# The Efficacy of Calcium Carbonate Scale Inhibition by Commercial Polymer Scale Inhibitors

Chan Boon Chew[*], Ramli Mat

Department of Chemical Engineering, Faculty of Chemical Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia
chanbc@i-Chemsolution.com

The efficacy of calcium carbonate scale inhibition by three selected inhibitors, Polymaleic Acid (PMA), Polyamino Polyether Methylene Phosphonic Acid (PAPEMP) and Acrylic Acid-Maleic Anhydride (AA/MA) copolymer was investigated via static beaker tests at 40 °C, pH 8.50 and incubated for 20 h. The calcium carbonate scales formed in the presence and absence of inhibitors have been examined by SEM. All the above compounds were found to be an effective calcium carbonate scale inhibitor at minimum concentrations ranging from 2.0 to 6.0 ppm depending on type of compound. PMA was found to be the most effective inhibitor. The normal crystal growth of calcium carbonate has been altered in the presence of all the above compounds as observed through SEM micrograph.

## 1. Introduction

Calcium carbonate has been identified as the main problem associated with industrial cooling water scaling or deposition. The formation of calcium carbonate scale in industrial cooling water system has been known to pose significant problems to the industrial processes. The calcium carbonate scales or deposits will serve as a heat insulating layer that reduces heat transfer efficiency and hence require higher energy consumption to attain the desired cooling or heating effect (Prisciandaro et al., 2013). Therefore, it is vital to ensure that heat transfer surfaces on industrial cooling water systems are relatively free from calcium carbonate scaling problems. Most of the research works on crystal growth inhibition of industrial cooling water treatment program were conducted by a few multinational water treatment companies at their own research center. This valuable information is unfortunately not available to others due to trade secret. As such smaller water treatment companies that have limited resources have limited information in developing the right formulation in their cooling water treatment program. This study aims to provide such information so that it can be made available to enhance the technical competency of calcium carbonate scale inhibition.

Calcium carbonate crystal growth inhibition by the simplest form of phosphate-containing compounds, orthophosphate, has been well studied by several researchers and orthophosphate concentration in the range of several milligrams per liter have been found to retard the crystal growth in seeded solutions. Adsorption of orthophosphate on calcium carbonate scale has been studied and found to change the structure of calcium carbonate crystal lattice (Millero et al., 2001). In another study, $CaHPO_4$ was found to be the responsible species that absorbs on the calcium carbonate surface and inhibits further precipitation (Lin and Singer, 2006). The use of polyphosphates for calcium carbonate crystal growth inhibition was also investigated (Lin and Singer, 2005) and sodium tri-polyphosphate was found to be the strongest inhibitor in a mono polyphosphate formulation followed by sodium pyrophosphate and sodium hexametaphosphate. However, orthophosphate and polyphosphates were excluded in this study, driven by market trend towards low or non-phosphorus compounds used for such application in consideration of environmental issues such as eutrophication associated with phosphorus compounds.

Calcium carbonate scale inhibition by organophosphorus compounds such as amino tris(methylene phosphonic acid) (ATMP), ethylene-diamine tetra(methylenephosphonic acid) (EDTMP), hexamethylene-diamine tetra(methylenephosphonic acid) (HDTMP), diethylenetriamine penta(methylenephosphonic acid)

(DTPMP) (Chen et al., 2013) and PAPEMP (Tang et al., 2008) were also being investigated. Results shown that the phosphonic group number and the methylene chain length play a vital role in the effectiveness of the inhibitors. Although the application of most organophosphorus compound contributes lesser phosphorus to the environment in relative term to orthophosphate and polyphosphates, some of the commonly used compounds such as ATMP still contains considerable amount of phosphorus (31 % as Phosphorus) and 1-hydroxyethane 1,1-diphosphonic acid (HEDP) (30 % as Phosphorus) (Hoffmann et al., 2012).

Owing to the environmental consideration, this study has selected non-phosphorous polymeric compound represented by PMA and AA/MA copolymer and low phosphorus contributor PAPEMP (about 20 % as Phosphorus) for the tests. The inhibition of calcium carbonate crystal growth by PMA, PAPEMP and AA/MA copolymer was investigated via static beaker tests at typical water chemistries encountered in Malaysia cooling water system.

This study provides a method that enables the evaluation of scale inhibitors at the practical dosage level and economically viable range at various water chemistries encountered in the market place, thus providing a practical and useful solution and background formulation information to water treatment professionals to mitigate industrial cooling water scaling and deposition problems for a given water chemistries and condition. The desired inhibition efficiency of minimum 90 % was set up to evaluate and compare the performance of the above inhibitors.

## 2. Experimental

### 2.1 Calcium carbonate crystal growth inhibition experiments
Static beaker tests were employed to study calcium carbonate crystal growth inhibition in oversaturated solutions containing $CaCl_2$ and $NaHCO_3$ in the absence and presence of various concentrations of selected inhibitors. Experiments were carried out using synthetic water that simulate the normal cooling water chemistry in Klang Valley, Malaysia and incubated for 20 h at 40 °C.

### 2.2 Materials and methods
250 mL of distilled water was filled in each conical flask and desired amount of scale inhibitor was added into each sample. 400 mg/L of analytical grade Calcium Chloride dihydrate (from Systerm) was added into each sample. The calcium content was analysed using Atomic Absorption Spectrometry and results were recorded. 150 mg/L of analytical grade Sodium Bicarbonate (from Systerm) was added into each sample. The solution was mixed by a magnetic stirrer at 150 rpm for 2 min to ensure homogenous and pH of the mixtures was adjusted to pH 8.50 with Analytical grade Sodium Hydroxide (from Systerm). All samples were capped and placed in the water bath and incubated for 20 h at 40 °C.  Scale inhibitors used were PMA (Belclene 200), PAPEMP (Mayoquest 2200) and AA/MA copolymer (Sokalan CP 5). Sample was removed from water bath after incubation period and supernatant was filtered through 0.20 µm filter. The filtrate of 0.20 µm filter was withdrawn for analysis and the concentration of soluble calcium ions was determined using Atomic Absorption Spectrometry and result recorded.

Calcium carbonate scale formation in the test solution will result in a reduction of soluble calcium ions still remaining in the test solution. As such, analysis of calcium ions of filtered (0.20 µm) aliquots of the test solution will determine the reaction progression and the efficacy of the inhibitors. The efficacy of the inhibitor was calculated as percent inhibition as illustrated in equation (1).

$$I = [(ion)_s - (ion)_c] \div [(ion)_l - (ion)_c] \times 100\% \qquad (1)$$

where:
 I = inhibition, %
$(ion)_s$ = Ion concentration in the presence of inhibitor at t = 20 h
$(ion)_c$ = Ion concentration in the absence of inhibitor at t = 20 h
$(ion)_l$ = Ion concentration at the beginning of the experiment

This study assumes that all calcium ions found in the filtered aliquots are soluble ion and all crystal formed will be rejected in the 0.20 µm filter paper. The assumption of rejection of crystal formed by 0.20 µm filter paper was thought to be reasonable considering 0.45 µm filter is used in the APHA test method [APHA TSS Method, 2540D (APHA, (1995)] on total suspended solids. Therefore, using 0.20 µm filter, an even smaller pore size filter should ensure no leakage of crystals into the filtered aliquots.

### 2.3 Scanning Electron Microscopy
The calcium carbonate scale samples formed both in the absence and presence of inhibitors were collected after it has been retained by the filter paper and scanned by Scanning Electron Microscopy to

examine the crystal morphology. SEM machine model EVO 50 of Carl Zeiss brand was used in this study. Carbon tape was used and stick to the sample stub. Calcium carbonate scale samples were sprinkled on the carbon tape so that the samples can stick on the stub. The sample was inserted into the sputter coater machine where platinum target sputtering was employed. Coating was used to increase conductivity of the samples. After coating is done, sample was removed and loaded into SEM machine for analysis.

## 3. Results and discussion

### 3.1 Calcium Carbonate Scale Inhibition efficacy

During the last decade a variety of calcium inhibitors have been developed and are currently used as components of water treatment formulations for scale inhibition Using the experimental procedure described above, performance of three different calcium scale inhibitors , namely, by PMA, PAPEMP and AA/MA copolymer as calcium inhibitors was investigated.The results of this static beaker test have been obtained and the percentage of inhibition of the scale inhibitors selected have been calculated using Eq(1) and results tabulated and graph plotted as shown in in Figure 1.
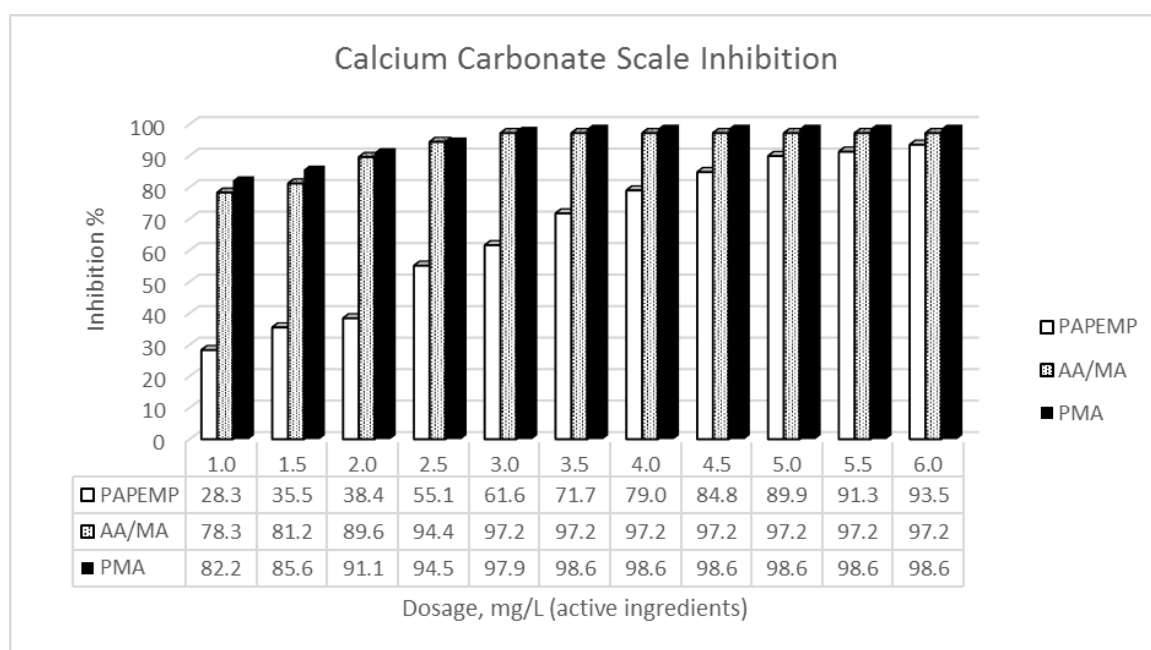


Figure 1: Calcium carbonate scale inhibition percentage

The results shown that PMA is the most effective calcium carbonate scale inhibitor with more than 90 % inhibition at relative low dosages (2.0 mg/L active ingredients) followed very closely by AA/MA copolymer and lastly PAPEMP which required dosages above 5.0 mg/L (active ingredients) to achieve 90 % inhibition. The poor performance observed for PAPEMP may be attributed to poor interaction of non-ionic group present in PAPEMP with the calcium ion present in the water.

As observed in figure 1, Inhibitor dosage is critical to the performance of calcium inhibitors. An increase in inhibitor dosage results in a significant increase in the inhibition of calcium especialy for PAPEMP. As may be seen, increasing PAPEMP concentration by three fold, i.e., 1.0 to 3.0 mg/L, increases % inhibitor for PAPEMP from 28.3% to 61.6% compared to 78.3 % to 97.2 % obtained for AA/MA. For AA/MA further increase of concentration does not improved the % inhibition after 3.0 mg/L.

### 3.2 Scanning Electron Microscopy morphology

Figures 2 and 3 show the SEM micrographs of Calcium Carbonate scale formed in the absence of and presence of selected inhibitors.
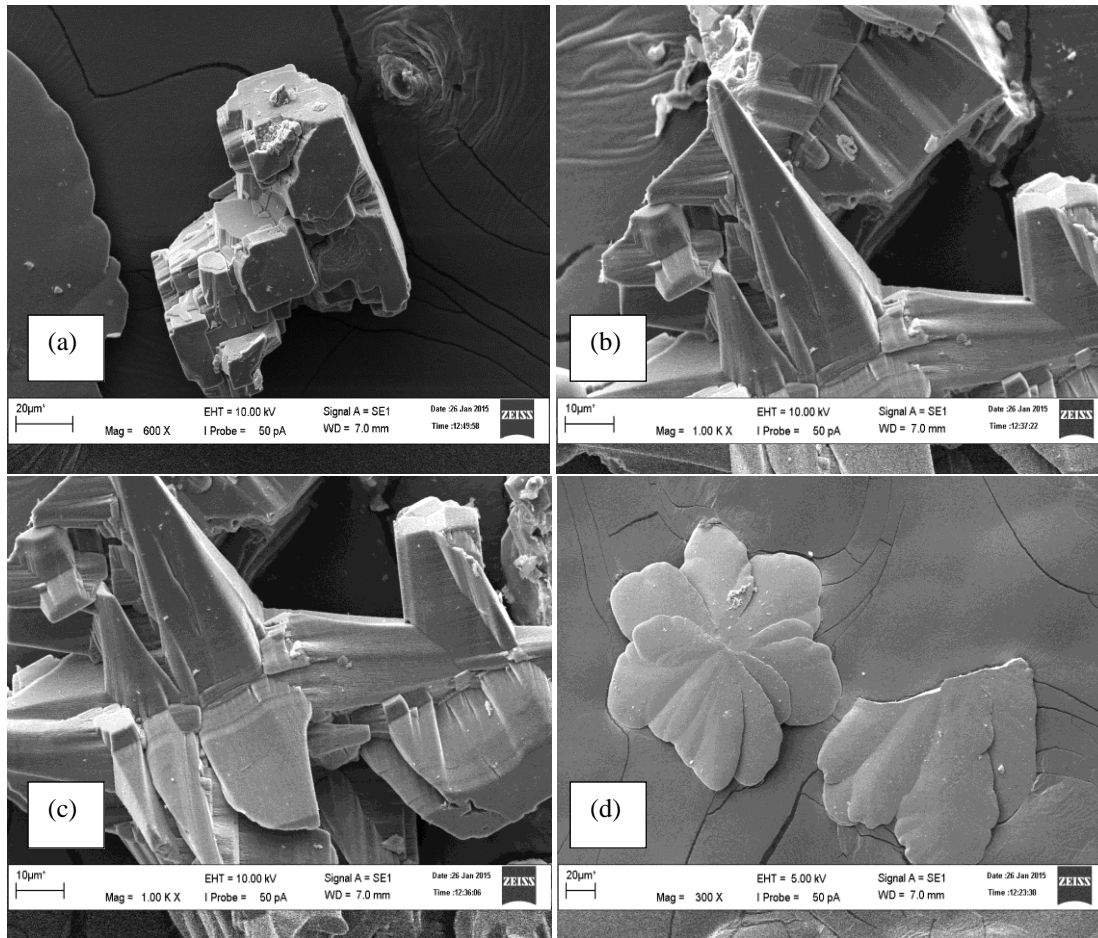
*Figure 2: SEM micrographs of calcium carbonate formed after 20 h of incubation in the absences of inhibitor. (a) Rhombohedral structure, (b) and (c) Needle-like structure, (d) dendritic structure*

It can be seen from the SEM micrographs in Figure 2 that calcium carbonate crystal exhibits distinctive smooth crystal surfaces in all forms of polymorphs. However, only rhombohedral calcite structure (Kirboga and Oner, 2013) and needle-like aragonite structure exhibits sharp edges.

The addition of scale inhibitor prevent the calcium scale formation by supressing the formation of nuclei in the supersaturated solution or by interfering with crystal growth and thus reducing their ability to adhere to the equipment surfaces. The present of scale inhibitor and adsorption at specific sites of the growing crystals may result to changes in crystal morphology as can be seen in Figure 3.

In the presence of the selected inhibitor PMA, AA/MA copolymer and PAPEMP, calcium carbonate crystal loses its distinctive sharp edges, and the crystal morphology has been modified and altered as shown in Figure 3. In the presence of PMA, calcium carbonate crystal exhibits lump shape with many tiny isolated pieces attached to it. In the presence of AA/MA copolymer, the crystal morphology changes and exhibits more rounded and smaller in size with loses of its distinctive sharp edges. However, with PAPEMP, the crystal morphology changes to irregular but elongated shape.

It was noted on the absence of dendritic vaterite structure in the presence of all selected inhibitors and this was believed to be due to its thermodynamically least stable form (Wang et al., 2014) among the calcium carbonate polymorphs.

The inhibitor molecules were believed to adsorb onto the active crystal growth sites (Xyla et al. 1992) during the crystal growth and disturbed or blocked the normal growth of calcium carbonate crystal (Yang et al., 2001). With the presence of inhibitors, the crystal lattice has been distorted and therefore the crystal morphology has been changed (Muresan et al., 2011).
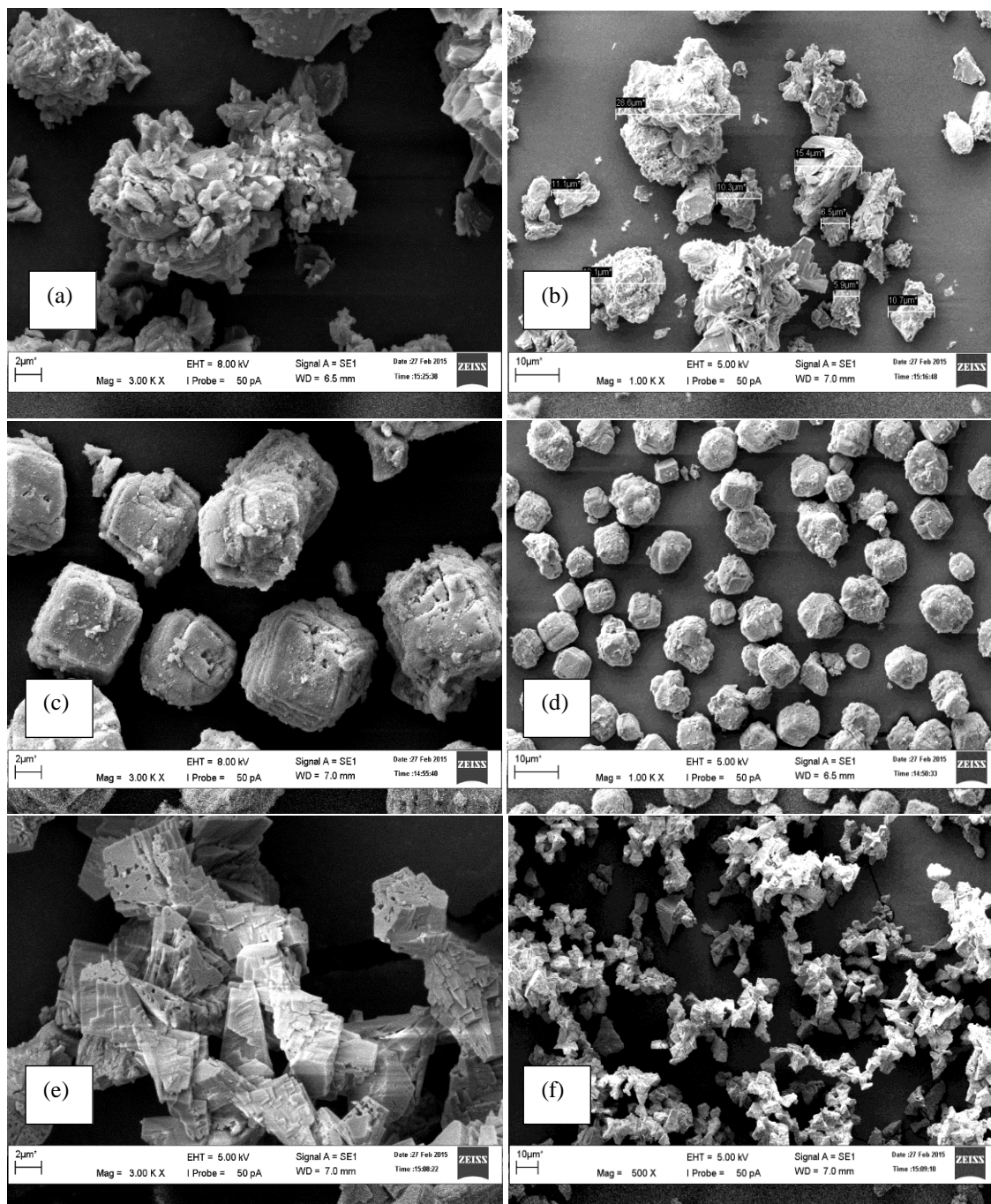
*Figure 3: SEM micrographs of Calcium carbonate formed after 20 h of incubation, in the presence of 5 mg/L active of (a) and (b) PMA, (c) and (d) AA/MA copolymer, (e) and (f) PAPEMP*

## 4. Conclusions

This study has demonstrated that low level of both non-phosphorus polymeric compounds, PMA and AA/MA copolymer and low phosphorus-containing compounds, PAPEMP can significantly inhibit calcium carbonate precipitation from the aqueous solution by modifying the crystal morphology. The results of this study shown that the efficacy of calcium carbonate scale inhibition also depends on the type and concentration of the inhibitors. PMA performed better for calcium carbonate scale inhibition under the test condition followed closely by AA/MA copolymer and then by PAPEMP.

## Acknowledgement

## References

Chen C.Y., Lei W., Xia M.Z., Wang F.Y., Gong X.D., 2013, Molecular modelling of several phosphonates onto the stepped calcite (011) surface, Desalination, 309, 208–212.

Hoffmann T., Friedel P., Harnisch C., Häußler L., Pospiech D., 2012, Investigation of thermal decomposition of phosphonic acids, Journal of Analytical and Applied Pyrolysis, 96, 43–53.

Kirboga S., Oner M., 2013, Effect of the experimental parameters on calcium carbonate precipitation, Chemical Engineering Transactions, 32, 2119-2124.

Lin Y.P., Singer P.C., 2005, Inhibition of calcite crystal growth by polyphosphates, Water Research, 39(19), 4835-4843.

Lin Y.P., Singer P.C., 2006, Inhibition of calcite precipitation by orthophosphate: Speciation and thermodynamic considerations, Geochimica et Cosmochimica Acta, 70, 2530–2539.

Millero F., Huang F., Zhu X.R., Li X.W., Zhang J.Z., 2001, Adsorption and Desorption of Phosphate on Calcite and Aragonite in Seawater, Aquatic Geochemistry, 7, 33–56.

Muresan L., Sinha P., Maroni P., Borkovec M., 2011, Adsorption and surface-induced precipitation of poly(acrylic acid) on calcite revealed with atomic force microscopy, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 390, 225-230.

Prisciandaro M., Lancia A., Di Celso G.M., Musmarra D., 2013, Antiscalants for gypsum precipitation in industrial equipments: Comparison among different additives, Chemical Engineering Transactions, 32, 2137-2142

Tang T.M., Yang W.Z., Yin X.S., Liu Y., Yin P.W., Wang J.T., 2008, Investigation of CaCO3 scale inhibition by PAA, ATMP and PAPEMP, Desalination, 228(1-3), 55-60.
.

Wang J.W., Zhang F.X., Zhang J.M., Ewing R.C., 2014, Carbonate orientational order and superlattice structure in vaterite, Journal of Crystal Growth, 407, 78-86.

Xyla A.G., Mikroyannidis J., Koutsoukos P.G., 1992, The inhibition of Calcium carbonate precipitation in Aqueous media by organophosphorus compounds, Journal of Colloid Interface and Science, 153(2), 537-551.

Yang Q.F., Liu Y.Q., Gu A.Z., Ding J., Shen Z.Q., 2001, Investigation of Calcium Carbonate Scaling Inhibition and Scale Morphology by AFM, Journal of Colloid and Interface Science, 240(1), 608–621.