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The application of biocides in the oil and gas industry

Introduction

Currently the world uses lots of technology, where enhanced recovery processes, desulfurization and denitrification of oil are initiated and controlled by microorganisms. Some species of bacteria were also isolated in the microbial oil survey technique [8]. On the other hand, the presence of bacteria and other microorganisms in deposits and transmission systems and in stored products is a very unfavorable phenomenon and often difficult to remove. A necessary condition for the emergence and development of micro-organisms is the presence of water and a carbon source in a given environment (fuel tanks, pipelines, gas storage, gas supply systems, etc.).

The phenomena of microbiological contamination of the oil and natural gas environment represent a broad issue. The negative effect of microorganisms is primarily associated with the degradation of petroleum hydrocarbons, leading to an increase in oil density, sulfur content and viscosity. These changes cause disruption in oil extraction and processing technology, bringing about significant economic losses. Problems also concern the ways crude oil is stored, products of its processing, drilling fluids, and natural gas [14, 27]. In addition to lowering the content of hydrocarbons in crude oil, adverse activity of microorganisms causes corrosion of transmission installations (oil and gas pipelines) and the production of undesirable substances (H_2S, polymers, organic acids, etc.) that affect the performance of oil and gas.

Attempts to eliminate microorganisms involve using chemicals, exhibiting biocidal properties, which besides the physical method is the most popular and most effective technique of eliminating microbiological contamination. The selection of appropriate antibacterial or antifungal agents requires the consideration of factors affecting the efficiency of the process. Such measures are primarily sought, which show the greatest spectrum of activity. The paper aims at the systematization of available literature data on biocides and their use and their efficiency in industrial environments.

Microorganisms responsible for the deterioration process of natural gas

The issue of deterioration of natural gas resulting from the metabolic activity of microorganisms is related to two main aspects – gas transmission and storage of this raw material in underground gas storage (UGS), i.e. exploited geological structures. Corrosion of metals, in this particular case of gas pipelines is one of the major problems of the gas industry, causing enormous economic losses. It is estimated that 40% of the corrosion occurring in the interior of gas pipelines is caused by the action of microorganisms (MIC – microbiologically influenced corrosion), mainly sulfate-reducing bacteria. These bacteria, using energy derived from organic compounds (light hydrocarbons contained in the gas), reduce sulfates to sulfides or directly to hydrogen sulfide. Development of microorganisms and their metabolic products accumulating in pipelines cause micro-changes on the metal surface, thereby initiating a complex process of corrosion. Microbiologically induced corrosion is involved in chemical and electrochemical corrosion of pipelines, facilities and tanks [6, 22, 23, 25]. So far, the mechanism of corrosion caused by microorganisms has not been fully elucidated, although there are various theories attempting to describe this phenomenon. One of these theories relates to a biofilm forming on the metal surface, consisting of anaerobic bacteria (primarily reducing sulfate and iron), which as a result of oxidation-reducing processes cause the dissolution of the protective oxide layer, covering the metal with forming iron sulfide.

Unfavorable activity of microorganisms is associated with a manner of storing this raw material – underground gas storages. The emergence of biogenic hydrogen sulfide [34], which is a product of sulfate-reducing bacteria (SRB) metabolism, lowers the value of the gas, furthermore there is the possibility of the formation of insoluble deposits of iron sulfides (Fe_xS_y) clogging manifolds, gas transmission installations, etc. Measurements of the quantity of produced hydrogen sulfide by *Desulfovibrio sp.* indicate that during the active division the bacteria are able to produce 10 g H_2S/l. One should also take into account the aspect of health risk to personnel working in the UGS facilities, because of exposure to the resulting hydrogen sulfide which is toxic (its toxicity is comparable to hydrogen cyanide).

Tab. 1. The examples of microorganisms responsible for the deterioration process of natural gas isolated from pipelines and UGS

Microorganisms	Place of samples collection	Bibliography
Arche		
Methanobacterium curvum, Methanocalculus halotolerans, Methanoculleus sp., Methanofollis liminatans, Methanofollis sp., Methanosarcina barkeri, Methanosarcina siciliae, Methanospirillum hungatei	pipelines	Zhu X.Y. et al., 2003 [35]
Aerobes		
Acinetobacter junii, Acinetobacter sp., E. coli, Pseudomonas aeruginosa, Staphylococcus auricularis	pipelines	Zhu X.Y. et al., 2003 [35]
Klebsiella pneumonia	pipelines	Jan-Roblero et al., 2004 [12]
Anaerobem		
Anaerobaculum mobile, Thermodesulfovibrio yellowstonii, Desulfovibrio vulgaris, Thermotoga neapaitana, Clostridium sporogenes, Clostridium bifermentas, Desulfomatoculum kuznetsorii, Thermotoga hypogea, Desulfovibrio sp., Desulfotomaculum sp.	pipelines, underground gas storage	Lohithesh M. D. et al., 2008 [16] Raczkowski J. et al., 2004 [20]
Desulfovibrio desulfuricans, Citrobacter freundii, Clostridium celerecrescens, Cetobacterium somerae	pipelines	Jan Roblero et al., 2008 [12]

Microorganisms responsible for the deterioration process of crude oil and its processing products

At each stage of oil processing from its exploitation, transport, processing and ending with the storage, it can be subjected to the action of microorganisms. They use hydrocarbons contained in crude oil as a source of carbon and modify the properties of this material, thus reducing its value. The complexity of the issue of microbiological contamination of the oil is due to the existence of the possibility of interactions between oil and water. It is extremely difficult to prevent microbiological contamination of oil, because it is impossible to maintain sterile conditions during the extraction, transport and storage of crude oil. An essential and necessary condition for the growth of microorganisms in oil, or products of its processing is the presence of water in the production well, accumulation of water in the pipelines during transmission or at the bottom of the tanks during storage.

There are several stages during which microbiological contamination of oil and its derivatives may occur [24, 25, 30, 32]:

- stage of application of drilling fluids, which may be contaminated – in this way allochtonous bacteria are introduced to the deposit,
- stage of supply – borehole watering with highly contaminated water,
- stage of oil transport – presence of microorganisms in contaminated water in transmission systems,
- petroleum processing stage,
- stage of storage of crude oil and its processing products.

The deterioration of crude oil and petroleum products under the influence of microbial activity reduces the hydrocarbon content, because they are being used as a carbon source in both aerobic and anaerobic conditions, which immediately translates to changing the physico-chemical parameters of this raw material. The occurrence and growth of microorganisms at the interface of water-crude oil phases produces a biofilm on the surface of pipelines and tanks, which presents excellent conditions for microbial growth. The effect of metabolic activity of microorganisms is the appearance of detergents, biosurfactants and hydrogen sulfide in crude oil, affecting the decrease in the energy value of this resource – acidification and sulfation. A particularly disadvantageous phenomenon is the secretion of hydrogen sulfide by some of the bacteria and the creation of a local area with reducing properties, causing corrosion of metals included in the material of tanks and transmission systems [6, 24, 27].

Such changes are a major economic problem for the mining and refining industry, as well as a huge threat to the environment. It is impossible to avoid the penetration of microorganisms into oil fields as a result of drilling, into oil and fuel storage tanks, oil pipelines and transmission facilities, which are the perfect place for colonization by both aerobic and anaerobic microorganisms. Development and metabolic activity of micro flora directly leads to the deterioration of the physico-chemical parameters of oil and fuel. A negative phenomenon is the precipitation of biomass (sludge), which are metabolic products of fungi, bacteria, yeast, which forms larger agglomerates. This causes the silting of reservoir rocks, clogging of pipelines and accumulation of sediments at the bottom of fuel tanks. Bacterial contamination is usually observed in crude oil, whilst fungi usually cause contamination of aviation fuel. The number of microorganisms (bacteria and fungi) in the aqueous layer contained in crude oil and petroleum products, determines the amount of contamination.

Tab. 2. The examples of microorganisms responsible for the deterioration process of crude oil and fuels isolated from drilling muds, flooding water and some fuels

Microorganisms	Place of samples collection	Bibliography
Fungi		
Penicillium spp., Fusarium spp., Cladosporium sp., Rhizopus sp., Aspergillus sp.	drilling mud, flooding water, drilling mud	Benka-Coker & Olumagin, 1995 [3] Elshafie et al., 2007 [8]
Yeast		
Candida tropicalis, *Candida albicans*, *Saccharomyces estuari*, *Saccharomyces cerevisiae*	aviation fuel	Itah et al., 2009 [11]
Candida viswanathii	biodiesel, diesel	Junior et al., 2009 [13]
Aerobic bacteria		
Serratia spp., Acinetobacter spp.	drilling mud, flooding water	Benka-Coker & Olumagin, 1995 [3]
Staphylococcus spp.	drilling mud	Benka-Coker & Olumagin, 1995 [3] Okpokwasili & Nnubia, 1995 [19] Nnubia & Okpokwasili, 1993 [18]
Alcaligenes sp.	drilling mud	Benka-Coker & Olumagin, 1995 [3] Okpokwasili & Nnubia, 1995 [19]
Pseudomonas sp.	stains from drilling wells	AL-Saleh et al., 2009 [2] Das & Mukherjee, 2007 [7]

Methods for suppression of biodegradation of crude oil and petroleum products and an overview of currently used biocides

The problem of microbiological contamination of natural gas, crude oil and its processing products represents a major problem in economic terms. Among the methods currently used, the following can be distinguished:

- physical and mechanical methods,
- chemical methods.

The article focuses on the second group of these methods – chemical control of microbiological contamination of natural gas and oil – using chemical agents (biocides). Biocides are compounds used to disinfect, decontaminate and sterilize materials (surfaces, objects) to eliminate microbiological degradation processes. Chemical compounds, exhibiting biocidal properties and used as antibacterial/antifungal preparations have a diverse structure. These are both inorganic substances (e.g. copper, tin, arsenate) and organic substances (e.g. aldehydes, hydantoins). Among biocides, there are substances with a simple chemical structure (e.g. glutaraldehyde) as well as a complex chemical structure (e.g. QUAT's), of which the mechanism of interaction with the microorganism is based on different mechanisms.

The mode of action of biocides is to suspend the current metabolic activity of microorganisms, causing changes in the proper functioning of cells, and consequently death of the microorganism [24, 28, 30]. Depending on the subject affected by a given biocide, there are antibacterial, antifungal and anti-algae formulations, although the most popular are agents which eliminate several types of microorganisms (bacteria, fungi, etc.). A given product may have a simultaneous activity against a specific group of bacteria and fungi, and thus can effectively eliminate only one bacterial strain of the species. The main areas of use of biocides are agriculture, forestry, the food industry and cosmetics, also, industrial water and swimming pools also undergo antibacterial decontamination.

Given the mechanism of chemical action of biocides, biocides can be divided into two groups, i.e., substances with oxidizing and non-oxidizing effect. The most commonly used oxidizing biocides are chlorine, bromine, ozone and hydrogen peroxide. However, use of oxidizing biocides is associated with negative effects:

- interaction with other chemicals (corrosion inhibitors),
- the possibility of interaction with non-metallic substances,
- initiation of corrosion of structural materials.

Before each treatment with oxidising preparations, these effects should be taken into account when considering the potential for oxidation, the dose and type of treatment (intermittent or constant).

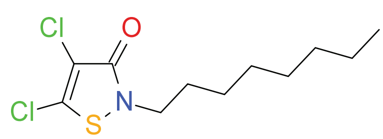
The group of non-oxidizing biocides includes aldehydes (formaldehyde, glutaraldehyde), acrolein, quaternary ammonium compounds, amines and diamines [29], and isothiazolones.

Often used in the industry, quaternary ammonium compounds are used as cationic corrosion inhibitors and biocides. Biocidal activity of these substances is to dissolve the lipid cell membrane, which leads to loss of the cell contents of the microorganism. Additionally, QUATS prevent the formation of polysaccharide secretions during bacterial colonization, thus showing antibacterial activity.

Often, biocides using QUATS have water, alcohol or potassium base as the dissolving phase, the use of alcohol increases the antibacterial activity of the preparation, since alcohol has biocidal abilities and facilitate penetration of an entity into the cell. QUATS generally work best in an alkaline environment. Inhibition of corrosion using these substances is to create a thin protective layer on the inner parts of the installation, thereby the possibility of interaction of oxidizing agents with steel components of the installation is reduced. Furthermore, these compounds were studied as a control substances, and even as substances preventing biofilm formation. These preparations are used in closed systems and gas manifolds. However, they are not used during the exploitation of oil because they may adversely affect the permeability of the crude oil deposit. Furthermore, they are not compatible with oxidizing agents, especially the chlorates, peroxides, chromates or permanganates. Most of these compounds are readily biodegradable.

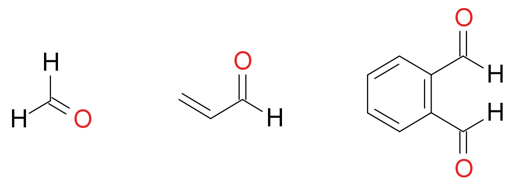
Another type of biocides is isothiazolones. They are fast-acting biocides inhibiting growth, metabolism and biofilm formation by algae and bacteria. They are used in combination with other biocides or individually, typically aqueous solutions of chloride- and methyl-derivatives of these compounds are used. Isothiazolones are used only in an alkaline medium, at pH < 7 they lose biocidal properties, moreover, these compounds can be used in combination with other chemicals without changes in performance. An exception is environment containing hydrogen sulfide, which causes deactivation of isothiazolones. The main application areas of isothiazolones are coolants and cooling and lubrication fluids.

A compound commonly used in biocidal formulations is methylchloromethyl-isothiazolone (MCMI) and 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOI), which causes inhibition of dehydrogenase and thus interferes with metabolic pathways. The following is a formula of this biocide:



In addition, commonly used substances with biocidal action are compounds containing an aldehyde group, which include:

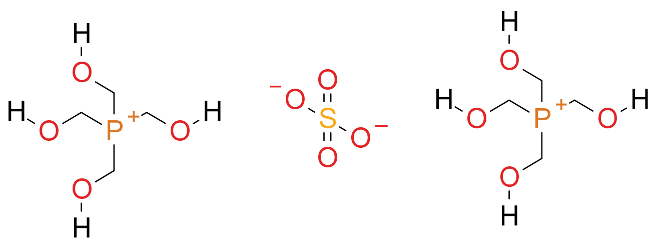
- formaldehyde,
- 2-propenal (acrolein),
- ortho-phthalic aldehyde (OPA),
- three-seven-carbon (C3-C7) compounds having aldehyde groups (e.g., pentane-1,5-dial) – formulas of aldehyde groups are shown:



Another discussed compound is glutaraldehyde (pentane-1,5-dial). This is the most common component of commercial biocides with powerful antibacterial and antifungal activity. An important advantage of this compound is the possibility of use in a wide range of temperatures and pH as well as solubility in water. Glutaraldehyde does not react with strong acids and alkalis, but reacts violently with ammonia and amine-containing substances, which causes exothermic polymerization reaction of an aldehyde, and thus its deactivation. It is not sensitive to the presence of sulfides and tolerates high salinity environments. Aldehyde interacts primarily with the basic amino acid groups (COOH and NH_2) and hydroxyl and thiol groups, present in the cell membrane, wall and cytoplasm. Preparations are commonly used in which the carrier is water, also products based on alcohols are known, mainly methanol and isopropanol. The use of alcohol increases the possibility of penetration of the aldehyde into the cell and prevents its solidification during storage. Often biocidal effectiveness is aided with addition of quaternary ammonium salt (2÷5%), surfactants or other biocides.

Among other non-oxidizing biocidal compounds, worth noting are biocides with methylene bis(thiocyanate) (MBT), which is effective against algae, fungi and bacteria including SRB. The undoubted disadvantage of this compound is its instability in alkaline medium, due to hydrolysis. Thus, preparations based on this compound are not used in refrigeration systems, in which the process water is above 8 pH. Optimum pH at which this compound does not lose its activity is 6.5÷8.0.

Another biocide used in industry is Tetrakis (hydroxymethyl) phosphonium sulfate (THPS), according to the following chemical formula:



It is water soluble, ionic biocide destroying bacteria, fungi and algae in industrial cooling installations and process water tanks. It is characterized by low toxicity and interacts with other chemicals used in aqueous environments, a particular advantage of this compound is its ability to remove residual iron sulfide in pipelines.

Biocides discussed in the article are used in many industries. Microbial control in the oil and gas industry is primarily practiced to prevent the detrimental effects of microbial growth on production equipment, pipelines, and the reservoir. Biocidal products are assigned to one of 23 different types. These types are divided into 4 main groups:

1) preservatives (e.g. biocides for liquid-cooling and processing systems, metalworking-fluids biocides, and biocides for oil and gas industry),
2) disinfectants (e.g. drinking water disinfectants),
3) pest control,
4) other biocidal products.

Antimicrobial agents and corrosion inhibitors are widely used in the oil and gas industry. Treatment chemicals are used in the natural gas industry from well development through transmission and storage of natural gas. Some papers [5, 10, 17] describe potential environmental impacts and effectiveness of biocides, corrosion inhibitors and their use in gas production, storage and transmission facilities. Potential environmental impacts were addressed by performing a screening environmental assessment on the use of glutaraldehyde, a widely used biocide. Scientific and technical biocorrosion and biocidal literature has descriptions and lists of numerous chemical compounds that exhibit inhibitive properties. Of these, only very few are actually used in practice. Considerations of cost, toxicity, availability and environmental friendliness are of considerable importance. Many of the new formulations tested had a lower environmental aquatic toxicity profile than either glutaraldehyde or THPS (tetrakis hydroxymethyl phosphonium sulfate) alone because of the favorable aquatic toxicity profiles of the complimentary did so with a better environmental footprint. Some papers describe H_2S formation and removal of hydrogen sulfide in Underground Gas Storage conditions. Hydrogen sulfide forms from the activity of sulfate reducing bacteria. Under anaerobic conditions, the sulfate ion is used as a source of oxygen for respiration by some bacteria. The main reason for decreased natural gas quality is the bioreduction of sulfates leading to sulfating of gas. The source of biogenic H_2S could be the water phase, including waste water processing, water disposal wells, etc.

Hydrogen sulfide must be removed to under 4 or 5 ppm in the gas stream for safe handling and for minimal formation of SO_2 during combustion. When used as petrochemical feedstock, methane, ethane and propane must have levels below < 1 ppm as the sulfur is a catalyst poison. The Oil and Gas Institute has obtained 3 patents in the area of biocide and H_2S Scavengers applications in the UGS. The results of these works, possessing practical applications in the oil and gas industry, have been implemented in the polish industry [28]. The microbiological methods are still attractive for the oil and gas industry, thus the methodologies are improved and modified depending on the actual needs and existing problems.

Generally, biocides are used in all stages of oilfield development, from the initial drilling of the wells, during production of oil and gas, and in all aspects of the maintenance of the field, including storage of oil and natural gas in geological conditions (in salt caverns or depleted reservoirs).

The mechanism of the impact of biocides

The chemical structure of biocides determines the manner of its impact on microorganisms, but it is not the only factor limiting antibacterial/antifungal effectiveness. Most of the biocidal agents penetrate into the cell and interfere with metabolic pathways, which in turn lead to the necrosis of the microorganism. Given the structural components of bacterial/fungal cell involved in these interactions, there are three basic types of biocides: binding to external cell structures (e.g. glutaraldehyde, phenols), binding to cell membranes (e.g. ethanol, i-propanol, copper, silver, arsenic compounds) and binding to cellular organelles (e.g. aldehydes, aryl methane, acridine dyes). The variety of biocides, resulting from the chemical structure is related to the different ways they interact with the cell of the microorganism. Depending on the mechanism of this impact, the biocide must fall into one of the following four groups:

- highly active substances whose speed of interaction is extremely short,
- oxidants (halogens and peroxides) – using a radical mechanism for the oxidation of organic compounds,
- electrophiles (formaldehyde, formaldehyde-releasing substances, Cu, Hg, Ag, isothiazolones) – covalently bind to cellular nucleophiles, leading to the inactivation of enzymes,
- compounds acting on the cell membrane, destabilizing the membrane, leading to the rapid decomposition of the cell – QUATS, phenols, alcohols,
- protonophores (parabens, weak acids: benzoic acid, sorbic acid) – causing acidification of the cytoplasm of the cell, disrupting the cellular metabolism.

The selection of appropriate biocides requires consideration of the following criteria. Low production costs, easy biodegradability, selectivity for specific microorganisms and ability to maintain inhibitory properties in the presence of other compounds and in industrial environments.

Characteristics of biocides for use in industrial conditions in petroleum and gas mining

Biocides for use in petroleum and gas mining industry should meet the following requirements. They should have high biocidal capabilities in a broad spectrum of activity, long duration of action, good solubility in water and hydrocarbons and chemical and thermal stability. Biocides also should be environmentally friendly, effective at low

Tab. 3. The example of results of MBO – 3.3'-metylenobis[5-methyloksazolidine] efficiency (one of biocidal agents tested in Microbiology Laboratory INiG. 2010)

Concentration of MBO [ppm]	Number of aerobic bacteria in liquid medium [CFU/ml] ± SD	Number of anaerobic bacteria in liquid medium [CFU/ml] ± SD	Number of fungi in liquid medium [CFU/ml] ± SD
0	**$9.2 \cdot 10^7 \pm 4.6 \cdot 10^6$**	**$6.0 \cdot 10^5 \pm 0.0$**	**$1.7 \cdot 10^4 \pm 5.8 \cdot 10^3$**
50	$8.9 \cdot 10^7 \pm 5.8 \cdot 10^5$	$9.3 \cdot 10^4 \pm 2.1 \cdot 10^4$	$9.3 \cdot 10^3 \pm 2.9 \cdot 10^3$
100	$6.2 \cdot 10^7 \pm 8.7 \cdot 10^6$	$3.7 \cdot 10^4 \pm 2.1 \cdot 10^4$	$5.7 \cdot 10^3 \pm 3.2 \cdot 10^2$
200	$5.0 \cdot 10^5 \pm 2.6 \cdot 10^5$	$6.0 \cdot 10^3 \pm 0.0$	$2.7 \cdot 10^3 \pm 5.8 \cdot 10^2$
400	$2.3 \cdot 10^5 \pm 1.1 \cdot 10^5$	$3.0 \cdot 10^3 \pm 0.0$	$4.7 \cdot 10^2 \pm 87$
600	$1.0 \cdot 10^5 \pm 0.0$	$1.0 \cdot 10^3 \pm 0.0$	$1.7 \cdot 10^2 \pm 35$
800	$3.3 \cdot 10^4 \pm 1.5 \cdot 10^4$	$2.9 \cdot 10^2 \pm 6.0 \cdot 10^1$	77 ± 25
1000	$1.0 \cdot 10^4 \pm 0.0$	$1.8 \cdot 10^2 \pm 36$	33 ± 58

concentrations (1÷100 ppm), not causing chemical contamination, made from cheap and commonly accessible materials. Very important is the lack of side effects such as destruction of the catalysts used in oil processing. Interaction with the components of the solution pumped into the hole must not cause any changes to its chemical and physical properties [15].

The use of many different biocidal chemical compounds in crude oil or petroleum products often causes slow degradation of these xenobiotics, which have mutagenic and carcinogenic properties, which in turn contributes to the chemical contamination of these environments.

The primary objective of the industrial application of biocides is to fight the development and growth of numerous microorganisms (bacteria, fungi, yeasts, etc.) which adversely affect the production, storage and transport of oil and its processing products. Effectiveness of biocidal agents is highly dependent on genus and species, and sometimes even the strain on which the substance has an impact [15, 26, 33]. Experiments show that both gram-negative bacteria and fungi are very sensitive to the presence of biocides, while *Mycobacterium* strains (gram positive), among all the microorganisms not forming spores, show the greatest resistance against biocides. Processing products of petroleum have certain toxicity, much higher than the oil, therefore microorganisms are sensitive in varying degrees lengthy contact with these substances, e.g. *Penicillium sp.* is able to survive much longer than *Cladosporium sp.* in the presence of the same biocidal compounds. Thus, preparations characterized by a wide range of activities against bacteria, fungi, yeasts, algae are highly valued and sought after. Prudent use of biocides requires consideration of several factors that affect the final result. Prior to injection procedures of antibacterial preparations, one should specify the type of microorganisms present in order to properly choose the efficiency

Tab. 4. The example of results of some biocidal agents: sym-triazine, oksazolidine, MgO_2 and CaO_2

Concentration of tested agent/ the kind of suspension	Number of microorganisms [CFU/ml] ± SD											
	Aerobic bacteria after cultivation				Anaerobic bacteria after cultivation				Fungi after cultivation			
	1 day	7 days	14 days	21 days	1 day	7 days	14 days	21 days	1 day	7 days	14 days	21 days
0% (suspension of bacteria/ fungi without biocide)	**$1.3 \cdot 10^8$ $\pm 3.5 \cdot 10^7$**	**$2.1 \cdot 10^8$ $\pm 6.4 \cdot 10^7$**	**$2.0 \cdot 10^8$ $\pm 1.4 \cdot 10^7$**	**$1.1 \cdot 10^8$ $\pm 1.3 \cdot 10^6$**	**$3.2 \cdot 10^6$ $\pm 3.5 \cdot 10^4$**	**$3.0 \cdot 10^6$ ± 0.0**	**$2.9 \cdot 10^6$ $\pm 1.4 \cdot 10^5$**	**$2.9 \cdot 10^6$ $\pm 0.7 \cdot 10^6$**	**$5.0 \cdot 10^2$ ± 0.0**	**$2.3 \cdot 10^3$ $\pm 1.3 \cdot 10^2$**	**$1.2 \cdot 10^4$ $\pm 4.8 \cdot 10^3$**	**$1.2 \cdot 10^5$ $\pm 1.4 \cdot 10^3$**
2% sym-triazine	$6.7 \cdot 10^5$ $\pm 1.1 \cdot 10^5$	< 1	< 1	< 1	$2.4 \cdot 10^6$ $\pm 3.6 \cdot 10^5$	$1.0 \cdot 10^4$ ± 0.0	< 1	< 1	50 $\pm 1.4 \cdot 10^2$	$2.3 \cdot 10^2$ $\pm 5.0 \cdot 10^1$	$6.5 \cdot 10^3$ $\pm 4.9 \cdot 10^2$	$5.5 \cdot 10^3$ $\pm 4.9 \cdot 10^2$
2% MBO	$4.0 \cdot 10^5$ $\pm 1.0 \cdot 10^5$	< 1	< 1	< 1	$1.9 \cdot 10^6$ $\pm 4.0 \cdot 10^4$	< 1	< 1	< 1	50 $\pm 2.8 \cdot 10^2$	< 1	< 1	< 1
Suspension of MgO_2	$5.7 \cdot 10^7$ $\pm 6.0 \cdot 10^6$	$1.3 \cdot 10^8$ $\pm 1.4 \cdot 10^7$	$1.0 \cdot 10^6$ ± 0.0	$2.5 \cdot 10^5$ $\pm 0.7 \cdot 10^5$	$2.4 \cdot 10^6$ $\pm 0.6 \cdot 10^5$	$2.8 \cdot 10^6$ $\pm 4.2 \cdot 10^3$	$2.2 \cdot 10^6$ $\pm 2.8 \cdot 10^3$	$1.9 \cdot 10^6$ $\pm 6.4 \cdot 10^4$	50 $\pm 1.4 \cdot 10^2$	$1.9 \cdot 10^2$ $\pm 2.0 \cdot 10^1$	$3.0 \cdot 10^2$ $\pm 2.0 \cdot 10^1$	$5.0 \cdot 10^2$ $\pm 0.7 \cdot 10^2$
Suspension of CaO_2	$1.0 \cdot 10^8$ $\pm 6.0 \cdot 10^5$	$1.0 \cdot 10^7$ ± 0.0	$3.0 \cdot 10^6$ ± 0.0	$4.0 \cdot 10^5$ $\pm 1.4 \cdot 10^5$	$1.0 \cdot 10^6$ $\pm 2.0 \cdot 10^4$	$7.0 \cdot 10^5$ ± 0.0	$4.0 \cdot 10^4$ ± 0.0	$3.5 \cdot 10^4$ $\pm 0.7 \cdot 10^4$	$1.0 \cdot 10^2$ $\pm 3.0 \cdot 10^1$	$4.0 \cdot 10^3$ $\pm 7.8 \cdot 10^2$	$7.0 \cdot 10^3$ $\pm 2.0 \cdot 10^1$	$1.1 \cdot 10^4$ $\pm 5.6 \cdot 10^2$
2% sym-triazine + MgO_2 (5%)	$1.3 \cdot 10^5$ $\pm 0.6 \cdot 10^5$	$1.0 \cdot 10^6$ ± 0.0	$1.0 \cdot 10^6$ $\pm 2.8 \cdot 10^5$	$4.5 \cdot 10^5$ $\pm 4.9 \cdot 10^3$	$1.9 \cdot 10^6$ $\pm 4.6 \cdot 10^3$	$5.0 \cdot 10^5$ ± 0.0	$5.0 \cdot 10^5$ ± 0.0	$1.8 \cdot 10^4$ $\pm 0.7 \cdot 10^4$	$3.0 \cdot 10^2$ ± 0.0	$2.2 \cdot 10^3$ $\pm 4.2 \cdot 10^2$	$2.4 \cdot 10^4$ $\pm 5.6 \cdot 10^2$	$5.0 \cdot 10^4$ $\pm 2.8 \cdot 10^2$
2% sym-triazine + CaO_2 (5%)	< 1	< 1	< 1	< 1	$9.7 \cdot 10^6$ $\pm 5.0 \cdot 10^5$	$1.5 \cdot 10^4$ $\pm 0.7 \cdot 10^4$	< 1	< 1	50 $\pm 1.0 \cdot 10^1$	$2.3 \cdot 10^3$ $\pm 4.2 \cdot 10^2$	$1.1 \cdot 10^4$ $\pm 6.4 \cdot 10^2$	$3.0 \cdot 10^4$ $\pm 2.8 \cdot 10^2$
2% r-r MBO + MgO_2 (5%)	< 1	< 1	< 1	$1.5 \cdot 10^5$ $\pm 7.0 \cdot 10^4$	$1.7 \cdot 10^6$ $\pm 2.0 \cdot 10^5$	< 1	< 1	< 1	$1.0 \cdot 10^2$ $\pm 0.7 \cdot 10^2$	$2.2 \cdot 10^3$ $\pm 1.4 \cdot 10^2$	$1.5 \cdot 10^4$ $\pm 0.7 \cdot 10^3$	$6.5 \cdot 10^4$ $\pm 3.5 \cdot 10^2$
2% MBO + CaO_2(5%)	< 1	< 1	< 1	< 1	$1.7 \cdot 10^6$ $\pm 2.9 \cdot 10^4$	< 1	< 1	< 1	$2.5 \cdot 10^2$ ± 0.0	30 $\pm 1.4 \cdot 10^2$	$2.2 \cdot 10^2$ $\pm 9.0 \cdot 10^1$	$4.5 \cdot 10^4$ $\pm 2.1 \cdot 10^2$

of the preparation. In addition, knowledge of activity, mechanism of impact and effective biocide concentration is essential.

Currently, in the domestic oil industry biocides are commonly used for drilling fluids. Also, H_2S Scavenger preparations are often used. There are compounds with varying chemical formula. Most of these types of agents work as antibacterial preparations and also have properties to absorb hydrogen sulfide produced by bacteria. These agents may be used on many gas and oil production installations. Some discussed formulations have been used worldwide for several years, for example in installations in the North Sea. Procedures were carried out with great success and resulted in lowering levels of hydrogen sulfide to acceptable values for the transmission of natural gas. An example of this process of neutralization of hydrogen sulfide is the application of hydrogen sulfide neutralizer (also with the characteristics of the biocide) to the stream of natural gas in amounts of about 3 to 10 parts of the preparation per 1 part H_2S, which resulted in a drastic reduction in the concentration of hydrogen sulfide. These preparations have a specific gravity usually within approximately 1.07÷1.1 g/ml, and the flash point is usually > 100°C.

Chemical formula of these types of preparations is usually based on amines, amino alcohols, mixture of amino alcohols and quaternary amines, triazine and derivatives, phenols. Some of these preparations are soluble in water, and some in oil, depending on the specific purpose of an agent. As a rule, they are used in systems transporting oil or gas and are characterized by high efficiency. Some of these products allow control over biogenic processes and cause neutralization of the hydrogen sulfide produced.

Removal of hydrogen sulfide from such media as oil, natural gas or water is necessary not only because of its very high toxicity, but also because of its corrosiveness, which can largely impede the course of operation. Corrosion processes are also associated with the action of other bacteria, apart from the group of SRB [1, 4, 24]. These bacteria give rise to the so-called biofilm layers in pipelines and tanks [6], which accelerate the corrosion of the equipment or installation. Hydrogen sulfide neutralizers generally are available in liquid form, while some of them are solid. Most of them are safe for the environment. For a particular application, the projected content of hydrogen sulfide and many other factors are taken into account, which are important from the standpoint of the operation. Systems based on the use of hydrogen sulfide neutralizers usually cause a large reduction in hydrogen sulfide, even below 1 ppm. The use of these agents does not cause changes in the gas. Amine compounds and derivatives of triazine are often used as the substances eliminating hydrogen sulfide from natural gas or oil. During gas extraction or operations, it is necessary to maintain constant levels of hydrogen sulfide below 4 ppm, for safety reasons and because of the need to avoid the corrosion process, which as mentioned can be caused by large concentrations of this highly corrosive gas.

Industrial systems which most apply hydrogen sulfide absorbers (neutralizers) are usually not complicated when it comes to their equipment. For this reason, the cost of application in industrial environments is not too high. Systems, using the biocide/H_2S Scavenger agents are used in many Western countries, the USA, and also in Poland. In some cases, the concentrations of hydrogen sulfide, which could have been removed due to their application, amounted to approximately 2.400 ppm, and various preparations differed with regard to the type of active ingredient and the carrier.

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