THE ROLE OF BIOCIDES AND H$_2$S SCAVENGERS IN EXPLOITATION OF HYDROCARBON RESERVOIRS AND LABORATORY TESTS IN THE FIELD OF HYDROGEN SULFIDE SCAVENGING

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Abstract: The article presents the problem of microbiological contamination of formation media (fluids) and discusses the role of biocides used to control and counteract harmful biogenic processes. The types of active substances used in biocidal products recommended for the oil industry are listed. The focus was also on issues related to the occurrence of hydrogen sulfide in natural gas and on the methods of elimination of this toxic compound (or decreasing its content in the gas). The article describes scavenging of hydrogen sulfide from natural gas by using liquid scavengers and the series of laboratory tests. Discussed research concerns the effect of two active substances on content of sulfur compounds in test samples, including: hydrogen sulfide, methyl mercaptan, carbon oxysulfide and dimethyl sulfide.

Keywords: biocides, H$_2$S scavengers, hydrocarbon reservoirs

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1. INTRODUCTION

Contamination of reservoir fluids (crude oil, natural gas, formation water), drilling fluids and stored crude oil, petroleum products and natural gas with biogenic hydrogen sulfide is one of the most important problems in oil and gas industry. In case of the environments rich in organic materials and sulphates, higher concentrations of reduced sulfur compounds (sulfides and H₂S) are the results of the uncontrolled actions of microorganisms, which have been generally introduced by industrial activities. The elimination or limitation of H₂S generation in microbiologically contaminated environments are the subject of many extensive studies.

Biocides, corrosion inhibitors and H₂S scavengers are widely applied to protect reservoir environment, gas and oil transmission and storage infrastructure (pipelines, storages, devices etc.) as well as drilling fluids from the negative effects of bacterial activities [1, 2, 3–6, 7]. The main industrial approach of prevention and control of microbial growth is application of special biocide-active substances that may eliminate microorganisms from drilling wells, transmission facilities etc. Chemically differentiated compounds revealing various toxicity may act as biocides. Taking into account chemical structure, biocides may be classified into the following groups:

- amines, ammonium salts, amino alcohols;
- imidazolines;
- quaternary ammonium salts;
- heterocyclic compounds containing nitrogen (N) atom.

2. BIOCIDAL PRODUCTS AND MICROBIAL CONTROL FOR HYDROCARBON RESERVOIR

Triazine derivatives are well known and widely used as biocides in the oil and gas industry. These substances are very effective in elimination of anaerobic bacteria, especially sulfate-reducing bacteria. They are substituted at the carbon and nitrogen atoms. Triazine-based products are mainly designed for neutral-high pH conditions. It was also found that long exposure time between triazine-based scavengers and H₂S can result in significant scavenging efficiency even at low pH values. In recent years triazine-based scavengers have been extensively used in stimulation treatments to remove H₂S from flowed back fluids [8]. Triazine derivatives were also applied as pesticides. Due to its low toxicity they have found widespread use in agriculture [9]. Besides, well-known are environmental studies which include determination of these antibacterial substances in water and soil samples [10, 11].
Biocides are often based on amines or amine salts [12, 13]. Amines are effective surfactants that can act as biocides due to their ability to kill aerobic and anaerobic microorganisms [14]. They were used in well-drilling technology to limit biodegradation of drilling fluids. Apart from water-soluble biocides [1, 15–17,] well known are oil-soluble amine compounds, which have biocidal properties. These products are dedicated for fuel applications.

Glutaraldehyde is the most common component of commercial biocides with powerful antibacterial and antifungal activity. Optimum pH for this substance is 6.5–8.0.

Biocidal products are assigned to the one of 23 different types [18]. Generally, a number of this chemicals have a two-pronged action (biocidal properties and H2S scavenging potential). The hydrogen sulfide scavenging compounds may also include quaternary amines as H2S scavengers [19]. Products based on quaternary amines, and mixtures of amines/amino alcohols were applied in UGS conditions. Application of this scavengers helps to reduce the potential for corrosion in equipment, tubulars and pipelines. Quaternary ammonium compounds accelerate the reaction between MEA-triazine and H2S to improve molar efficiency [20, 21].

There are many requirements that the biocide, used in oil and gas industry, should meet [22]. Selection of the compound depends on the anti-microbial efficacy, stability, applied effective concentration, environmental safety, economic aspects and characteristics of the environment in which this substance should effectively act. Therefore, various parameters are evaluated before introduction of the mentioned compound into the medium. For example, the permeability of reservoir rock may be affected due to biocidal treatment. Thus, the changes of the mentioned parameter bring crucial information for the selection of biocide, which may be applied in the underground gas storages. It is worth mentioning here that the used compound will not always play as an anti-microbial agent in the given environment. Instead of bacterial proliferation’s inhibition, in some cases the applied compound can be used as a substrate for microorganisms. This situation may also take place in case of dissolution of biocide in water or brine. Too low concentration may stimulate the microbial growth since the substance is not toxic for microorganisms and they start to metabolize it. Moreover, wrong choice of biocides may even generate the economic loss or environmental danger.

Application of biocides is one of the most popular and effective strategy to decrease microbiological contamination affecting numerous fields of oil and gas industry. In formation waters can exist many of aerobic (Fig. 1) and anaerobic bacteria (Desulfovibrio sp., Desulfobacterium sp., Pseudomonas sp., Bacillus sp., Flavobacterium sp., Thiobacillus sp., Acidithiobacillus sp., Bacillus sp., Arthrobacter sp.). Some of this species live in water polluted with oil products [7] or drilling fluids. Some of aerobic bacteria can neutralize H2S and sulphides. This species (sulphur-oxidizing bacteria) are also able to eliminate heavy metals [23].
Among many well-studied antibacterial substances, 1,3,5-tris(2-ethyl)hexahydro-1,3,5-triazine and 3,3'-methylenebis[5-methyl]oxazolidine] are characterized by good biocidal activities. The first mentioned compound is successfully applied to control bacterial growth in natural gas wells. Both transmission and storage of natural gas may be affected by metabolic activities of microorganisms. Their actions led to deterioration of gas as well as \( \text{H}_2\text{S} \) generation. The occurrence and activities of autochthonous and introduced (allochthonous) bacteria are involved in the above mentioned problems. Sulfate reducing bacteria (SRB) play a pivotal role in decreasing quality of natural gas due to produc-
tion of hydrogen sulfide. Moreover, the formation of undissolved precipitates such as ferrous sulfides (Fe$_x$S$_y$) is also problematic since these compounds plugged the collectors, transmission pipelines etc.

The occurrence and activities of microorganisms in hydrocarbon deposits and drilling muds may lead to CO$_2$ generation. This compound is a final product of some metabolic processes. Its presence may be involved in decreased pH of medium (e.x. drilling fluids). The change of an initial, alkaline pH of drilling mud is an essential signal of the existing biodegradation processes. Therefore, this observation indicates the presence of alive bacterial cells in analyzed material.

Some microorganisms introduced to the drilling mud, are able to degrade natural, semi-synthetic and synthetic polymers. These substances are the main components of fluid circulating in the well. The bacterial presence in this kind of materials is undesirable, since microbial action may decrease the quality of drilling fluids and destroy their functions.

Biodegradation, chemical degradation, decomposition of polymers and increase of H$_2$S concentration may easily and rapidly change the initial chemical composition of drilling fluid and its rheological parameters. To avoid these phenomena, the appropriate biocide-protected drilling mud formulations are the essential aspect of well-drilling technology.

3. H$_2$S SCAVENGING IN THE OIL AND GAS INDUSTRY

Hydrogen sulfide is a toxic and pungent gas and, because it behaves as a weak acid in water, can cause corrosion of steel equipment and pipelines. Natural gas must ordinarily contain less than 4–5 parts per million (ppm) of hydrogen sulfide before it can be sold. When used as petrochemical feedstock’s, methane, ethane and propane must have levels below < 1 ppm as the sulfur is a catalyst poison.

Not all sulfur in crude oil is H$_2$S. In fact it is usually only a small portion. Most are other non volatile sulfur compounds [24]. On the other hand, H$_2$S is usually the dominant sulfur compound in natural gas. Non volatile compounds are normally allowed in fuels like gasoline and diesel at higher concentrations (100 ppm):

- thiophenes,
- non volatile mercaptans,
- sulfides and disulfides.

Hydrogen sulfide can be present not only in natural gas, but it can also be a component of biogas. The biogas desulphurisation technique used various methods, as evidenced by numerous literature data [25, 26]. Their common feature is maintaining good quality of gas (no conflict with the basic component – methane).
According to American standards, the composition of natural gas must guarantee the quality of this product, so that limits of impurities should be at the following rates:

- \( \text{H}_2\text{S} \): < 4 ppm,
- \( \text{CO}_2 \): < 2\% mol.,
- \( \text{H}_2\text{O} \): < 0.1 g/Nm\(^3\) (< 120 ppm),
- amount of inert gases (N\(_2\), He, Ar): < 4\% mol.

Limits of impurities in the gas by Polish standards should be at the following rates:

- \( \text{H}_2\text{S} \): 7 mg/Nm\(^3\),
- \( \text{CO}_2 \): 3\% mol.,
- total sulfur content: 40 mg/Nm\(^3\).

Accordingly, production fluids may be “sweetened” through a process of removing the hydrogen sulfide. Typical hydrogen sulfide removal processes use an active treatment compound that reacts with the hydrogen sulfide \[19\]. For removing high levels of \( \text{H}_2\text{S} \) are used regenerable amine or other solvent systems require multiple towers, heat exchangers, surge drums and filters. Regenerable amine systems remove \( \text{H}_2\text{S} \), most of the \( \text{CO}_2 \) and very little other sulfur compounds.

Low volume \( \text{H}_2\text{S} \) removal is based on non-regenerable scavengers. Non regenerable scavengers only require an injection nozzle and pump or single tower. These scavengers may have a higher annual chemical cost than an equivalent regenerable system, but much less capital and utility costs. They are more selective to \( \text{H}_2\text{S} \) vs. \( \text{CO}_2 \) and other sulfur compounds. The liquid scavengers are not very soluble in the gas and the droplets will quickly fall out of the gas phase. With higher gas velocities, the droplets will remain dispersed in the gas longer. With lower velocities, the droplets will coalesce on the pipe walls and the scavenger is ineffective \[27\].

Water injection for enhanced oil recovery always carries risk of reservoir souring, whether produced water or sea water is injected. Various mitigation strategies can be employed to reduce the risk, including injection of biocide, nitrate, and liquids scavenger chemicals. Selection of the most appropriate treatment strategy will depend on a variety of factors, including \( \text{H}_2\text{S} \) concentration, gas volume and process conditions. Operating conditions will also influence the selection of treatment strategies and ultimate application locations \[28\]. As mentioned above, effective antimicrobial substance and scavenger for industrial applications is triazine. Three variations of triazine exist, based on the location of the substitution of nitrogen atoms, as shown in Figure 2.

In direct-injection applications, the triazine is sprayed directly into gas, usually with an atomizing quill. This method is excellent for removing \( \text{H}_2\text{S} \) when there is good annular-mist flow and sufficient time to react. Typical efficiencies are lower due to the \( \text{H}_2\text{S} \) dissolution into the product, but ca 40\% removal efficiency can reasonably be expected.
In order for direct injection to be effective, careful consideration of injection location and product selection must be used. Hydrogen sulfide is converted to a water-soluble, non-corrosive and non-toxic product. One mole of triazine reacts with two moles of $\text{H}_2\text{S}$ to form dithiazine, the main byproduct. An intermediate product is formed, but rarely seen. Continued reaction can result in the formation of an insoluble trithiane product [28]. Another data, based on industrial applications, indicate that several moles of $\text{H}_2\text{S}$ react with one mole of scavenger when applied properly. It concerns liquid scavengers such as cyclic amines, heterocyclic and polymeric amines or alkyl amines [27]. Applications of liquid $\text{H}_2\text{S}$ scavengers include natural gas, NGL’s, LPG, refined fuels, crude oil, sewage treatment, and water.

4. LABORATORY TESTS IN THE FIELD OF HYDROGEN SULFIDE SCAVENGING

The method of gas chromatography was used in laboratory tests. Four test samples were prepared in 250 ml glass bottles with glass stoppers, each containing 200 ml of suspension, i.e. formation water with hydrogen sulfide. The degree of hydrogen sulfide neutralization was evaluated in comparison to the control sample (i.e. the sample without the addition of a scavenger). Sample 1 contained a scavenger based on the active substance N-methyl bis (2-hydroxyethyl) amine of 2% vol., time of the exposure to the preparation was 2 hours. Sample 2 contained the same active compound of 2% vol. and time of its exposure to the test fluid was 4 hours. Sample 3 contained a scavenger based on the active substance hexahydro-1,3,5-trimethyl-1,3,5-triazine of the same concentration, and time of the exposure was 2 hours. The last sample (4) was the triazine derivative mentioned above which was tested after 4 hours of exposure, in the same concentration and in a manner analogous to the previous samples.

After the specified time of incubation of the control samples (exposure to the preparations), each sample was subjected to the degassing process, i.e. the separation of the gas phase from the liquid phase with the use of a formation water and fluid degassing set.
The method consists in measuring the volume of the gas released from the formation fluid and taking it into a syringe. For this purpose, control samples (in 250 ml glass bottles, connected tightly with the use of a rubber tube with a burette) were heated in the water bath and then gas was collected in two fractions, to the temperature of 30°C and 60°C. The degassing time was 40 minutes. The separated gas phase, containing hydrogen sulfide at the given concentration, was collected in burette containers.

Then, a series of analyses of the content of hydrogen sulfide and other sulfur compounds was performed by GC methods. Before performing the analyses, validation of the chromatographic system was carried out. GC analyses of sulfur compounds were conducted with the use of AGILENT 7890 A two-channel valve gas chromatograph with ChemStation version B.04.03 software and a system of columns and detectors:

- thermal conductivity detector (TCD), column: Molecular Sieve 5A Ultimetal 9FT ×1/8IN × 2.00, Supelco Analytical,
- flame photometric detector (FPD), capillary column: DB-1, length 60 m, inner diameter 0.32 mm, Agilent Technologies.

During the analyses, nitrogen with a constant flow of 3 ml/min was used as the carrier gas. The temperature gradient of the columns from 30°C to 240°C was used. The temperature of 30°C was maintained for five minutes and the temperature was rising 25°C every minute. The working temperature of the TCD thermal conductivity detector was 200°C and of the FPD flame photometric detector was 250°C.

The standard curves were determined for the following chemical compounds:

- hydrogen sulfide,
- methyl mercaptan,
- carbon oxysulfide,
- dimethyl sulfide.

Then, the stability of the chromatographic system was checked based on the standard mixtures for individual sulfur compounds and after determination of the calibration curves, subsequent determinations were carried out. The measurement uncertainty for hydrogen sulfide was from 3/mol/mol to 15/mol/mol, while for other sulfur compounds from 2/mol/mol to 5/mol/mol.

As the first, a control sample (containing no neutralizer) was subjected to the degassing process, and the gas collected was injected with the Hamilton syringe into the chromatograph. The one-off amount of the injected gas sample was 20 microliters. The result was converted into microliters/100 millilitres of gas obtained from the degassing process for each control sample. It was the arithmetic mean of three chromatographic analyses.

After analysing the control sample, after the determined incubation time, other control samples containing the specified scavenger of 2% by volume were analysed with
the use of the GC method. For the hydrogen sulfide present in the control sample, a result of 90 microliters H₂S/100 millilitres of gas released was obtained during the degassing process.

As a result of the 2-hour and 4-hour exposure to the first active substance (contained in samples 1 and 2), from 24.2 microliters to 35.5 microliters of hydrogen sulfide/100 ml of the released gas was obtained. This means that the neutralization degree for these samples ranged from 60.56% to 73.11%. The second active substance (contained in samples 3 and 4) caused complete neutralization of H₂S, both after 2 hours and after 4 hours of incubation. Methyl mercaptan was neutralized from 27.33% to 36.65% with the use of the amine active substance. Analyses of the second active substance (triazine derivative) showed a higher degree of neutralization of CH₃SH, ranging from 72.05% to 91.30%.

In addition to H₂S and mercaptans, carbon oxysulfide was another analysed compound. Under the influence of the first active substance, it was neutralized in 40.82% to 44.90%. However, after two hours of exposure to the second active substance tested, more than half of the initial COS content, i.e. 51.02% was neutralized. As a result of a 4-hour incubation, complete neutralization of carbon oxysulfide was stated under the influence of the triazine derivative, as compared to the control sample.

In contrast to other test results, chromatographic analyses of the last sulfur compound tested, i.e. dimethyl sulfide, showed an increase in the value of the analysed gas component (compared to the control sample) under the influence of the amine neutralizer. This means that in this case no beneficial effect of the active substance on the (CSH₃)₂S was observed. The test result for the second active substance was different. After a 2-hour incubation, a 75% decrease in the dimethyl sulfide content was observed under the influence of the triazine derivative. However, after a 4-hour incubation, the total content of the tested substance, i.e. (CSH₃)₂S has been neutralized in relation to the control sample (without the addition of a neutralizer).

Summing up the above test results, it should be stated that the high efficacy of the tested triazine derivative has been laboratory confirmed in the process of neutralization (absorption) of sulfur compounds, and above all hydrogen sulfide, for the needs of the oil and gas industry. The second tested preparation, based on the active substance N-methyl bis (2-hydroxyethyl) amine, also has the absorption properties of H₂S and other sulfur compounds (except for dimethyl sulfide), but its efficacy is much lower than Hexahydro-1,3,5-trimethyl-1,3,5-triazine. The results of the tests are presented in a tabular (Tab. 1), and graphical form in Figures 3 and 4.

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Table 1
Results of the efficiency test of hydrogen sulfide scavengers – 2% volume solutions; exposure time: 2–4 hours

| Sample number | Active substance/ exposure time                          | Content of sulfur compounds [μl/100 ml of gas] |
|---------------|----------------------------------------------------------|-----------------------------------------------|
|               |                                                         | Hydrogen sulphide (H₂S) | Methyl mercaptan (CH₃SH) | Carbon oxysulfide (COS) | Dimethyl sulfide (CH₃)₂S |
| 1             | N-methyl bis (2-hydroxyethyl)amine 2 hours of exposure  | 35.5                          | 11.7                      | 2.9                      | 2.3                    |
| 2             | N-methyl bis (2-hydroxyethyl)amine 4 hours of exposure  | 24.2                          | 10.2                      | 2.7                      | 2.6                    |
| 3             | Hexahydro-1,3,5-trimethyl-1,3,5-triazine 2 hours of exposure | n.s.                          | 4.5                       | 2.4                      | 0.2                    |
| 4             | Hexahydro-1,3,5-trimethyl-1,3,5-triazine 4 hours of exposure | n.s.                          | 1.4                       | n.s.                     | n.s.                   |
| 5             | Control sample (no scavenger)                           | 90.0                          | 16.1                      | 4.9                      | 0.8                    |

n.s. - not found

**Fig. 3.** The changes of sulfur compounds content in gas (obtained after degassing the formation fluid) under the influence of the scavenger based on Hexahydro-1,3,5-trimethyl-1,3,5-triazine [μl/100 ml of gas]
Fig. 4. The changes of sulfur compounds content in gas (obtained after degassing the formation fluid) under the influence of the scavenger based on N-methyl bis (2-hydroxyethyl) amine

[μl/100 ml of gas]

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Streszczenie: W artykule przedstawiono problematykę zanieczyszczenia mikrobiologicznego mediów ( płynów) złożowych oraz omówiono rolę biocydów stosowanych w celu kontroli i przeciwdziałania niepożdanym procesom biogennym. Wymieniono rodzaje substancji czynnych używanych w produktach biobójczych, polegających na stosowaniu w przemyśle naftowym. Skoncentrowano się także na zagadnieniach związanych z występowaniem siarkowodoru w gazie ziemnym i na sposobach eliminacji tego toksycznego związku (lub zmniejszeniu jego zawartości w gazie). W artykule scharakteryzowano działanie płynnych neutralizatorów siarkowodoru i opisano przebieg badań laboratoryjnych dotyczących wpływu dwóch substancji czynnych (typu H₂S scavengers) na zmiany zawartości związków siarki w próbkach testowych, w tym: siarkowodoru, merkaptanu metylowego, tlenosiarczku węgla i siarczku dimetylowego.

Słowa kluczowe: biocydy, neutralizatory H₂S, złoże węglowodorów