

## Synthesis And Evaluation of Different Numbers of Phosphonate Group Containing Compounds As Scale Inhibitors For Crude oil Production

Abubaker K. Elayatt<sup>1</sup>, Mahjoub A. M. Elaoud<sup>2</sup> and Mukhtar Shaglouf<sup>3</sup>  
<sup>1,3</sup>(Chemical Engineering Department Faculty of Engineering the University of Sirte P.O. Box 674 Sirte – Libya)  
<sup>2</sup>(Jowfe Oil Technology, Benghazi, Libya)

**Abstract:** Oil fields were seriously affected by the mineral scale formation, mainly calcium deposition. This paper focused on the synthesis and scale prevention of oilfield scaling, especially carbonates scale and sulfate scale. Scale can cause loss of production due to blockages in the near-well formation, in the tubing or in the surface facilities. Phosphonates are widely accepted as the most effective inhibitors for calcium carbonate and calcium sulfate, also are widely used in many water treatment applications. Most good scale inhibitors should work at dosage levels between 5 and 25 ppm on most production systems depending on calcium concentration. The treatment rates can be affected by contaminants which take the scale inhibitor out of solution. Six different compounds of phosphonate containing groups have been synthesized and evaluated for scale inhibition property. Evaluation of synthetic phosphonate compounds as scale inhibitors has been done by using NACE Standard TM-0374-2001. From the results clear that one and two phosphonate group containing compounds do not show any characteristic of prevention of scales of either calcium carbonate or calcium sulphate. The compounds which have phosphonate group three or more show characteristics of prevention of both types of scales.

**Keywords:** Phosphonate, Calcium carbonate, Calcium Sulfate, Scale, Inhibition

---

### I. Introduction

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<sup>[1]</sup>. Scale and sludge are differentiated on the basis that scale is a deposit formed in place on surfaces in contact with water, while the sludge may form in one place and be deposited in another. Sludges may collect in areas of a system where the flow rate is low or where there are bends in the lines, and thus build up a deposit which will reduce the flow. 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<sup>[2]</sup>. Scale deposition can occur in any place where a significant temperature differential occurs, such as in well tubulars, in pipelines and heat exchangers, it can seriously degrade performance, it can also cause problems at point where significant amount accumulate in separators. It is therefore not a local problem, but may occur anywhere within the production process<sup>[3]</sup>. In addition to scales formed from substances deposited from water, scale may form as a result of a chemical reaction between the water or some impurity in the water and the pipe itself. The bacteria reduce sulfate and liberate hydrogen sulfide, which reacts with iron to form ferrous sulfide scale. Scales deposited on a surface or collected sludges are seldom pure. These usually are a mixture of any sparingly soluble salts present in the water, plus any corrosion products formed on the pipe surface. This often makes it difficult to classify deposits according to a specific acid radical. The deposits may be classified generally as scale, sludge, corrosion products, and biological deposits.

Phosphonates have three main properties: they are effective chelating agents for two divalent and trivalent metal ions, they are inhibiting crystal growth and scale formation and they are quite stable under high temperature, low and high pH and in the presence of oxidants (harsh chemical conditions)<sup>[4]</sup>. An important industrial use of phosphonates is in cooling waters, desalination systems, and in oil fields to inhibit scale formation. In pulp and paper manufacturing and in textile industry they are used as peroxide bleach stabilizers, acting as chelating agents for metals that could inactivate the peroxide<sup>[4]</sup>. In detergents they are used as a combination of chelating agent, scale inhibitor and bleach stabilizer<sup>[5]</sup>. Phosphonic acids and its salts (phosphonates) are among the most potent scale inhibitors next to the polyphosphates. These compounds inhibit the crystal growth at concentrations far below those required to chelate stoichiometric amounts of the reactive cations<sup>[4]</sup>. Models for this retardation include inhibition of nucleation, adsorption onto growth sites, distortion of the crystal lattice, changes in surface charge, and association with precursors of crystal formation<sup>[6,7]</sup>.

Ethylene diamine tetra methylene phosphonic acid (EDTMP) showed superior performance compared to Diamine ethylene triamine methylene phosphonic acid (DETMP) under extensive studies of the effect of various phosphonates on the crystal growth of sparingly soluble salts<sup>[8]</sup>. The performance of various polyphosphates and phosphonates on deposition of gypsum on cellulose acetate and composite membranes at different recovery ratios show that compared to phosphonates (i.e., AMP, HEDP), polyphosphates (i.e., sodium tripolyphosphate STPP, and sodium hexametaphosphate SHMP) exhibit superior performance<sup>[9]</sup>. The investigation the inhibition of calcium carbonate by various phosphonates: AMP, HEDP, PTBTC, under harsh condition shows the order of effectiveness is HEDP >> AMP = PBTC<sup>[4]</sup>. Sherbondy and Vanderpool 1995<sup>[10]</sup>, show that the polyether polyamino methylene phosphonate and corresponding N-oxides of the compositions and methods of the present invention are prepared first by phosphonomethylation of the appropriate primary amine which already contains the polyoxyethylene and polyoxypropylene moieties, followed by an oxidation step which provides the N-oxide moieties. The polyether polyamino methylene phosphonate scale Inhibitors and their use in controlling calcium carbonate scale under severe conditions, the polyether polyamino methylene phosphonates described herein can be used in the same range of amounts as threshold inhibitors to prevent the formation and deposition of calcium carbonate scale<sup>[2]</sup>. Jordan et al 1997<sup>[11]</sup>, present an experimental confirmation of some predictions by analyzing core flooding experimental results using both outcrop and reservoir cores. Results are presented from a series of resin coated core floods conducted at 70°C and reconditioned reservoir conditioned core floods at 90°C to 110°C. It is shown that precipitation of a generic scale inhibitor, either a polymeric or a phosphonate species, will give a longer squeeze lifetime at higher inhibitor concentrations than the same product when applied purely as an adsorption treatment. Performance tests of various phosphonates for 24 hours at ambient temperature using 3 mg/L of inhibitor in water with 224 mg/L calcium at a pH of 8.3 shows that the general calcium carbonate inhibition: phosphonates > homopolymers > co- and ter-polymers. AMP [Aminotri (methylene phosphonic acid)], HEDP [1-hydroxyethylidene 1,1-diphosphonic acid], and PBTC [2-phosphonobutane-1,2,4-tricarboxylic acid]<sup>[12]</sup>. El-Shall et al 2002<sup>[13]</sup> studied the effect of Aminotris (methylene phosphonic acid) [ATMP] on calcium sulfate dehydrate (gypsum) crystallization, and their results indicate that: ATMP increases the induction time at all the supersaturation ratios studied due to decrease the regular crystal growth. Surface energy is decreased in the presence of ATMP compared with the baseline. Nucleation rate is increased in the presence of ATMP compared with the baseline. The Critical nucleus diameter and hence size is smaller with addition of 100 ppm ATMP. The crystal growth rate is lower with ATMP compared with the baseline. The crystal growth rate is generally lower at lower supersaturation ratio with and without ATMP additive.

Amjad et al 2003<sup>[14]</sup>, showed that phosphonates and polyphosphates prevent scale formation at "substoichiometric" dosages by adsorbing onto crystal growth sites of micro-crystallites thereby interfering with crystal growth and altering the crystal growth morphology. In addition, both phosphonates and polyphosphates have been shown to exhibit metal chelation and dispersancy activities.

Baraka-Lokmane and Sorbie 2006<sup>[15]</sup>, present results from four core floods (P2, RC1, RC2 and RC3) from the Jurassic Portlandian (UK) chalk using 5000 ppm, 10000 ppm and 25000 ppm of partly neutralized diethylene triamine penta phosphonic acid (DETPP) at pH 4 and 2. They found that the degree of dissolution increases as injection fluid pH decreases. A relatively high level of mixing (dispersion) was observed in floods RC1 and RC2. Flood RC3 performed with 25000 ppm DETPMP at pH 2 gives higher inhibitor adsorption than for flood RC1 performed with 5000 ppm DETPMP at pH 4 and flood RC2 performed with 10000 ppm DETPMP at pH 4. This indicates that the effect of pH on inhibitor adsorption is more important than the inhibitor concentration under these conditions. Flood RC3 also shows more calcium carbonate dissolution and thus higher permeability after treatment than did floods RC1 and RC2.

Nano-metal-phosphonates are used as an inhibitor to prevent scale formation in water processes. The nano-Ca-DTPMP (nano-calcium-diethylene triamine penta (methylene phosphonate)) particles are synthesized and utilized in CaCO<sub>3</sub> scaling inhibition experiments. The precipitation/inhibition curves were obtained through the online electrochemical measurement of Ca<sup>2+</sup> concentration and pH against time show that nano-Ca-DTPMP inhibitors delay the precipitation of CaCO<sub>3</sub>, decelerate the Ca<sup>2+</sup> and pH reduction and increase the final Ca<sup>2+</sup> concentration in the bulk solution<sup>[16]</sup>.

## II. Experiments

### Chemicals Used

All chemicals used is reagent grade, were purchased from BDH (UK). UHQ water was used throughout this study. All experiments were conducted at least in triplicate, and the average of the results reported. Variation in the experimental results is presented as average ± standard deviation of the mean values.

### Synthesis of Phosphonate Compounds

Six different compounds of phosphonate containing groups have been synthesized and evaluated for scale inhibition property. These compounds were prepared by reaction of amines, phosphorous acid and

formaldehyde. During reaction hydrogen atoms of amine group converted to phosphate groups with reaction of phosphorous acid and formaldehyde in the presence of concentrated hydrochloric acid as catalyst. On neutralization with sodium hydroxide they can be converted to phosphonates. The selection of amine will give required phosphonate compound since the replaceable hydrogen of amine will convert to phosphonate group during reaction. As many replaceable hydrogens are present in amine as many phosphonate containing compounds can be prepared by using required amount of formaldehyde and phosphorous acid stoichiometrically. Table1 shows the lists the synthesized compounds and the amine used for their synthesis.

**Table1.** Synthesized phosphonate containing compounds

Name of Compound	No. of Phosphonate Groups	Amine Used
MMP	1	Morpholine-methylenephosphonic acid
DMPDMP	2	3-Dimethylaminopropylamine-dimethylenephosphonic acid
AEETMP	3	Aminoethylethanolamine-trimethylenephosphonic acid
EDTMP	4	Ethylenediamine-tetramethylenephosphonic acid
DTPMP	5	Diethylenetriamine-pentamethylenephosphonic acid
TTHMP	6	Triethylenetetramine-hexamethylenephosphonic acid

### Reaction Conditions

The process of addition of reaction was as follows [17]:

- 1) Slowly added amine to a mixture of phosphorous acid and water with keeping the temperature below 60 °C.
- 2) Required concentrated hydrochloric acid on the stoichiometry was then added slowly.
- 3) Reaction mixture was heated to reflux at temperature between 105 °C and 110 °C with slowly addition of aqueous formaldehyde for four hours.

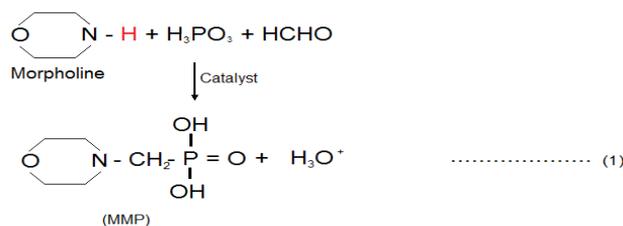
The quantities of chemicals for reaction to produce the certain chemical are shown in the table 2. The reaction equations of each synthesis of phosphonate containing compound are shown below in figures from 1 to 6.

### Reactants:

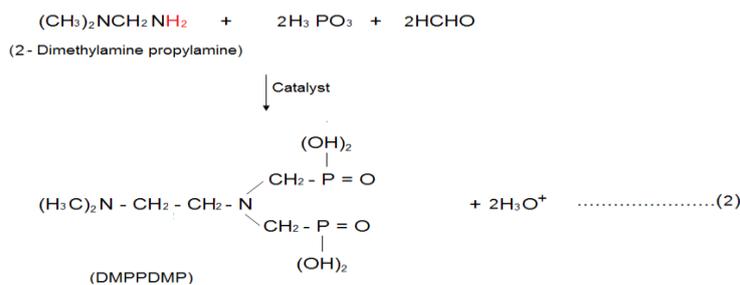
**Table2.** The reactants for synthesis of phosphonate containing compound

Products	Chemicals	W/W %
(MMP) Containing one phosphonate compound	Distilled water	6.72
	Phosphorus acid	26.89
	Morpholine	27.24
	Hydrochloric acid (37%)	10.77
	Formaldehyde solution (37%)	28.38
(DMPDMP) Containing tow phosphonate compound	Distilled water	7.71
	Phosphorus acid	30.83
	3-Dimethylaminopropylamine	16.57
	Hydrochloric acid (37%)	12.35
	Formaldehyde solution (37%)	32.54
(AEETMP) Containing three phosphonate compound	Distilled water	8.16
	Phosphorus acid	32.65
	Aminoethylethanolamine	13.81
	Hydrochloric acid (37%)	13.09
	Formaldehyde solution (37%)	32.29
(EDTMP) Containing four phosphonate compound	Distilled water	8.67
	Phosphorus acid	34.69
	Ethylenediamine	6.14
	Hydrochloric acid (37%)	13.9
	Formaldehyde solution (37%)	36.6
(DTPMP) Containing five phosphonate compound	Distilled water	8.44
	Phosphorus acid	33.81
	Diethylenetriamine	8.51
	Hydrochloric acid (37%)	13.55
	Formaldehyde solution (37%)	35.69
(TTHMP) Containing six phosphonate compound	Distilled water	8.32
	Phosphorus acid	33.3
	Triethylenetetramine	9.9
	Hydrochloric acid (37%)	13.34
	Formaldehyde solution (37%)	35.14

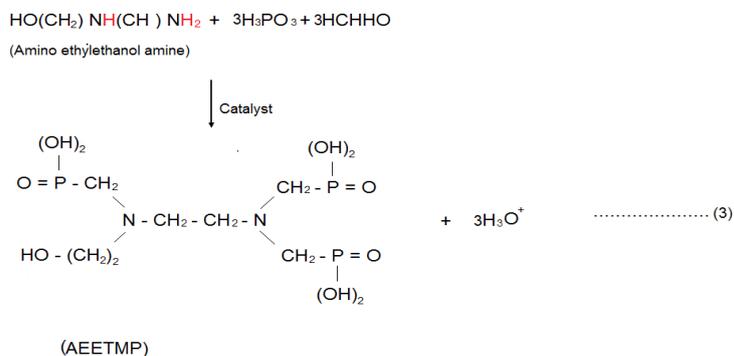
Equations of reaction of each synthesis of phosphonate containing compound are shown in figures from 1 to 6. The catalyst used in all synthesis equations is concentrated hydrochloric acid, reflux at temperature 105 - 110 °C.



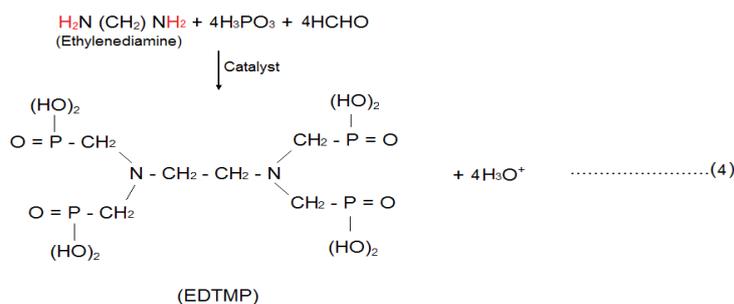
**Figure1.** Reaction of synthesis of compound contains one phosphonate group



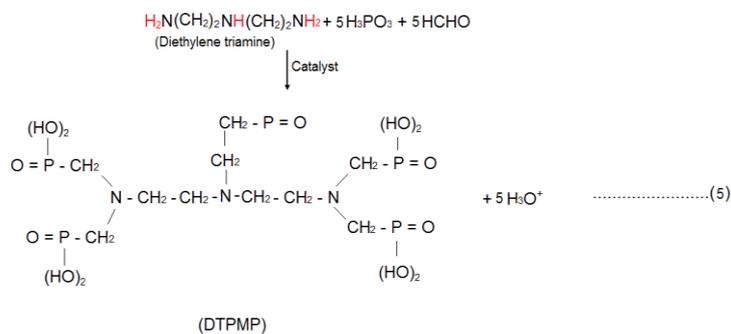
**Figure2.** Reaction of synthesis of compound contains two phosphonate groups



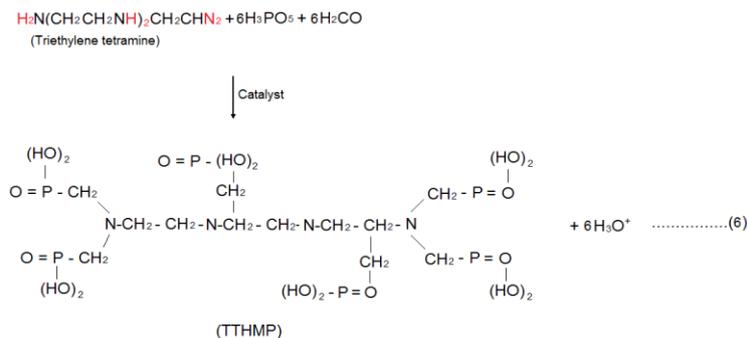
**Figure3.** Reaction of synthesis of compound contains three phosphonate groups



**Figure 4.** Reaction of synthesis of compound contains four phosphonate groups



**Figure5.** Reaction of synthesis of compound contains five phosphonate groups



**Figure 6.** Reaction of synthesis of compound contains six phosphonate groups

### III. Results and Discussion

#### Evaluation of Synthesized Phosphonate Groups Containing Compounds as Scale Inhibitors

Evaluation of synthetic phosphonate compounds as scale inhibitors has been done by using NACE Standard TM-0374-2001 “laboratory screening tests to determine the ability of scale inhibitors to prevent the precipitation of calcium sulfate and calcium carbonate from solution”. These are the static laboratory tests designed to give a measure of the ability of scale inhibitor to prevent the precipitation of calcium carbonate and calcium sulfate from solution at 71°C. These test methods are recommended only for ranking the performance of different chemicals under laboratory conditions. Many factors, such as reaction kinetics, fluid velocity and composition, variable temperatures and pressures, scale adherence and solids dispersion can significantly affect scale deposition under field conditions. These considerations are outside the scope of this method, but field brine composition and other variables should at some point be considered in inhibitor evaluation prior to field use.

#### Calculation of Percent Inhibition

After that the concentration level of calcium ions remained in the solution was evaluated. Using these data percent of scale inhibition was calculated:

$$\% \text{ Inhibition} = 100 \times \frac{C_a - C_b}{C_c - C_b}$$

Where:

$C_a - C_a^{2+}$  concentration in the traded sample after precipitation

$C_b - C_a^{2+}$  concentration in the blank after precipitation

$C_c - C_a^{2+}$  concentration in the blank before precipitation

Tables (3, 4) show the visual test for six synthetics chemicals at different dosing (1,3, 5, 10, and 20 ppm) against both calcium carbonate and calcium sulfate respectively for 24 hours, where the samples are inspection at 0, 1, 2, 4, 8 and 24 hours. Tables (5, 6) are showing the inhibitions calculations at the same dosing chemicals to show the efficiency of prevention of calcium carbonate and calcium sulfate scales respectively. Chemical MMP and DMPDMP which presented one and two phosphonate group respectively do not show any inhibition at all concentrations. Chemical AEETMP which presented three phosphonate groups before 10 ppm show no inhibition, after 10 ppm start to prevent the scale formation for bout types. The other three chemicals (EDTMP, TTHMP and TTHMP) which presented four, five and six phosphonate group respectively show inhibition from 5 ppm.

**Table 3.** Visual Evaluation of six synthetic chemicals against calcium carbonate scale

Visual Evaluation of product MMP against calcium carbonate scale							
MMP	Dose (ppm)	0 hr	1 hr	2 hrs	4 hrs	8hrs	24 hrs
	0	C&B	C&B	C&B	C&B	sl haze	CO <sub>3</sub> ppt
	1	C&B	C&B	C&B	C&B	sl haze	CO <sub>3</sub> ppt
	3	C&B	C&B	C&B	C&B	sl haze	CO <sub>3</sub> ppt
	5	C&B	C&B	C&B	C&B	sl haze	CO <sub>3</sub> ppt
	10	C&B	C&B	C&B	C&B	sl haze	CO <sub>3</sub> ppt
	20	C&B	C&B	C&B	C&B	sl haze	CO <sub>3</sub> ppt
Visual Evaluation of product DMPDMP against calcium carbonate scale							
DMPDMP	Dose (ppm)	0 hr	1 hr	2 hrs	4 hrs	8hrs	24 hrs
	0	C&B	C&B	C&B	C&B	sl haze	CO <sub>3</sub> ppt
	1	C&B	C&B	C&B	C&B	sl haze	CO <sub>3</sub> ppt
	3	C&B	C&B	C&B	C&B	sl haze	CO <sub>3</sub> ppt
	5	C&B	C&B	C&B	C&B	sl haze	CO <sub>3</sub> ppt
	10	C&B	C&B	C&B	C&B	sl haze	CO <sub>3</sub> ppt
	20	C&B	C&B	C&B	C&B	sl haze	CO <sub>3</sub> ppt
Visual Evaluation of product AEETMP against calcium carbonate scale							
AEATMP	Dose (ppm)	0 hr	1 hr	2 hrs	4 hrs	8hrs	24 hrs
	0	C&B	C&B	C&B	C&B	sl haze	CO <sub>3</sub> ppt

	1	C&B	C&B	C&B	C&B	sl haze	CO <sub>3</sub> ppt
	3	C&B	C&B	C&B	C&B	sl haze	CO <sub>3</sub> ppt
	5	C&B	C&B	C&B	C&B	C&B	sl haze
	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
Visual Evaluation of product EDTMP against calcium carbonate scale							
<b>EDTMP</b>	0	C&B	C&B	C&B	C&B	sl haze	CO <sub>3</sub> ppt
	1	C&B	C&B	C&B	C&B	sl haze	CO <sub>3</sub> ppt
	3	C&B	C&B	C&B	C&B	C&B	sl haze
	5	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
Visual Evaluation of product DTPMP against calcium carbonate scale							
<b>DTPMP</b>	0	C&B	C&B	C&B	C&B	sl haze	CO <sub>3</sub> ppt
	1	C&B	C&B	C&B	C&B	sl haze	CO <sub>3</sub> ppt
	3	C&B	C&B	C&B	C&B	C&B	sl haze
	5	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
Visual Evaluation of product TTHMP against calcium carbonate scale							
<b>TTHMP</b>	<b>Dose (ppm)</b>	<b>0 hr</b>	<b>1 hr</b>	<b>2 hrs</b>	<b>4 hrs</b>	<b>8hrs</b>	<b>24 hrs</b>
	0	C&B	C&B	C&B	C&B	sl haze	CO <sub>3</sub> ppt
	1	C&B	C&B	C&B	C&B	sl haze	CO <sub>3</sub> ppt
	3	C&B	C&B	C&B	C&B	C&B	sl haze
	5	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

**Table 4.** Visual Evaluation of sex synthetic chemicals against calcium sulfate scale

Visual Evaluation of product MMP against calcium sulfate scale							
<b>MMP</b>	<b>Dose (ppm)</b>	<b>0 hr</b>	<b>1 hr</b>	<b>2 hrs</b>	<b>4 hrs</b>	<b>8hrs</b>	<b>24 hrs</b>
	0	C&B	C&B	C&B	C&B	sl haze	SO <sub>4</sub> ppt
	1	C&B	C&B	C&B	C&B	sl haze	SO <sub>4</sub> ppt
	3	C&B	C&B	C&B	C&B	sl haze	SO <sub>4</sub> ppt
	5	C&B	C&B	C&B	C&B	sl haze	SO <sub>4</sub> ppt
	10	C&B	C&B	C&B	C&B	sl haze	SO <sub>4</sub> ppt
20	C&B	C&B	C&B	C&B	sl haze	SO <sub>4</sub> ppt	
Visual Evaluation of product DMPDMP against calcium sulfate scale							
<b>DMPDMP</b>	0	C&B	C&B	C&B	C&B	sl haze	SO <sub>4</sub> ppt
	1	C&B	C&B	C&B	C&B	sl haze	SO <sub>4</sub> ppt
	3	C&B	C&B	C&B	C&B	sl haze	SO <sub>4</sub> ppt
	5	C&B	C&B	C&B	C&B	sl haze	SO <sub>4</sub> ppt
	10	C&B	C&B	C&B	C&B	sl haze	SO <sub>4</sub> ppt
	20	C&B	C&B	C&B	C&B	sl haze	SO <sub>4</sub> ppt
Visual Evaluation of product AEETMP against calcium sulfate scale							
<b>AEATMP</b>	0	C&B	C&B	C&B	C&B	sl haze	SO <sub>4</sub> ppt
	1	C&B	C&B	C&B	C&B	sl haze	SO <sub>4</sub> ppt
	3	C&B	C&B	C&B	C&B	sl haze	SO <sub>4</sub> ppt
	5	C&B	C&B	C&B	C&B	C&B	sl haze
	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
Visual Evaluation of product EDTMP against calcium sulfate scale							
<b>EDTMP</b>	0	C&B	C&B	C&B	C&B	sl haze	SO <sub>4</sub> ppt
	1	C&B	C&B	C&B	C&B	C&B	sl haze
	3	C&B	C&B	C&B	C&B	C&B	sl haze
	5	C&B	C&B	C&B	C&B	C&B	sl haze
	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
Visual Evaluation of product DTPMP against calcium sulfate scale							
<b>DTPMP</b>	0	C&B	C&B	C&B	C&B	sl haze	SO <sub>4</sub> ppt
	1	C&B	C&B	C&B	C&B	C&B	sl haze
	3	C&B	C&B	C&B	C&B	C&B	sl haze
	5	C&B	C&B	C&B	C&B	C&B	sl haze
	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
Visual Evaluation of product TTHMP against calcium sulfate scale							
<b>TTHMP</b>	<b>Dose (ppm)</b>	<b>0 hr</b>	<b>1 hr</b>	<b>2 hrs</b>	<b>4 hrs</b>	<b>8hrs</b>	<b>24 hrs</b>
	0	C&B	C&B	C&B	C&B	sl haze	SO <sub>4</sub> ppt
	1	C&B	C&B	C&B	C&B	C&B	sl haze
	3	C&B	C&B	C&B	C&B	C&B	sl haze

	5	C&B	C&B	C&B	C&B	C&B	sl haze
	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

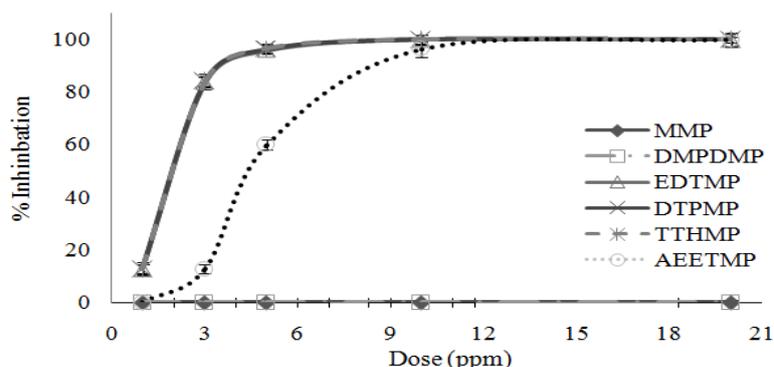
CO<sub>3</sub> ppt = Carbonate Precipitate

SO<sub>4</sub> ppt = Sulfate Precipitate

**Table 5.** Evaluation of six synthetic chemicals against calcium carbonate scale

Evaluation of a product MMP against calcium carbonate scale					
Dose(ppm)	Ca <sup>2+</sup> concentration after precipitation (ppm)				Inhibition (%)
	Sample (1)	Sample (2)	Sample (3)	Average	
1	390	388	392	390	0
3	389	390	391	390	0
5	392	388	390	390	0
10	390	389	391	390	0
20	388	391	391	390	0
Evaluation of product DMPDMP against calcium carbonate scale					
1	388	392	390	390	0
3	391	390	389	390	0
5	389	391	390	390	0
10	391	391	388	390	0
20	392	389	389	390	0
Evaluation of product AEETMP against calcium carbonate scale					
1	390	390	390	390	0
3	549	549	552	550	12.64
5	1150	1152	1148	1150	60.03
10	1610	1615	1610	1610	96.37
20	1657	1656	1658	1656	100
Evaluation of product EDTMP against calcium carbonate scale					
1	551	548	551	550	12.64
3	1452	1448	1450	1450	83.73
5	1605	1604	1606	1605	95.97
10	1658	1655	1655	1656	100
20	1655	1655	1659	1656	100
Evaluation of product DTPMP against calcium carbonate scale					
1	552	548	550	550	12.64
3	1462	1458	1460	1460	84.2
5	1611	1611	1608	1610	96.37
10	1658	1654	1656	1656	100
20	1653	1658	1657	1656	100
Evaluation of a product TTHMP against calcium carbonate scale					
1	552	547	551	550	12.64
3	1452	1458	1455	1455	84.12
5	1616	1613	1616	1615	96.76
10	1654	1656	1658	1656	100
20	1659	1654	1655	1656	100

Figures 7 presented the efficiency of six synthetics chemicals at different dosing (1, 3, 5, 10, and 20 ppm) against calcium carbonate, where clear no inhibition for one and two phosphonate groups (MMP, DMPDMP) respectively and moderate inhibition shown by three phosphonate groups (AEETMP), where at 3 ppm give inhibition of 12.6%, 60% inhibition was at 5 ppm, 96.4% was at 10 ppm and 100% inhibition was at 20 ppm. Four, five and six phosphonate group (EDTMP, DTPMP and TTHMP) respectively, show perfect inhibition where the inhibition start at 1 ppm to give 12.6% inhibition, 84.1% was at 3 ppm, 96.7% was at 5 ppm and full inhibition was at 10 and 20 ppm against calcium carbonate scale.

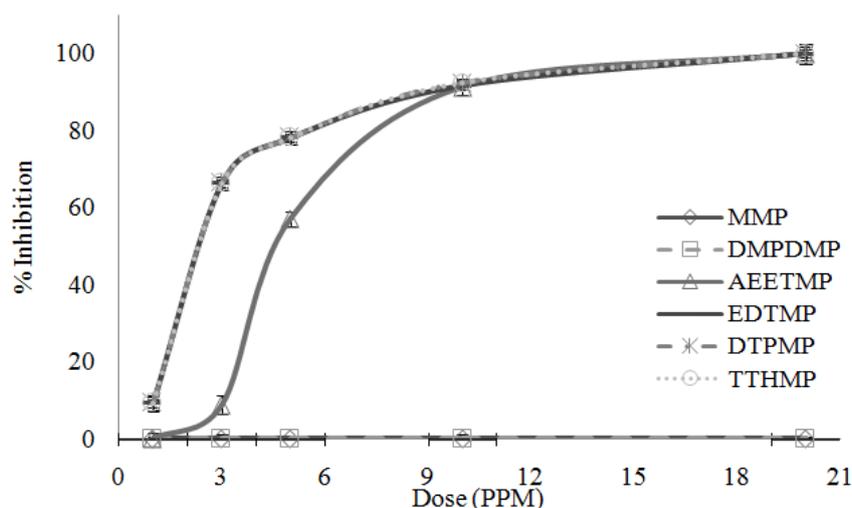


**Figure 7.** Evaluation of six synthetic chemicals against calcium carbonate scale

**Table 6.** Evaluation of six synthetic chemicals against calcium sulfate scale

Evaluation of product MMP against sulfate scale					
Dose (ppm)	Ca <sup>2+</sup> concentration after precipitation (ppm)				Inhibition %
	Sample (1)	Sample (2)	Sample (3)	Average	
1	601	601	600	601	0
3	600	602	602	601	0
5	601	601	602	601	0
10	602	600	601	601	0
20	601	601	601	601	0
Evaluation of a product DMPDMP against sulfate scale					
1	601	601	601	601	0
3	601	601	602	600	0
5	601	601	601	601	0
10	601	600	600	602	0
20	601	600	601	601	0
Evaluation of product AEETMP against sulfate scale					
1	601	603	600	601	0
3	681	684	680	680	8.81
5	1122	1122	1124	1120	57.13
10	1433	1431	1433	1435	91.23
20	1513	1514	1515	1510	100
Evaluation of product EDTMP against sulfate scale					
1	685	685	687	683	9.25
3	1205	1203	1206	1206	66.29
5	1314	1315	1313	1314	78.18
10	1436	1436	1437	1435	91.56
20	1513	1511	1516	1512	100
Evaluation of product DTPMP against sulfate scale					
1	685	686	686	683	9.25
3	1206	1206	1207	1205	66.34
5	1314	1315	1315	1312	78.18
10	1443	1435	1433	1434	92.32
20	1513	1512	1515	1512	100
Evaluation of product TTHMP against sulfate scale					
1	685	685	686	684	9.25
3	1206	1207	1206	1205	66.34
5	1314	1313	1315	1314	78.18
10	1443	1443	1442	1444	92.32
20	1513	1514	1512	1513	100

Figures 8 presented the efficiency of six synthetic chemicals at different dosing (1, 3, 5, 10, and 20 ppm) against calcium sulfate, where clear no inhibition for one and two phosphonate groups (MMP, DMPDMP) respectively and moderate inhibition shown by three phosphonate groups (AEETMP), where at 3 ppm give inhibition of 8.8%, 57.1% inhibition was at 5 ppm, 91.2% was at 10 ppm and 100% inhibition was at 20 ppm. Four, five and six phosphonate group (EDTMP, DTPMP and TTHMP) respectively, show perfect inhibition where the inhibition start at 1 ppm to give 9.2% inhibition, 66.3% was at 3 ppm, 78.2% was at 5 ppm, around 92.0% at 10 ppm and full inhibition was at 20 ppm against calcium sulfate scale.



**Figure 8.** Evaluation of six products against sulfate scale

Standard test method (NACE Standard TM-0374 – 2001) has been used for testing the scale inhibition efficiency of all the six synthesized compounds. The results are presented in Tables from 3, 4, and 5 for all compounds. The summary of performance of scale prevention of all synthesized compounds is given in Table 5 and 6. It is clear from the results that one and two phosphonate group containing compounds do not show any characteristic of prevention of scales of either calcium carbonate or calcium sulphate. The compounds which have phosphonate group three or more show characteristics of prevention of both the types of scales.

#### IV. Conclusions and Recommendations

1. Scale formation is a major water problem in industries especially in production of oil and gas. Therefore, scale prevention is a priority in the industry for efficient operation, prevention of shutdowns and economical benefits.
2. The successful method used in industries to prevent the deposition of scale from scale forming waters are: (a) treatment of water i.e. the removal of scale forming cations and anions in water, or (b) the prevention of scale formation by addition of chemicals or the combination of both methods.
3. The most common organic compounds used as scale inhibitors are phosphonates, diphosphonates, phosphate esters and polyacrylates. The phosphonate containing compounds exhibit greater temperature stability and do not have any adverse environmental impact.
4. The synthesized phosphonate group containing compounds have been evaluated for their scale inhibition property by using standard method (NACE Standard TM-0374-2001). Compounds containing phosphonate group one or two do not show any characteristics of prevention of scales of either calcium carbonate or calcium sulfate.
5. The compounds which have phosphonate group three or more show scale prevention characteristics. The scale prevention efficiencies of these compounds have been determined and presented in this study.
6. It is recommended to test their thermal stability at reservoir conditions (i.e. at high temperature and high pressure) before using them in commercial scale.
7. It is also recommended to test their toxicity (LC<sub>50</sub> value) before using them in the industries.

#### References

- [1]. M. B. Tomson, SPE, G. Fu, M. A. Watson and A. T. Kan, Rice U, Mechanisms of mineral scale inhibition, 2002, international symposium on oilfield scale, Aberdeen, United Kingdom.
- [2]. Ostroff, Introduction to Oilfield Water Technology, 1979, 2<sup>nd</sup> Ed.
- [3]. Dawe, Modern Petroleum Technology, 2001, 6<sup>th</sup> Ed, p 318 Z. Amjad, Scale Inhibition in Desalination Applications, The NACE International Annual Conference and Exposition, 1996, paper No. 230.
- [4]. B. Davenport, A. DeBoo, F. Dubois, and A. Kishi, CEH Report: Chelating agents. SRI Consulting, 2000, Menlo Park, Ca, USA.
- [5]. G. Müller and U.Förstner, Experimental mobilization of copper and zinc from aquatic sediments by some polyphosphate substitutes in detergents. Z. f. Wasser- und Abwasser-Forschung 1976, 9, 150.
- [6]. J.Y. Gal , J.C. Bollinger, H. Tolosa and N. Gache, Calcium carbonate solubility: a reappraisal of scale formation and inhibition. Talanta, 1996, 43, 1497–1509.
- [7]. A.J. Gratz and P.E. Hillner, Poisoning of calcite growth viewed in the atomic force microscope (AFM). J. Cryst. Growth 129, 789–793.
- [8]. S.T. Liu and G.H. Nancollas, J. Colloid Interface Sci., 1993, 44, 422, 1973.
- [9]. A. Pervov, Desalination, 83, 77, 1991.
- [10]. Ann M. Sherbondy, D. Vanderpool, Stabilization of polyether polyaminomethylene phosphonate scale inhibitors against degradation by bromine and chlorine biocides, united state patent, 1995, patent number 5,433,886.
- [11]. P. Bailey and Cristina A. Bailey, Organic Chemistry (A Brief Survey of Concepts and Applications), 1981, 2<sup>nd</sup> Ed, p 243.
- [12]. Jordan M. M; Sorbie K. S; Chen P; Armitage P; Hammond P; Taylor K, The design of polymer and phosphonate scale inhibitor precipitation treatments and the importance of precipitate solubility in extending squeeze lifetime. 1997, International Symposium on Oilfield Chemistry, 18-21 February, Houston, Texas.
- [13]. H. El-Shall, M. M. Rashad, E. A. Abdel-Aal, Effect of phosphonate additive on crystallization of gypsum in phosphoric and sulfuric acid medium, Crystal research technology, 2002, 37, 1264-1273.
- [14]. Zahid Amjad, Robert W. Zuhl, P.E. Noveon and John F. Zibrida, Factors Influencing the Precipitation of Calcium-Inhibitor Salts in Industrial Water Systems. Association of Water Technologies, Inc. Annual Convention 17 to 20 September 2003, Phoenix, AZ .
- [15]. Bin Merdiah, A. B and Yassin, A. M. Laboratory Study and Prediction of Calcium Sulphate at High-Salinity Formation Water. The Open Petroleum Engineering Journal, 2008, 1, 62-73
- [16]. S. Baraka-Lokmane and K. Sorbie, Effect of phosphonate scale inhibitor (DETPMP) concentration, application pH and adsorption on inhibitor and cation return concentrations in carbonate cores, 2006. 3rd European Geosciences Union General Assembly.