Sirte University Scientific Journal(Applied Sciences) *Vol. 1 1(2), Dec 2021*

Corrosion Inhibition of Mild Steel using Morpholine Methylene Phosphonic Acid (MPA) in Oil Field Water

Abubaker Elayatt[1] , Elfitouri Ahmied Mohamed[2]

[1]Chemical Engineering Department, Faculty of Engineering, Sirte University, Libya

[2]Petroleum Engineering Department, Faculty of Engineering, Sirte University, Libya

e.ahmied@su.edu.ly

Abstract

The formation of scales and sludges deposited from waters is troublesome. These deposits may form in distribution lines, domestic hot water heaters, various types of cooling equipment, boilers, heat exchangers, or on nearly any surface which water contacts. Phosphonates are used in cooling waters, desalination systems, and oil fields to inhibit scale formation.

The Dynamic test has been carried out using dynamic scale rig test to determine the efficiency of scale inhibitor (MMPA) at injection rates of (3, 5, 7, 10, and 20 ppm) at 40 °C. The experiments shows that the scale inhibitor (MMPA) is effective in preventing formation of calcium carbonate $CaCO_3$ scale, where it has achieved efficiency from 94.83% to 98.20% at concentration of scale inhibitor of 10 ppm.

It has been found that the rate of change in pressure with respect to the time is constant, and this proves that the scale inhibitor (MMPA) achieved a very good efficiency as it managed to prevent formation of calcium carbonate $CaCO_3$ scale through a time period with respect to the injection of both the scale inhibitor and sample (scaling solution). The scale inhibitor (MMPA) achieved a very good efficiency at injection rates of 10ppm.

Keywords: *Morpholine methylene phosphonic acid, Scale formation, scale Inhibitors, oil field water, Inhibitor efficiency.*

1. Introduction

It is very important to add corrosion inhibitors to prevent metal dissolution and minimize acid consumption [1-3]. Dissolved gases such as oxygen and carbon dioxide increase the corrosives of the water[1].

In fact; dissolved gases are the primary cause of most corrosion problems. If they could be excluded and the water maintained at a neutral pH or higher, most oilfield waters would cause very few corrosion problems [2]. Then, corrosion is a problem with certain waters.

Corrosion is undesirable for several reasons. Foremost; the corrosion represents damage of equipment and replacement costs. All types of oilfield equipment exposed to water are subject to corrosion. Corrosion can cause not only a shutdown in production operations, but also causes a safety hazard by weakening high pressure equipment. Leaks in flow lines or pipelines can also result in costly damages to a farmer's property.

Corrosion products removed by turbulent water flow can deposit in processing equipment to reduce permeability in water injection wells. Damage caused by corrosion can, therefore, decrease the operational efficiency of a system [1].

These deposits often prove expensive due to shutdowns of equipment for removal of deposits or replacement of the equipment.

Scale formation in gas and oil wells is a common and persistent problem during production, treatment, transportation, and disposal of co-produced salt water; inhibition of this scale formation is a priority [3].

Scales and sludges are formed from waters, as the waters adjust to changes in equilibrium. Calcium and magnesium carbonates exhibit a negative solubility characteristic. This is the characteristic of a decreasing solubility with increasing temperature. Therefore, water saturated with either of these salts at a given temperature would precipitate these salts in adjusting to equilibrium, if the temperature were increased [1].

Example of scale problems which occur in an evaporator when such a solution is heated or concentrated, the solubility of the solute is a minimum at the tube wall, where the temperature is at maximum. Precipitation therefore takes place at tube wall. Precipitation from solutions possessing normal solubility takes place in the bulk of the fluid rather than at the wall [4].

Chemical changes in the system can also cause scale to form. For example, the solubility of calcium carbonate is dependent on the partial pressure of carbon dioxide. A decrease in carbon dioxide partial pressure will often cause calcium carbonate scale to form in tubing and flow lines [1].

Scale control can be achieved through operation depending on formation of scale. If the scale

produced from mixing of two different water, one of them contains high concentration of anions (carbonate ion) and the other contains high concentration of cations (calcium ions), which mostly comes from different reservoirs. In this case the methods of inhibition are separation of the different waters and prevent it from mixing again. While if the formation of
scale depending on other factors, the most direct method of inhibiting formation of scale deposits is using the scale inhibitors [5].

Scale inhibitors (or antiscalants) are agents that inhibit deposition of adherent, crystalline deposits at surfaces, especially heat transfer surfaces. Antiscalants and antiprecipitants are both classified as antinucleation agents [6]. Antiscalant can prevent the precipitation of scale
forming salts by preventing formation of crystals larger than the critical size (preventing nucleation) and by surface modification of those crystals which do form. Several types of antiscalants are commercially available now and the proper selection of an antiscalants depends upon the water chemistry and system design [7].

The surfactant inhibitor has many advantages such as high inhibition efficiency, low price, low toxicity and easy production [8-13]. The adsorption of the surfactant on the metal surface can markedly change the corrosion resisting property of the metal [14- 16], and so the study of the relationship between the adsorption and corrosion inhibition is of great importance. The aim of this study is investigating the Corrosion Inhibition of carbon steel using Morpholine methylene phosphonic acid (MMPA) in oil field water.

2. Materials And Methods

The main material used for this research work are Mild steel samples.

Table 1. The composion of the Mild Steel Sample.

Element	C	Si	Mn	Cu	Fe
Weight Percent (%)	0.203	0.152	0.627	0.204	Balance

The reactants used for synthesizing the compound are shown in table 2.

Table 2: The reactants for synthesis of one phosphonate containing compound

Chemical	**W/W %**
Distilled water	6.72
Phosphorus acid	26.89
Morpholine	27.24
Hydrochloric acid (37%)	10.77
Formaldehyde solution (37%)	28.38

Morpholine contains one replacement hydrogen atom which reacts with phosphorus acid as shown in figure 1 to produce moropholine-methylene phosphonic acid (MMPA). This contains one phospnonic acid group which partially neutralized with 50 % caustic soda to get
the one phosphonate group. pH of sodium salt of partially neutralized of product was found to be 5 + 0.1.

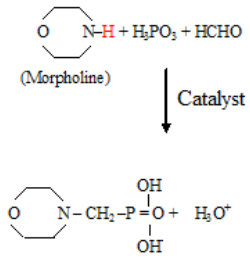

Figure 1: The Moropholine-methylene phosphonic acid (MMPA).

2.1 Sample Preparations

Two solutions are made up. One contains the anions and the other containing the cations. These two solutions are then heated separately to the required temperature before mixing. This procedure ensures that no scaling occurs before the start of testing. In highly scaling brines, it is quite possible to find that major scaling has occurred by the time that they have been transported to the lab and this can lead to erroneous results.

Most scale inhibitors work by modifying or preventing crystal growth and so are only effective if introduced to the system before any scale is formed.

1- Analysis of the brine is carried out and the concentration of cations and anions are determined for formation water of the well Q-25. These concentrations for cations and anions are carried into the Oddo and Tommson program which calculate the amount of the synthetic brines.

Table 3. Synthetic Brine

Synthetic Brine Composition.					
Volume of brain required		Chemical Purity	Chemical Required g/l	g Chemical Required For x ml of Solution	g Chemical Required For x ml of Separate Solutions
1000	ML (x)				
CATIONS					
Sodium Chloride Na		0.999	68.0226	68.0226	136.0452
Sodium Chloride Cl		0.999	68.0451	68.0451	136.0903
Potassium Chloride		0.995	0.0000	0.0000	0.0000
Calcium Chloride $2H_2O$		0.995	22.7763	22.7763	45.5526
Magnesium Chloride $6H_2O$		0.980	9.3755	9.3755	18.7510
Barium Chloride $2H_2O$		0.990	0.0000	0.0000	0.0000
Strontium Chloride $6H_2O$		0.985	0.0000	0.0000	0.0000
Ferric Chloride soln		0.414	0.0493	0.0493	0.0986
ANIONS					
Sodium Sulphate $10H_2O$		0.990	2.0346	2.0346	4.0691
Sodium Carbonate $10H_2O$		0.990	0.0000	0.0000	0.0000
Sodium Bicarbonate anhyd		0.995	0.3875	0.3875	0.7751
Sodium Sulphide anhyd		0.995	0.0000	0.0000	0.0000

2- The Cations as shown in the table (3) above were weighted and transferred in a 1000 ml calibrated volumetric flask. The flask was then filled up using deionized water and adjust the pH to that the system for sample well Q-25, and deionized water was added drop wise using a pastel pipette to bring the level to the mark.

3- The Anions as shown in the table (3) above were weighted and transferred in a 1000 ml calibrated volumetric flask. The flask was then filled up using deionized water adjust the pH to that the system for the sample well Q-25, and deionized water was added drop wise using a pastel pipette to bring the level to the mark.

All two solutions (Cations & Anions) were filtered through a 0.45 micro membrane filter before used and each of solutions (Cations & Anions) were transferred into a separate Pyrex dispenser bottle and cap, and invert the bottles as is necessary to dissolve the solids, and to make homogenous solution.

2.2 Procedure

It is first necessary to carry out a full and thorough field investigation with full water analysis.

Two solutions are made up. One contains the anions and the other contains the cations. These two solutions are then heated separately to the required test temperature before mixing. This procedure ensures that no scaling occurs before the start of testing.

In highly scaling brines, it is quite possible to find that major scaling has occurred by the time that they have been transported to the lab and this can lead to erroneous results.

Most scale inhibitors work by modifying or preventing crystal growth and so are only effective if introduced to the system before any scale is formed.

Enter the analysis and volume of the brine that conduct testing into the spreadsheet program. The program will then calculate the weight of each of the salts required.

Use this information to prepare the required volume of anions solution and cations solution. Adjust the pH as the system for sample (Q-25) and then place the solutions into a separate Pyrex dispenser bottle and cap.

Prepare the required number of new clean 100 ml wide neck screw cap bottles (12 bottles for each sample) and mark them up with the scale inhibitor (MMPA) being tested and the dose rate (3, 5, 7, 10 and 20 ppm).

The test should be carried out in duplicate with two blanks i.e. containing no chemical. Remove the bottle of cation solution from the oven and fit a clean dry repeat dispenser. Set the dispenser to 50 ml and prime it to remove any air from the pump mechanism and Dispense 50 ml of cation solution into each of the 100 ml test bottles. Set the two blanks to one side.

Using a micro syringe 50 µl, add the required volume of 10% scale inhibitor solution to each bottle (3, 5, 7, 10 and 20 ppm) ,cap all bottles and shake to mix. Remove the anion solution from the oven and fit a clean dry repeat dispenser.

Set the dispenser to 50 ml and prime it to remove any air from the pump mechanism and Dispense 50 ml of anion solution into each of the 100 ml test bottles, cap each of the bottles and shake to mix. Note the time, inspect each of the bottles for signs of scaling or scale inhibitor, and note all observations on the test sheet, after that immediately place all the test bottles in the oven. Repeat the observation procedure at 1, 2, 4, 8 and 24 hours and note all observations.

1- Carbonate scale will tend to form a "scum" on the surface of the liquid.

2- Sulphate scale will tend to form a crystalline layer on the bottom of the bottle.

3- Incompatibility and precipitation of the scale inhibitor will tend to show as a fairly even haze throughout the liquid.

At the end of the 24 hour test period, allow the bottles to cool. Remove an aliquot from each bottle and filter it through a 0.4 micron Millipore filter. Analyze immediately for calcium on each filtered solution and record all results on the observation sheet.

From the equation below, the calcium concentration in the sample (CaCO3) can be calculated as:

$$Ca^{++} \text{ as } Ca\,CO_3 \text{ (ppm)} = \frac{\text{Eq.Wt (CaCO3).(0.02N)EDTA, TR, 1000}}{\text{Sample x Volume x ml}} \qquad (1)$$

A. *Where:*

N = Normality of EDTA solution = 0.02 N

V= Volume of sample (ml),

T = Titration Reading of Burette (ml),

Eq. Wt. for $CaCO_3$ = 50 g/mol

Multiply all the original calcium test results obtain as $CaCO_3$ by 0.4 to give calcium ion (Ca^{++}) in the sample and record all calcium readings as (mg/l Ca^{++} Sample) in the table above.

C_a = Ca^{++} concentration

We have used the calcium ion from the static jar test to calculate the percent inhibition by using the following equation:

$$\% \text{ Inhibitor} = \frac{Ca - Cb}{Cc - Cb} \times 100 \qquad (2)$$

Where: in the treated sample after precipitation

$C_b = Ca^{++}$ concentration in the blank after precipitation

$C_c = Ca^{++}$ concentration in the blank before precipitation

2.3 Evaluations of scale inhibitors (Dynamic Test) using the P-MAC (Pressure, Measurement and Control) Dynamic Scale Rig.

2.3.1. Principle of Operation

This equipment consists of a micro-bore tube housed in a temperature controlled fan oven. Separate anion and cation solutions are first pumped through a mixing tube before entering the micro-bore scaling tube. This is achieved by means of a speed controllable peristaltic pump. When the two mixed solutions enter the scaling tube, scale is formed and adheres to the walls causing the bore to be reduced and a pressure increase. The pressure differential across the scaling tube is measured by means of a pressure transducer. The electronics then process this signal to give an output to the chart recorder. The required dose rate of scale inhibitor can be introduced into the scaling solutions by means of a second speed controllable peristaltic pump feeding into a T piece at the entrance to the scaling tube.

3. Results And Discussion

Table 4: Scale Test Observations at 40°C (Well No. Q-25)

Inhibitor	Dose (ppm)	0 hr	1 hr	2 hrs	4 hrs	8hrs	24 hrs
Blank	0	C&B	C&B	C&B	C&B	sl haze	CO_3 ppt
(MMPA)	3	C&B	C&B	C&B	C&B	C&B	C&B
	5	C&B	C&B	C&B	C&B	C&B	C&B
	7	C&B	C&B	C&B	C&B	C&B	C&B
	10	C&B	C&B	C&B	C&B	C&B	C&B
	20	C&B	C&B	C&B	C&B	C&B	C&B
Blank	0	C&B	C&B	C&B	C&B	sl haze	CO_3 ppt
(MMPA)	3	C&B	C&B	C&B	C&B	C&B	C&B
	5	C&B	C&B	C&B	C&B	C&B	C&B
	7	C&B	C&B	C&B	C&B	C&B	C&B
	10	C&B	C&B	C&B	C&B	C&B	C&B
	20	C&B	C&B	C&B	C&B	C&B	C&B

C&B = Clear and bright

sl haze = Slight haze

sl CO_3 ppt = Slight Carbonate Precipitate

CO_3 ppt = Moderate Carbonate Precipitate

hvy SO_4 ppt = Heavy Sulphate Precipitate

SO_4 ppt = Moderate Sulphate Precipitate

sl SO_4 ppt = Slight Sulphate Precipitate

hvy CO_3 ppt = Heavy Carbonate Precipitate.

Table 4 shows the observation test for the evaluation of scale inhibitor (MMPA) with different dosage rate (3, 5, 7, 10, and 20 ppm) for 24Hrs period at 40°C. From the observation, the blank shows slight haze after 8Hrs and the precipitation of carbonate becomes clear after 24 Hrs. In the

other bottles where the inhibitor was injected at different concentrations it observed that all bottles were clear and bright. It can conclude that the scale inhibitor gave very good results with all concentrations. This observation is attributed to the fact that the rate of chemical reaction increases with increasing concentration.

Table 5: Scale test analysis at 40°C (Well No. Q-25)

Product	Dose (ppm)	mg/l Ca Sample	mg/l Ca Sample -mg/l Ca Blank (C_1)	Percent Inhibition %
Blank	0.00	5556	0.00	0.00
(MMPA)	3	6118	562	96.23
	5	6124	568	97.26
	7	6124	578	98.9
	10	6140	584	100.00
	20	6140	584.0	100.0
Blank	0.00	5556	0.00	0.00
(MMPA)	3	6119	563	96.40
	5	6123	567	97.10
	7	6136	580	99.32
	10	6139	583	99.83
	20	6140	584	100.00

Dosage/ ppm	0.0	3.0	5.0	7.0	10.0	20.0

Average % inhibition	0.00	96.32	97.18	99.11	99.92	100.00

Calcium content of fresh Brine before test =6140 mg/l

Therefore the Blank has Precipitated = 2840 mg/l

Calcium ($Cc-C_b$) =584 mg/l

We have used the calcium ion to calculate the percent inhibition by using the following equation:

$$\% \text{ Inhibition} = \frac{C_a - Cb}{Cc - Cb} \; x \; 100 \qquad (2)$$

Where:

C_a = Ca^{++} concentration in the treated sample after precipitation

C_b = Ca^{++} concentration in the blank after precipitation

C_c = Ca^{++} concentration in the blank before precipitation

Calculations:

From the equation below, the calcium concentration in the sample

($CaCO_3$) can be calculated as:

$$Ca^{++} \text{ as Ca } CO_3 \text{ (ppm)} = \frac{\text{Eq.Wt (CaCO3).(0.02N)EDTA, TR, 1000}}{\text{Sample Volume}} \qquad (3)$$

B. Where:

N = Normality of EDTA solution = 0.02 N

V= Volume of sample (ml)

T = Titration Reading of Burette (ml)

Eq. Wt. for $CaCO_3$ = 50 g/mol

Multiply all the original calcium test results obtain as $CaCO_3$ by 0.4 to give calcium ion (Ca^{++}) in the sample and record all calcium readings as (mg/l Ca^{++} Sample) which shown in Table 4.

(1) For Blank Titration (Calcium content of fresh brine before precipitate)

$$Ca^{++} \text{ (ppm)} = \left[\frac{50 \times 0.02N \times 15.35ml \times 1000}{1.0ml}\right] \times 0.4 = 6140\text{mg/l as } Ca^{++}$$

(2) For 3 ppm concentration

$$Ca^{++}\ (ppm) = \left[\frac{50 \times 0.02N \times 15.295ml \times 1000}{1.0ml}\right] \times 0.4 = 6118\ mg/l \text{ as } Ca^{++}$$

From (1) and (2) above, the efficiency can be calculated as:

$$\text{Efficiency of Scale Inhibitor \%} = \left[\frac{C_a - C_b}{C_c - C_b}\right] \times 100$$

Where:

$C_a = Ca^{++}$ concentration in the treated sample after precipitation

$C_b = Ca^{++}$ concentration in the blank after precipitation

$C_c = Ca^{++}$ concentration in the blank before precipitation

C. *For 3ppm dose rate Scale Inhibitor:*

D. *Efficiency of Scale Inhibitor %* $= \left[\frac{C_a - C_b}{C_c - C_b}\right] \times 100$

$$= \left[\frac{6118mg/l - 5556mg/l}{6140mg/l - 5556mg/l}\right] \times 100 = 96.23\%$$

This value was recorded as percentage inhibition as shown in Table 4. The procedure was repeated with treated samples of 5, 7, 10 and, 20 ppm.

From the results obtained from Well No. Q-25 Table 4 it is observed that the 3 ppm dose rate of scale inhibitor gave a very good result at 40 ^{o}C. The inhibitor efficiency was found to increase with increased inhibitor concentration.

3. Conclusions

From the results of this study, we can conclude that:

1. The experiments shows that the scale inhibitor (MMPA) is effective in preventing formation of calcium carbonate $CaCO_3$ scale, where it has achieved efficiency from 94.83% to 98.20% at concentration of scale inhibitor of 10 ppm.
2. The rate of change in pressure with respect to the time is constant, and this proves that the scale inhibitor (MMPA) achieved a very good efficiency as it managed to prevent formation of calcium carbonate $CaCO_3$ scale through a time period with respect to the injection of both the scale inhibitor and sample (scaling solution).
3. The inhibitor efficiency was found to increase with increased inhibitor concentration.

References

[1]. Nash, J. F. & Tanner, P. R. (2009) Sunscreens. In Z. D. Draelos & L. A. Thaman (Eds). *Cosmetic Formulation of Skin Care Products* (pp. 3-14). Taylor & Francis Group, 270 Madison Avenuem, New York, US.

[2]. Begoun, P. (2009) *The Original Beauty Bible: Skin Care Facts for Ageless Beauty*, 3rd, Washington, Beginning Press.

[3]. Murphy, G. B. & Hawk, J. L. M (2009) Sunscreens and Photocarcinogenesis. In H. W. Lim & Z. D. Draelos (Eds.), *Clinical Guide to Sunscreens and Photoprotection* (pp. 11-38). New York, NY, Informa Healthcare USA, Inc.

[4]. Fonseca A. P. & Rafael, N. (2013). Determination of sun protection factor by UV-vis spectrophotometry. *Health care current*. *1*(1), 108.

[5]. González-Arjona, D., López-Pérez, G., Domínguez, M. M., Looken S. C. V. (2015) Study of Sunscreen Lotions, a Modular Chemistry Project, *Journal of Laboratory Chemical Education, 3*(3), 44-52.

[6]. Bartholomey, E., House, S. & Ortiz, F. A. (2016) Balanced Approach for Formulating Sunscreen Products Using Zinc Oxide. *sofwjournal 142* (3), 18-25.

[7]. Klimová, Z., Hojerová, J. & Pažoureková, S. (2013) Current problems in the use of organic UV filters to protect skin from excessive sun exposure, *Acta Chimica Slovaca, 6* (1). 82—88.

[8]. Osterwalder, U. & Herzog, B. (2009) Chemistry and Properties of Organic and Inorganic UV Filters. In H. W. Lim & Z. D. Draelos (Eds.), *Clinical Guide to Sunscreens and Photoprotection* (pp. 11-38). New York, NY, Informa Healthcare USA, Inc.

[9]. Donglikar, M. M. & Deore, S. L. (2016) Sunscreens: A review, *Pharmacognosy Journal*, *8* (3), 171-179.

[10]. Gabriel, J. (2008), *The green beauty guide: your essential resource to organic and natural skin care, hair care, makeup, and fragrances*, Florida, Health Communications, Inc.

[11]. Diffey, B. L., Ferguson, J. (2009) Assessment of Photoprotective Properties of Sunscreens. In H. W. Lim & Z. D. Draelos (Eds.), *Clinical Guide to Sunscreens and Photoprotection* (pp. 11-38). New York, NY, Informa Healthcare USA, Inc.

[12]. Acker, S., Hloucha, M. & Osterwalder, U., (2014) The Easy Way to Make a Sunscreen. *sofwjournal 140* (7), 24-30.

[13]. Mansur, J. S., Breder, M. N. R., Mansur, M. C. A., Azulay, R. D. (1986) Determinação do fator de proteção solar por espectrofotometria. *An. Bras. Dermatol., 61* (3), 121-124.

[14]. Dutra, E. A., Oliveira, D. A. G. C., Kedor-Hackmann, E. R. M.; Santoro, M. I. R. M. (2004) Determination of sun protection factor (SPF) of sunscreens by ultraviolet spectrophotometry. *Braz. J. Pharm. Sci. 40* (3), 381-385.

[15]. Sayre, R. M., Agin, P. P., Levee, G. J., Marlowe, E. (1979) Comparison of in vivo and in vitro testing of sun screening formulas. *Photochem Photobiol Oxford., 29* (3), 559-566.

[16]. Emsley, J. (2007) *Better Looking, Better Living, Better Loving. How Chemistry can Help You Achieve Life's Goals*. Weinheim, WILEY-VCH Verlag GmbH & Co.KGaA.