hydrogen sulphide). We have detected bacteria *Thiobacillus* sp. and *Acidithiobacillus* sp. in formation water samples from the horizontal wells called WM-B7H, WM-B4H, and from the samples of collective water in the cycles XVIII, XIX, and XXII. Monitoring studies conducted to determine the content of hydrogen sulphide and organic sulphur compounds proved the presence of hydrogen sulphide and organic sulphur compounds in the observation and production wells of the Wierzchowice UGS facility (Supplementary materials Tables S1–S3, Figures 8 and 9). In addition, the results of isotope studies suggest that the dominant process responsible for the formation of hydrogen sulphide in the Wierzchowice UGS facility is microbiological processes, consisting in the bioreduction of sulphates by SRB (MSR).

Considering the hydrogeological aspects of the Wierzchowice deposit and the cyclical studies of changes in the hydrogen sulphide content in natural gas from the operational and observation wells of the Wierzchowice UGS facility, the following conclusions can be drawn: (i) the appearance of hydrogen sulphide in the gas received from the Wierzchowice UGS facility was not a sudden and violent phenomenon, but it is a gradually growing process, (ii) so far the tendency of this phenomenon has been increasing

within the cycle along with the increase in the amount of gas extracted, and (iii) the content of hydrogen sulphide in the gas shows an upward trend towards the gas-water contact (Figures 10 and 11)

The above regularities seem to confirm the probable thesis that the biogenic hydrogen sulphide present is of migration origin and its source is reservoir waters, because: (i) the solubility of hydrogen sulphide in reservoir waters, while maintaining a constant temperature, depends on the size of the reservoir pressure, and therefore increases with its increase the amount of dissolved hydrogen sulphide and vice versa, with a decrease in pressure, its amount decreases, (ii) the intensity of hydrogen sulphide release (desorption) and migration to the gas zone depends on the degree of pressure reduction in the warehouse.

The content of hydrogen sulphide and organic sulphur compounds in the gas withdrawn from the Wierzchowice UGS facility is kept at a satisfactorily low level thanks to the monitoring of their content and the use of optimal doses of hydrogen sulphide neutralizing preparations.

5. Conclusions

1. Biomonitoring of the formation waters and cyclical analyses of the composition of the stored gas at Wierzchowice UGS enable the assessment of the microbiological condition of the formation environment and individual storage wells of UGS Wierzchowice over the next years of operation.
2. The composition of the microflora isolated in the previous work cycles of UGS included sulphate reducing bacteria (SRB) from the *Desulfovibrio* and D*esulfotomaculum genera* and bacteria oxidizing sulphur compounds (including accumulated biogenic hydrogen sulphide). After the injection of biocide/H_2S scavenger preparations was applied, the metabolic activity of SRB strains was significantly reduced, and in some wells, it was completely eliminated. There is a tendency towards the gradual disappearance or limitation of the microbial reduction of sulphates in the studied environment (after a series of treatments with the use of H_2S scavengers on UGS wells). It should be mentioned that the active hydrogen sulphide producing bacteria isolated from the formation fluids of the UGS Wierzchowice facility constitute material for the further testing of H_2S scavengers and which also have an antibacterial effect.
3. The effects of the process of using H_2S scavenger solutions in previous years can be considered satisfactory, as evidenced by the data contained in the article on the content of hydrogen sulphide in formation waters and recovered natural gas. In the course of the research, a number of changes in the technology of using preparations neutralizing hydrogen sulphide were introduced, including changing the type of carrier (solvent) or increasing the concentration of the active substance (aimed at combating contamination using the so-called "shock dose", and then introducing a continuous dose, turned out to be effective especially in endangered wells—showing the highest biogenic hydrogen sulphide contamination.
4. The chromatographic analysis of the gas pumped into the UGS Wierzchowice facility ruled out the possibility of introducing contaminants in the form of sulphur compounds together with the pumped gas. This leads to the conclusion that the processes taking place in the formation result in the generation of sulphur compounds causing contamination of the gas recovered from the Wierzchowice Underground Gas Storage facility.
5. The article contains detailed data from the chromatographic analyses of natural gas recovered from the Wierzchowice UGS facility (Tables 5, S1 and S3, Figures 2–7) in the last cycles of exploitation. These data show the range of variability of the content of H_2S and organic sulphur compounds in the gas over the subsequent stages of gas recovery from UGS.

6. Summing up, it should be stated that monitoring the content of sulphur compounds in natural gas from UGS Wierzchowice is extremely important, as it allows for controlling the effectiveness of actions taken to reduce the hydrogen sulphide content in gas recovered from UGS. In addition, chromatographic analyses of sulphur compounds in natural gas are helpful on an ongoing basis in correcting the project of pumping H_2S scavenger solutions in next work cycles of the UGS Wierzchowice facility.

Supplementary Materials: The following are available online at www.mdpi.com/article/10.3390/en14175463/s1, Table S1: The content of sulphur compounds in natural gas from selected horizontal wells in clusters A and B of the Wierzchowice Underground Gas Storage facility in the XXV exploitation cycle (I series—15 January 2020; state of gas depletion from UGS: 255 million Nm^3), Table S2: The content of sulphur compounds in natural gas from selected horizontal wells in clusters A and B of the Wierzchowice Underground Gas Storage facility in the XXV UGS exploitation cycle (II series—15 January 2020; gas depletion from the UGS facility: 497 million Nm^3), Table S3: The content of sulphur compounds in natural gas from selected horizontal wells in clusters A and B of the Wierzchowice Underground Gas Storage facility in the XXV exploitation cycle (II series—15 January 2020; gas depletion from the UGS facility: 750 million Nm^3), Table S4. A comparison of hydrogen sulphide content in natural gas from horizontal wells in clusters A and B of the Wierzchowice Underground Gas Storage facility (III series of tests), Figure S1. Scheme of biomonitoring studies, Figure S2. Diagram illustrating the theoretical possibilities of hydrogen sulphide formation.

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