



CONTROL OF SULFATE REDUCING BACTERIA THROUGH THE APPLICATION OF SODIUM MOLYBDATE IN COMPLETION FLUIDS.

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Abstract

Numerous studies have demonstrated that the use of sodium molybdate inhibits the activity of the adenosine 5 phosphosulphate reductase enzyme in different dosages: 0.2-20 mM (Smith, 1981), 10 mM (Hilton, 1988), 2 mM (Lo, 1990) and 3.2 mM (Yodar, 1988). In our experiments, we detected that the lowest concentration to inhibit the activity of this enzyme in the planktonic Sulfate Reducing Bacteria (SRB) and in Total Anaerobic Bacteria (TAB) was of 0.2 mM or 48 ppm. Sodium molybdate bears very low toxicity and it is, therefore, very attractive to minimize the possible environmental impacts associated to the use of completion fluids by using glutaraldehyde or triazine as bactericide. In addition to that, it has been pointed out as an excellent anodic inhibitor of corrosion (Shams, 1996), (Mainier, 1991), (O'Neal, 1975) and (Vukasovich, 1977). Moreover, this work not investigates this characteristic, but only evaluates the corrosion rates in four completion fluids under specific conditions.

Introduction

This study tried to make the use of sodium molybdate viable as an inhibitor of the bacterial activity of SRB, where the results have pointed it as a possible substitute for glutaraldehyde or for the triazine used in completion fluids. Thus, this study was performed in four stages:

1. Establish the ideal concentration for the use of sodium molybdate;
2. Study of the compatibility of the sodium molybdate among the salts composing the completion fluids;

3. Performance of acute toxicity tests with *Mysidopsis juniae*, according to the CETESB NT L5.251 policy;
4. Corrosion tests in aerated and deaerated media.

Material and Methods

Study of the Ideal Inhibitory Concentration of Sodium Molybdate

The sample is inoculated in an adequate culture medium, with the absence of oxygen, containing the ferrous ion as indicator of bacterial development and in different concentrations of sodium molybdate. After the incubation in oven at a temperature of 35°C we noticed the growth in a period of up to 28 days. This method is applied for the detection of the presence of SRB in waters, solid residues, petroleum and derivatives. We noticed the inhibitory effect on planktonic SRB up to 0.2 mM, corresponding to 48 ppm.

In this experiment, we have also evaluated the capacity of the sodium molybdate to inhibit the activity of the TAB, according to results shown in **Table 1**. The efficiency of the molybdate was considered high up to 0.2 mM, since there was absence of growth of SRB and TAB in solution.

Photos 1 and **2** refer to the results of experiments performed in the Microbiology Laboratory in Macaé.

Study of the Compatibility between Sodium Molybdate and The Salts used on Completion Fluids

The completion fluids selected to evaluate the compatibility of the sodium molybdate were: on the basis of KCl, of NaCl, of CaCl₂, of NH₄Cl and of NaHCOO salts. After the preparation of the completion fluids

shown in **Table 2**, they were submitted to vacuum filtration using a Millipore filter of 45 μm of pore for the removal of fine solids and afterwards a solution of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$. Finally, the behavior of the solutions was observed at temperatures of 30°C and 75°C using a vacuum oven during two hours. At the end of the study we concluded that the sodium molybdate is compatible with Na^+ , K^+ , NH_4^+ and with sodium formate. However, with calcium, the formation of precipitates at 514 g/l and 60 g/l was observed. It will be necessary to establish the limits of saturation of calcium in order to avoid the formation of precipitates.

Separately, the tests performed with calcium and barium ions, in the presence of sodium molybdate yielded the results shown in **Table 3**.

It will be necessary to perform more specific tests in order to determine the adequate value to work in different concentrations of barium. However, it has been reported that in seawater or in industrial water, the barium concentration is below 5 ppm, which probably would not cause problems in using sodium molybdate to produce the completion fluids related to the formation of precipitates.

Test of Acute Ecotoxicity of Completion Fluids

The tests were made by LABTOX – Laboratório de Análise Ambiental Ltda, using the testing organism, *Mysidopsis juniae*. The composition of the evaluated fluids and the results are shown in **Table 4**. Initially, the saline fluids were tested and afterwards, the fluids were tested in the presence of glutaraldehyde (**Table 5**) and finally, the fluids only with sodium molybdate (**Table 6**).

In summary, we noticed that the toxicity of the completion fluids with sodium molybdate at a concentration of 1000 ppm is much inferior to the toxicity of fluids using glutaraldehyde in their composition, as the presentation of bar graphic (**Figure 1**) generated from data on **Table 7**.

Experimental

Completion fluids preparation

The completion fluids were prepared from basic formulations (1 liter) with artificial sea water, inorganic salt and Ultrawet 70 (dispersant), which are showed in **Tables 8, 9, 10, and 11**. After, the solutions were filtered by vacuum process with membrane 0.45 μm pore, and then, from this solutions, four aliquots were obtained in order to prepare the completion fluids formulations with the characteristics as follows:

- Fluid 1 - Deaerated environment with addition of sodium bisulfite;
- Fluid 2 - Blank (environment aerated);
- Fluid 3 - Environment deaerated with glutaraldehyde compound (bactericide) and
- Fluid 4 - Environment aerated with sodium molybdate salt.

Corrosion tests

In order to evaluate the corrosion rate, the method of mass loss based on standard ASTM G1-30 (2004) was used. Rectangular specimens of size 2 cm x 0,8 cm x 0,5 cm were mechanically polished on wet SiC paper (grade 400), degreased ultrasonically in acetone and dried on hot air. After, the specimens were weighed to the 10^{-4} g and immersed in solutions with artificial sea water, completion fluids, bactericide (molybdate salt solution and glutaraldehyde compound) and a oxygen scavenger (sodium bisulfite salt) giving a volume to surface ratio equivalent to 83 mL/cm³. Tests were performed in coated TEFLON™ stainless steel cylinders, assembled in a roller oven for 96 h during four days at 70°C. At the end of this period, the specimens were cleaned, dried and reweighed. The corrosion rate was calculated from corrosion rate equation in accordance with ASTM G1-30 (2004) Standard. Corrosion tests were duplicated and the corrosion rate values were obtained from the average of three coupons. The results are presented as average corrosion rate given in mils per year (mpy).

In **Table 12** is collected the corrosion rate results, with respective standard deviations, of 1020 carbon steel in completion fluid formulations tested.

KCl - based fluid completion: In this case, Formulation 1 (deaerated environment) presented the 1020 carbon steel lowest rate value. The formulations 2 and 4, aerated blank and aerated environment with sodium molybdate salt, respectively, showed the same corrosion rate values, namely, 24 mpy. The formulation 3 in deaerated environment with glutaraldehyde compound exhibited corrosion rate less value than formulations 2 and 4.

NaCl - based fluid completion: The formulations 1 and 3 deaerated environment and deaerated environment with glutaraldehyde, respectively, presented the same corrosion rates, on the other hand, formulations 2 and 4 showed corrosion rate values above the fluid 1 and fluid 3 values.

HCOONa - based fluid completion: In this case, completion fluid formulations 2 (aerated blank), 3 (deaerated environment with glutaraldehyde) showed similar values. Similar corrosion rates between KCl 1 and HCOONa 1 completion fluids (both in deaerated environment) were observed.

NH_4Cl - based fluid completion: In formulation 1 as well KCl and HCOONa completion fluid formulations, the presence of the sodium bisulfite decreased the corrosion rate value of the 1020 carbon steel. In relation to formulations 2 and 4, significant differences on corrosion rate values was not observed.

Incompatibility between NH_4Cl salt solution / glutaraldehyde compound not permit to evaluate the behavior of the formulation 3.

Conclusions

The study developed regarding the sodium molybdate fluids in the completion works, as a possible substitute for current bactericidal agents such as glutaraldehyde and triazine proved that:

1. Sodium molybdate was able to inhibit the activity of planktonic Sulfate Reducing Bacteria and of Total Anaerobic Bacteria in a concentration superior to 48 ppm (0,2 m M), using formation water and oil in the experiments.

2. The compatibility tests limited the use of the concentration of molybdate to 250 ppm for the respective concentrations of calcium and barium of 1000 ppm and 50 ppm. However, it is totally compatible with the other cations of potassium, sodium, ammonia and with fluids with a sodium formiate base.

3. The ecotoxicity tests determined that the completion fluids with sodium molybdate as bactericide at the 1000 ppm concentration are not toxic. The tests demonstrated that the fluids with glutaraldehyde are significantly more toxic than the fluids on the molybdate basis. Glutaraldehyde, differently from molybdate, is easily degraded and although it reduces the activity of SRB, it is capable of increasing the growth of the biofilm, thus accelerating the corrosion of steel.

4. Regarding of the corrosion test results, we have verified the impossibility of application of the sodium molybdate salt in completion fluids as a corrosion inhibitor on protection of 1020 carbon steel. However, this salt not demonstrated to be a corrosive agent.

5. By analysing the corrosion rate values of 1020 carbon steel with glutaraldehyde as bactericide, although in environment deareated, in general showed similar values to the aerated fluids with sodium molybdate salt. Besides, fluids with gluraraldehyde compound presented higher toxicity in relation to the completion fluid with sodium molybdate salt.

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Table 1. MPN/ml: most probable number of microorganisms per ml. Temperature: 35° C.

Concentration of Sodium molybdate (nM)	Sample: formation water from P-35 Concentration in MPN/ml after 28 days		Sample: oil from P-35 Concentration in MPN/ml after 28 days	
	SRB	TAB	SRB	TAB
0.5	N.D	N.D	N.D	N.D
0.2	N.D	N.D	N.D	N.D
0.125	110×10^4	110×10^4	110×10^4	110×10^4
0.063	110×10^4	110×10^4	110×10^4	110×10^4
0.031	110×10^4	110×10^4	110×10^4	110×10^4

N.D = Non-Detected.

TAB = Total Anaerobic Bacteria.

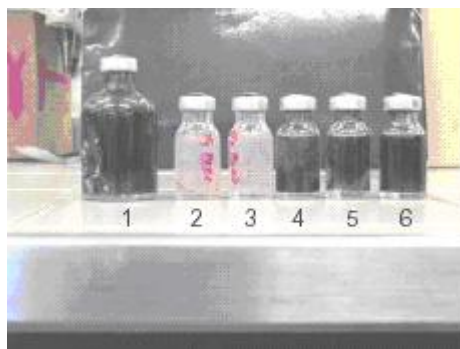


Photo 1. The darkened color of culture medium 4, 5 and 6 indicates the formation of ferrous sulphide due to the production of sulphide gas produced by the activity of the planktonic SRB, yielding positive results. Since there was no color alteration in medium 2 and 3, we concluded that in the presence of the sodium molybdate, SRB were totally inhibited. The samples were originated from the formation of water. The concentration of the medium:

1. Positive control; 2. 0.5 mM; 3. 0.2 mM; 4. 0.125 mM; 5. 0.063 mM and 6. 0.031mM.

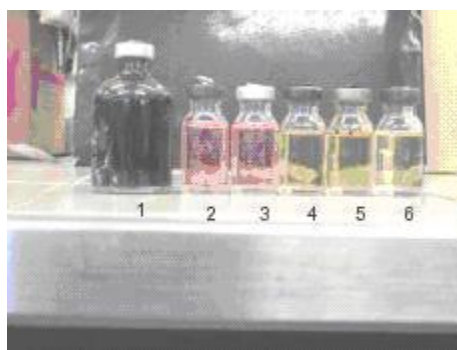


Photo 2. The yellowish color of culture media 4, 5 and 6 gave a positive result due to the activity of the TAB. Since there was no color alteration for medias 2 and 3, we concluded that the sodium molybdate in solution was able to completely inhibit the activity of the TAB. The samples were taken from formation water. The concentration of the medium:

1. Positive control; 2. 0.5 mM; 3. 0.2 mM; 4. 0.125 mM; 5. 0.063 mM and 6. 0.031mM.

Table 2. Composition of completion fluids – Formulations tested.

Components	Fluid at KCl basis	Fluid at NaCl basis	Fluid at CaCl₂ basis	Fluid at NH₄Cl basis	Fluid at NaHCOO basis
Sea Water, ml	350	350	350	350	350
KCl,g/l	20	-	-	-	-
NaCl,g/l	-	291	-	-	-
CaCl ₂ ,g/l	-	-	514	-	-
NH ₄ Cl,g/l	-	-	-	15.2	-
NaHCOO g/l	-	-	-	-	542
Ultrawet 70, % vol.	0.3	0.3	-	0.3	0.3
Sodium molybdate, ppm	1000	1000	1000	1000	1000
Sodium bisulfite, % vol.	0.045	0.045	0.045	0.045	0.045
Ultrawet 110, % vol.	-	-	-	0.2	-

Table 3. Incompatibility tests with Ba⁺² and Ca⁺² ions

Calcium (ppm)	Molybdate at 500 ppm	Molybdate at 250 ppm
5000	White precipitate	White precipitate
2000	White precipitate	turbidity
1000	White precipitate	N.D.
Barium (ppm)	Molybdate at 500 ppm	Molybdate at 250 ppm
5000	White precipitate	White precipitate
2000	White precipitate	White precipitate
1000	White precipitate	White precipitate
500	-	White precipitate
250	-	White precipitate
100	White precipitate	Slight turbidity
50	White precipitate	N.D.

N.D. = Not detected.

Table 4. LC(I) 50; 96 hours (initial dilution lethal to 50 % of the organisms in test in a period of 96 hours).

Components	Fluid at KCl basis	Fluid at NaCl basis	Fluid at NaHCOO basis
Sea Water, ml	350	350	350
KCl,g/l	20	-	-
NaCl,g/l	-	291	-
CaCl ₂ ,g/l	-	-	-
NH ₄ Cl,g/l	-	-	-
NaHCOO g/l	-	-	542
Ultrawet 70, % vol.	0.3	0.3	0.3
Sodium molybdate, ppm	-	-	-
Sodium bisulfite, % vol.	0.045	0.045	0.045
Glutaraldehyde at 40%, % vol.	-	-	-
LC(I)50; 96 hours	86,369.55 ppm	172,377.88 ppm	109,969.96 ppm

Table 5. LC(I); 96 hours (initial dilution lethal to 50% of the organisms in test in a period of 96 hours).

Components	Fluid at KCl basis	Fluid at NaCl basis	Fluid at NaHCOO basis
Sea Water, ml	350	350	350
KCl,g/l	20	-	-
NaCl,g/l	-	291	-
CaCl ₂ ,g/l	-	-	-
NH ₄ Cl,g/l	-	-	-
NaHCOO g/l	-	-	-
Ultrawet 70, % vol.	0.3	0.3	0.3
Sodium molybdate, ppm	-	-	-
Sodium bisulfite , % vol.	0.045	0.045	0.045
Glutaraldehyde at 40 %, % vol.	0.053	0.053	0.053
LC(I)50; 96 hours	42,198.44 ppm	31,476.58 ppm	44,926.53 ppm

Table 6. LC(I); 96 h (initial dilution lethal to 50% of the organisms in test in a period of 96 hours).

Components	Fluid at KCl basis	Fluid at NaCl basis	Fluid at NaHCOO basis
Sea Water, ml	350	350	350
KCl,g/l	20	-	-
NaCl,g/l	-	291	-
CaCl ₂ ,g/l	-	-	-
NH ₄ Cl,g/l	-	-	-
NaHCOO g/l	-	-	542
Ultrawet 70, % vol.	0.3	0.3	0.3
Sodium molybdate salt, ppm	1000	1000	1000
Sodium bisulfite salt , % vol.	0.045	0.045	0.045
Glutaraldehyde at 40%, % vol.	-	-	-
LC(I)50; 96 hours	119,355.20 ppm	106,840.07 ppm	152,87.18 ppm

Table 7. Results of acute toxicity in ppm of the completion fluids in the presence of glutaraldehyde and sodium molybdate.

Fluid (ppm)	with Molybdate	with Glutaraldehyde
KCl	119,355.20	42,198.44
NaCl	106,840.07	31,476.58
Formiate	152,870.18	44,926.53
LC(I)50; 96 hours in ppm.		

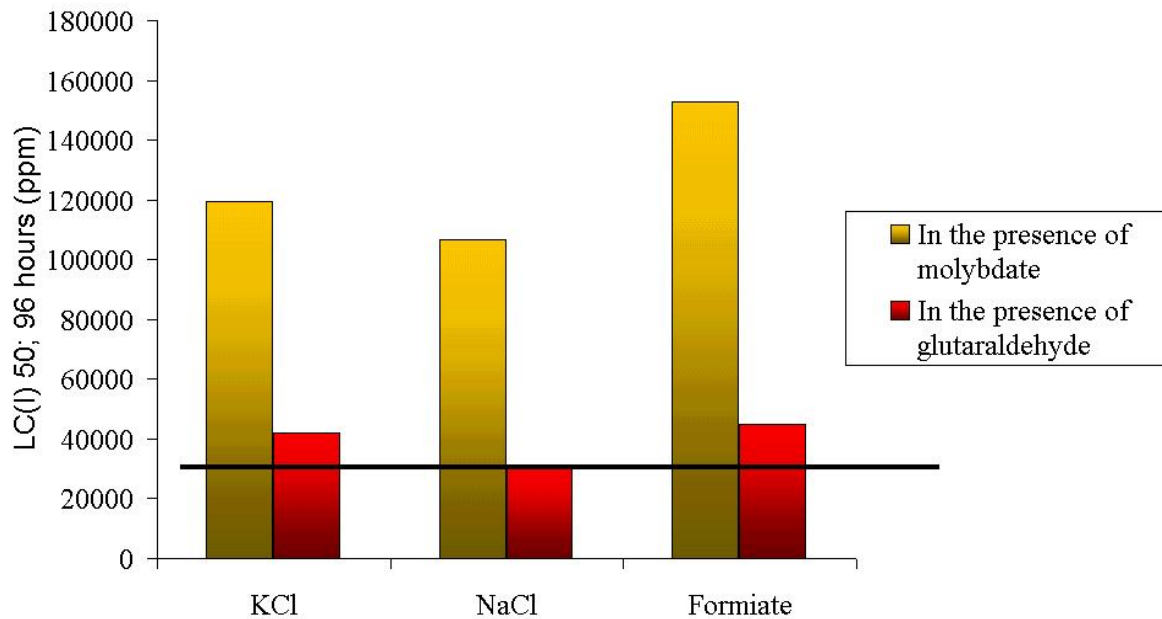


Figure 1. This bar graphic shows that the completion fluids with glutaraldehyde are closer to the toxicity limit of 30,000 ppm, which is currently accepted by IBAMA (government environment agency) for licenses of fluids in exploitation and production activities, become them more toxic than the fluids with sodium molybdate.

Table 8. KCl - Based Completion fluids.

Compounds	Basic formulation	KCl - based Fluid completion			
		1	2	3	4
Sea water, ml	970	1/4 from total volume	2/4 from total volume	3/4 from total volume	Volume remaining
KCl, ppm	20,000	-	-	-	-
Ultrawet 70, ml	3	-	-	-	-
Sodium bisulfite at 40 %, µl	-	115	-	115	-
Na ₂ MoO ₄ (100 ppm), ml	-	-	-	-	5
Glutaraldehyde at 40%, µl	-	-	-	135	-
Total volume, ml	1000	250	250	250	250

Table 9. NaCl - Based Completion fluids.

Compounds	Basic formulation	NaCl - based Fluid completion			
		1	2	3	4
Sea water, ml	970	1/4 from total volume	2/4 from total volume	3/4 from total volume	Volume remaining
KCl, ppm	291,000	-	-	-	-
Ultrawet 70, ml	3	-	-	-	-
Sodium bisulfite at 40 %, μl	-	115	-	115	-
Na_2MoO_4 (100 ppm), ml	-	-	-	-	5
Glutaraldehyde at 40%, μl	-	-	-	135	-
Total volume, ml	1000	250	250	250	250

Table 10. NH_4Cl - Based Completion fluids.

Compounds	Basic formulation	NH_4Cl - based Fluid completion			
		1	2	3	4
Sea water, ml	970	1/4 from total volume	2/4 from total volume	3/4 from total volume	Volume remaining
KCl, ppm	15,200	-	-	-	-
Ultrawet 70, ml	3	-	-	-	-
Sodium bisulfite at 40 %, μl	-	115	-	115	-
Na_2MoO_4 (100 ppm), ml	-	-	-	-	5
Glutaraldehyde at 40%, μl	-	-	-	135	-
Total volume, ml	1000	250	250	250	250

Table 11. HCOONa – Based Completion fluids.

Compounds	Basic formulation	HCOONa - based Fluid completion			
		1	2	3	4
Sea water, ml	970	1/4 from total volume	2/4 from total volume	3/4 from total volume	Volume remaining
KCl, ppm	542,000	-	-	-	-
Ultrawet 70, ml	3	-	-	-	-
Sodium bisulfite at 40 %, µl	-	115	-	115	-
Na ₂ MoO ₄ (100 ppm), ml	-	-	-	-	5
Glutaraldehyde at 40%, µl	-	-	-	135	-
Total volume, ml	1000	250	250	250	250

Table 12. Average corrosion rate of 1020 carbon steel in different completion fluids.

Average corrosion rate (mpy)														
KCl				NaCl				HCOONa				NH ₄ Cl		
1	2	3	4	1	2	3	4	1	2	3	4	1	2	4
8±0.1	24±2	20±0.5	24±1.2	12±0.8	14±0.5	12±0.7	19±1.1	8±0.4	19±0.6	20±2	14±0.5	9±0.3	18±0.4	20±1.2