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## **LABORATORY TESTS FOR THE APPLICATION OF NITRATE-BASED INHIBITOR AGAINST H<sub>2</sub>S FORMATION**

### **1. INTRODUCTION**

The questions of the occurrence of hydrogen sulfide and hydrogen sulfide hazards in deposit conditions are directly linked to the application of H<sub>2</sub>S Scavengers preparations in oil and gas industry. As it is commonly known, the majority of crude oil deposits in Poland contain hydrogen sulfide. Hydrogen sulfide is a highly toxic chemical compound. Its dangerous concentration amounts to ca. 6 mg/m<sup>3</sup>, and at the concentration exceeding 1 g/m<sup>3</sup> it can have an immediate lethal effect. Moreover, H<sub>2</sub>S as the ingredient of wet gas causes the interference in microcrystalline structure of the material in contact points, which results in its weakening due to atypical corrosion processes as well as in breakability and may lead to catastrophic results, such as cracks in the pipeline material. Breakdowns of this type constitute a serious threat to the health and life of the staff together with potential pollution of the environment.

Natural gas deposits as well as gas accompanying crude oil often contain an important amount of hydrogen sulfide (Barnówko-Mostno-Buszewo oil field may constitute an example as the content of this substance was reaching 40 g/Nm<sup>3</sup>). In order to protect the atmospheric air, the system of constant hydrogen sulfide detection is used in this type of deposits. In connection with the presence of contamination described above, there exists the necessity to monitor sulfur compounds in deposit media [21].

Apart from using amine systems, biocides and typical preparations serving as hydrogen sulfide neutralizers, other solutions are also applied in the oil industry, including

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nitrate treatments in order to limit the H<sub>2</sub>S emission from deep-seated hydrocarbon deposits [2, 11, 14, 15, 20].

## **2. MATERIALS AND METHODS**

### **2.1. The procedure of efficiency testing of hydrogen sulfide inhibitor**

Laboratory tests presented in tables 1 and 2 include the results of two tests of the BMF Bac (nitrate-based inhibitor), substance acting as hydrogen sulfide scavenger intended for use in the conditions of hydrocarbon deposits. Tests presented in the tables were conducted in the range of concentration of the preparation from 100 to 2000 ppm. In total, 24 test liquids and two control samples were prepared. Test liquid was constituted by pooled formation water and the mixture of pooled formation water with sulfate-reducing bacteria (SRB) in the 1:1 volume ratio. Breeding was performed in sterile glass bottles with ground glass joint, to which test liquid was poured and the neutralizer added and after 24-hour and 48-hour incubation, the concentration of hydrogen sulfide was measured in subsequent test samples with the iodometric method applied [9, 18]. The results were compared with the level of hydrogen sulfide in the control sample which did not contain the nitrate-based inhibitor.

In laboratory tests, the mixtures of several strains of sulfate-reducing bacteria were used. In the last years, they were isolated from different exploitation wells during the reception of natural gas from national underground gas storage facilities, following the high level of H<sub>2</sub>S production. Bacteria contained in the suspension, i.e. test mixture, included sulfate-reducing bacteria *Desulfovibrio spp*, *Delulfomicrobium spp*. as well as *Desulfotomaculum spp*. and other [4, 10, 13, 17]. Test liquids with the content of sulfate-reducing bacteria in the solution amounting to 10<sup>3</sup> cells/ml were used in tests. The results of tests of the preparation performed within the scope of the present work reflect the effectiveness of its action at different concentrations, with reference to the elimination of biogenic H<sub>2</sub>S forming in deposit conditions.

### **2.2. The procedure of testing permeability changes**

The permeability of a reservoir is a measure of how much fluid can flow through a rock for a specified pressure drop. Permeability can be measured in a laboratory from core analysis. While this sometimes done with the core in its native or restored state. In a petroleum reservoir, the rock is usually not fully saturated with a single phase fluid. Generally saturations in the reservoir rock will consist of different amounts of gas, oil, and water.

Tests were conducted on sandstones, having similar parameters to the stone in an exemplary underground gas storage facility. Due to insufficient amount of material (cores) from the storage facility, measurements were performed on sandstone samples obtained from the open-pit mine located near Szydłowiec. The sandstone is yellow, characterized by medium compactness and loose framework of grains. Samples with effective permeability for gas were prepared for tests, while in the majority of cases permeability amounted from ca. 700 to 1200 mD.

Six test solutions were prepared within the scope of works. The content of preparation in the solution amounted from 1 to 10% of volume. Tests were also performed on medium samples for the active substance, i.e. methanol.

Laboratory tests regarding the changes in the permeability of reservoir rock samples under the influence of test solutions were performed with the use of:

- HTHP filter press (OFI USA), modified by INiG-PIB (measurements of drilling fluids filtration through cores in static and dynamic conditions at  $\Delta p_{\max} = 0.7$  MPa and  $T_{\max} = 80^{\circ}\text{C}$ ),
- permeability measuring device manufactured by the TEMCO company for the measurements of gas permeability,
- devices described above enable conducting the tests in the following conditions (so called simulated deposit conditions):
  - measurement temperature – up to  $150^{\circ}\text{C}$ ,
  - simulated pressure of overburden stones – up to 21 MPa,
  - simulated reservoir pressure (differential) – up to 17.5 MPa.

All measurements were performed in simulated deposit conditions, in accordance with measurement procedures applied in renowned laboratories of the world. The first part of the realized laboratory works consisted in obtaining irreducible ( $S_{wi}$ ) saturation of sandstone samples with formation water. Stages of the procedure applied in the described tests are presented below:

**A) Sample preparation process according to the applicable procedures consisted of the following stages:**

- saturation core sample with formation water (2% NaCl solution):
  - stone samples were seasoned in 2% NaCl solution for 5 days;
  - brine was pumped through the sample at the outlet backpressure of 1.4 MPa in order to enable the air to dissolve in it and be completely removed from the pore space of the sample;
- obtaining irreducible saturation with formation water through removing the brine from the sample with gas (nitrogen);
- measuring the initial permeability of the sample for gas  $k_0$ .

**B) Simulation of the process of pumping the inhibitor solution and receiving the gas from the storage facility was conducted as follows:**

- stone sample, prepared according to the abovementioned procedure, was placed in the HTHP filter press;
- stone sample was subject to the impact of the biocide/neutralizer/inhibitor solution (the solution was pumped) in the amount of 20 pore volumes of the sample, at differential pressure of 0.7 MPa and the temperature of 35°C;
- then the sample was seasoned in the test solution for 14 days at the temperature of 40°C;
- the sample was placed in the Temco permeability measuring device in order to determine final permeability for gas  $k_{kb}$ , after seasoning in the determined solution and to evaluate the change (degree of damage – loss) of permeability  $UP_B$  after the action of a particular preparation (or SRB suspension).

### **2.3. The method of determining the change (loss) of sandstone sample permeability**

Loss of permeability  $UP$ , defined as the decrease in permeability of initial sample expressed in percent, after the filtration of drilling or fracturing fluids to the pore space (in this case – the determined test solution), is expressed the following formula:

$$UP = (1 - k_k/k_0) \cdot 100 \text{ [%]}$$

where:

$k_k$  – final stone permeability, [mD],

$k_0$  – initial stone permeability (of the undamaged porous rock), [mD].

If the permeability of damaged rock  $k_k = 0$ , then the loss of permeability amounts to 100%.

## **3. RESULTS**

### **3.1. Efficiency tests of nitrate-based inhibitor in the elimination of biogenic hydrogen sulfide**

The results of laboratory tests aiming at determining the efficiency of the BMF Bac 4 nitrate-based preparation are presented in Tables 1–2. Works were divided into 2 stages, i.e. tests of the mixture of pooled formation water and sulfate-reducing bacteria active suspension as well as tests of pooled formation water itself. According to the rules for tests performed in order to determine the efficiency of preparations neutralizing hydrogen sulfide, SRB suspension was used for tests, obtained from a specific UGS deposit environment, with high metabolic activity, as well as formation water contaminated with hydrogen sulfide, constituting a mixture of water from different wells of the underground gas storage facility.

**Table 1**

Results of efficiency tests of BMF Bac 4 – nitrate-based inhibitor  
in the process of biogenic hydrogen sulfide elimination

Sample label	Concentration of BMF Bac 4 [ppm]	H <sub>2</sub> S content in test samples [mg/dm <sup>3</sup> ] (pooled formation water + SRB suspension in 1 : 1 volume ratio)	
		24 hours of incubation	48 hours of incubation
A-1	100	94.9	88.6
A-2	200	92.9	90.3
A-3	300	94.5	95.2
A-4	400	94.0	94.0
A-5	600	93.0	88.5
A-6	800	91.5	91.1
A-7	1 000	69.2	70.2
A-8	1 200	69.0	72.0
A-9	1 400	75.5	69.1
A-10	1 600	75.5	71.9
A-11	1 800	71.7	71.7
A-12	2 000	72.8	72.9
K-1 control sample (without preparation)	–	96.5	96.5

Number of sulfate-reducing bacteria in test solution: 10<sup>3</sup> SRB/ml

Pooled formation water contains the material from several exploitation wells (with natural biogenic H<sub>2</sub>S). As far as the discussed tests are concerned, they were performed at the concentrations from 100 to 2000 ppm. The content of hydrogen sulfide was measured after adding the inhibitor to the solution and it was compared with control solution (not containing the inhibitor). According to the results (Tab. 1), at the highest concentration of BMF Bac 4 inhibitor amounting to 2000 ppm, ca. 23 mg/dm<sup>3</sup> of hydrogen sulfide were neutralized after 24 hours of incubation. After 48 hours of incubation, no statistically important change was observed. The results of the efficiency of BMF Bac 4 preparation at the concentrations of 1000–1400 ppm, after 24 hours and 48 hours of incubation showed the decrease in the content of hydrogen sulfide by ca. 21.0–27.5 mg/dm<sup>3</sup>. This test demonstrated a slight decrease in the content of hydrogen sulfide in test samples at the concentrations of the inhibitor from 100 to 500 ppm. The level of H<sub>2</sub>S fell from 96.5 mg (suspension without the addition of inhibitor) to the range of 91.5–94.9 mg/dm<sup>3</sup> after 24 hours of incubation. This represents ca. 5.18–1.66% in comparison with the control sample.

The second series of tests was performed on natural formation water (not contaminated with bacteria). At the highest concentration, i.e. 2000 ppm (Tab. 2), decrease in the content of hydrogen sulfide was observed in the tested liquid from the initial value of 35.8 mg/dm<sup>3</sup> to the value within the range of 27.9–21,1 mg/dm<sup>3</sup> after the predetermined incubation period of 24 and 48 hours. At the concentration of 2000 ppm, the efficiency of hydrogen sulfide neutralization ranged between 22.07% and 41.06%. Good results were also obtained at the concentration of the inhibitor amounting to 1000–1400 ppm; in this case the level of H<sub>2</sub>S decreased from the initial value of 35.8 mg/dm<sup>3</sup> to the value within the range of 25.0–28.7 mg/dm<sup>3</sup> after 24 hours of incubation. After 48 hours of incubation, the level of hydrogen sulfide decreased to the range of 24.1–25.8 mg/dm<sup>3</sup>. It corresponds to ca. 32.68–27.93%. At the concentrations of the inhibitor ranging from 100 to 800 ppm (Tab. 3), the content of neutralized hydrogen sulfide in the solution was low and amounted to ca. 0.9–6.6 mg/dm<sup>3</sup>. It shows that efficient content of the tested inhibitor in laboratory conditions concerns the concentrations exceeding 1000 ppm. In view of the performed tests, the preparation is suitable for application in oil and gas industry, separately as the agent for neutralizing biogenic hydrogen sulfide or as the adjuvant agent for biocides and H<sub>2</sub>S Scavengers.

**Table 2**  
Results of efficiency tests of BMF Bac 4 – nitrate-based inhibitor  
in the process of biogenic hydrogen sulfide elimination

Sample label	Concentration of the preparation [ppm]	H <sub>2</sub> S content in test samples [mg/dm <sup>3</sup> ] (pooled formation water)	
		24 hours of incubation	48 hours of incubation
B-1	100	33.0	33.0
B-2	200	29.9	29.2
B-3	300	30.3	31.3
B-4	400	31.9	31.1
B-5	600	32.8	32.8
B-6	800	32.0	34.9
B-7	1 000	28.7	24.1
B-8	1 200	22.8	23.2
B-9	1 400	25.0	25.8
B-10	1 600	25.0	21.5
B-11	1 800	27.4	27.4
B-12	2 000	27.9	21,1
K-2 control sample (without preparation)	–	35.8	35.8

Number of sulfate-reducing bacteria in test solution: 10<sup>3</sup> SRB/ml

**Table 3**

The effect of nitrate-based inhibitor and methanol on the sandstone permeability. Samples A – BMF Bac 4, samples M – methanol (solvent for the active substance)

Concentration of BMF Bac 4 (% of volume)	Initial permeability $k_0$ [mD]	Final permeability after the application of solution $k_0$ [mD]	Loss of permeability after the application of solution UPB	FE ratio (flow efficiency)	SKIN ratio
A-1%	1 280	988	22.9	0.90	0.80
A-2%	1 530	1 192	22.1	0.90	0.77
A-4%	1 548	1 120	27.6	0.87	1.03
A-6%	862	657	23.8	0.89	0.84
A-8%	1 049	800	23.7	0.89	0.84
A-10%	952	697	26.8	0.88	0.99
Average value for all tested concentrations of BMF Bac 4				0.888	0.878
M1 (Methanol – sample 1)	1244	1250	–0.5	1.00	–0.01
M2 (Methanol – sample 2)	804	802	0.2	1.00	–0.005
Average value for methanol				1.00	–0.0075

### 3.2. Tests of permeability changes in reservoir rock

Formation damage may occur during several processes mainly drilling, coring, well completion, and production, workover and injection of water or chemicals for enhanced oil recovery. There are four types of formation damage; the first type results from the blocking of pore channels by solids introduced by drilling fluids or completion or workover or injection fluid. The second type is related to clay water reaction that yields clay hydration and swelling or dispersion of clay particles and plugging of pores by movement of produced or injected water. A third type is developed from extraneous water introduced into the formation at the wellbore causing liquid blocking during drilling, coring, completion or workover. A fourth type is due to caving and subsequent flow of unconsolidated sands into the wellbore [1, 3, 5, 22].

While discussing the issues closely related to a very important physical parameter being the permeability of reservoir rock, it is necessary to mention that cost-efficient exploitation of the existing natural gas and crude oil deposits together with geological structures for underground gas storage requires among others the knowledge of mechanisms governing the flow of hydrocarbons through porous rocks. In this type of rocks, the decrease in permeability is usually caused by the penetration of drilling fluid filtrate

or slurry as well as partially the solid phase (loam, bentonite, charging materials, bore dust and other) to the pore space. It results in an important decrease (damage, loss) in stone permeability.

Loam particles with the dimensions smaller than stone pores will deposit in pore space of the rock [7]. The discussed phenomena are often caused by strongly dispersing clay rocks. Other factors include colmatage caused by the accumulation of certain chemical substances or excessive and uncontrolled development of bacteria in the pore space.

The results obtained in tests concerning the influence of nitrate-based inhibitor on reservoir rock are reflected in the average flow efficiency ratio (FE), for the concentrations of 1–10% amounting to ca. 0.888. With the increase in the concentration of the inhibitor, the ratio is subject to insignificant changes, ranging from 0.90 to 0.88. Tests performed within the scope of the present work still need to be completed with comparative data. They would consider analogical tests with the use of biocide/H<sub>2</sub>S Scavenger type preparations intended for oil industry. What seems interesting is the comparison of the same parameters for nitrate-based inhibitors as well as for biocides and H<sub>2</sub>S Scavengers (acting according to a different principle). However, the realized series of tests may constitute the basis for potential use in the industry, at a not too high concentration, i.e. up to ca. 10%, which has been proved in the present work.

The results of tests performed with the use of the BMF Bac 4 preparation intended for the neutralization of hydrogen sulfide in deep-seated deposits constitute a valuable source of information concerning its potential use in industrial procedures. It is in general necessary to emphasize that phenomena connected with chemical colmatage of deposits, as well as with the colmatage of a biochemical character, were many times described in literature [4, 5, 6, 10, 16, 17]. The results of research on the influence of active substances pumped to the deposit zone constitute a very important parameter. They should be taken into account while planning industrial procedures, apart from testing the level of efficiency of a given parameter in the process of eliminating hydrogen sulfide contamination.

#### **4. CONCLUSIONS**

The following conclusions can be drawn after the performance of laboratory tests described in the present article:

1. The adopted methodology made it possible to perform both the research on the influence of the BMF Bac 4 nitrate-based preparation on the concentration of hydrogen sulfide in formation water (first series of analysis) and the mixture of formation water and SRB suspension (second series of analysis), as well as the research on the influence of the abovementioned preparation on the permeability of reservoir rock.



2. In the samples with the maximum concentration of the preparation (used in the tests), i.e. 2000 ppm it was determined that the level of hydrogen sulfide in the tested media decreased by ca. 23 mg/dm<sup>3</sup> in comparison with control samples in the first series of analysis. It means that the neutralization of hydrogen sulfide amounted in the case of this series to the range of 24.46–24.56%. In the second series, at lower concentrations, a positive effect was observed. The level of neutralization when the concentrations from 1000 to 2000 ppm were applied reached between 20.67% and 41,06% in relation to control samples.
3. At low concentrations of the preparation (100–500 ppm) a slight decrease in the content of hydrogen sulfide in test samples was observed, at the concentrations of the inhibitor from 100 to 500 ppm. The level of H<sub>2</sub>S decreased from 96.5 mg (suspension without the addition of inhibitor) to 91.5–94.9 mg/dm<sup>3</sup> after 24 hours of incubation. It constituted ca. 5.18–1.66% for the first series. While in the second series, at inhibitor concentrations from 100 to 800 ppm the content of neutralized hydrogen sulfide in the solution was low and amounted to ca. 0.9–6.6 mg/dm<sup>3</sup>, which fell within the range 2.51–18.43%.
4. Basing on the results of the abovementioned tests, BMF Bac nitrate-based preparation has a positive effect reflected in the decrease in the content of hydrogen sulfide in the analyzed fluids. Minimum recommended concentration of the preparation acting efficiently in laboratory conditions amounts to >1000 ppm.
5. Moreover, tests connected with the influence of nitrate-based preparation on the permeability of reservoir rock were performed. The adopted methodology made it possible to test the changes in the permeability of sandstone cores as a result of the action of nitrate-based inhibitor. In the tests connected with the influence of nitrate-based inhibitor on reservoir rock the obtained results were reflected in the average flow efficiency ratio (FE), for the concentrations of the tested preparation of 1–10% of volume. Average FE ratio amounted to ca. 0.888 and with the increase in the concentration of the inhibitor, the ratio was subject to insignificant changes, ranging from 0.90 to 0.88. It means that the accumulation of the abovementioned preparation in the selected concentrations does not cause disturbances in the flow of deposit media. In this way, the preparation (at the tested range of concentrations) is safe for the deposit.

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