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# Effect of antiscalants for inhibition of calcium sulfate deposition in thermal desalination systems

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## ABSTRACT

Antiscalants are used in desalination and water treatment plants to reduce or prevent scale formation on heat transfer equipments surfaces. For this purpose, an experimental apparatus has been designed to study the effect of various types of antiscalants on the deposition of calcium sulfate on the surface of stainless steel tubes. Three antiscalants are used in this study, sodium hexametaphosphate (SHMP), Belgard EV2030 and ethylenediamene-tetraacetic acid (EDTA). Two levels of antiscalants used in this work are 1 and 3 ppm, while $CaSO_4$ concentrations are 3000 and 7000 ppm. Collected results revealed that 33% decrease in fouling can be achieved by using SHMP, while 19% fouling reduction with Belgard EV2030 and 40% decrease in fouling when using EDTA. Also, the effect of the antiscalants is decreased by increasing the concentration of calcium sulfate from 3000 to 7000 ppm. This observation was extracted from graphical plots of obtained results. For antiscalant concentration above 1.5 ppm, it was found that the increase in its concentration has almost no effect on fouling resistance.

*Keywords*: Calcium sulfate; SHMP; EDTA; Belgard EV2030, Fouling resistance

## 1. Introduction

Fouling can be defined as the deposition of an insulating layer of foulant material on heat transfer surfaces leading to an increase in the resistance to heat transfer and subsequent loss of thermal exchange capacity of the heat transfer equipment [1], and the result is more equipment cost and higher maintenance cost. Prevention of scale formation on heat exchange surface is important in the desalination of brackish water and seawater [2].

One of the most effective methods for controlling scale formation is the use of inhibitors. It has been shown that the addition of scale inhibitor to feed water would be an effective method to reduce or prevent scale formation in industrial water systems [3].

Antiscalants 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 during its formation. The surface modification of the crystals causes them to distort as they grow. This distortion can slow and actually stop the growth of the usually highly-ordered crystals. Several types of antiscalants are commercially available now, and the proper selection of an antiscalant depends upon the water chemistry and system design [4].

Antisclants may act in one or more ways for its inhibition effect [5]:

1. It may destroy the activity of the scale deposit.
2. It may physically affect the fouling process by changing the physical interaction between the foulant and the heat exchanger surface.

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3. The additive may modify the nature of the deposit residing on the surface so that it is more susceptible to the removal surface.
4. It may react chemically with the fouling species to modify its fouling potential.

The question of the most efficient seed concentration for prevention of scale formation was considered theoretically by Linnikov [2]. He mentioned that seed crystals decrease super saturation of scale-forming salts in a solution and hence the growth rate of scale also decreases.

El-Dahan et al. [6] used organic phosphate ester as a scale inhibitor to prevent calcium sulfate dehydrate (gypsum) deposition. They found that the dose required for inhibition is small at a low temperature and increases with a rise in temperature. They also reported that gypsum has been inhibited through threshold inhibition as well as stabilization by adsorption onto crystal growth sites of nascent crystals.

The effect of copolymer of acrylic acid-diphenyl amine sulphonic acid (AA-DBSA) addition on the crystals of $CaSO_4$ and $CaCO_3$ scales morphology and structures were examined through scanning electron microscopic (SEM) and X-ray diffraction studies (XRD) [7]. The results show that the AA-DPSA polymer acts as a very good antiscaling inhibitor both in the carbonate and sulfate brines, and can be used safely in cooling water industries.

Atamanenko et al. [8] studied the effect of caboxymethyl cellulose (CMC), polyacrylamide (PAA) and poly-hexamethylene-$N_1N_2$NN-tetramethyl-1,5-dimethylene-naphthalene-diammonium chloride (PE-1) on the water state in $CaSO_4$-containing solution. Better results were established by the presence of polyacrylamide and carboxymethyl cellulose while those with the presence of PE-1 polyelectrolyte were somewhat worse.

Sodium hexametaphosphate (SHMP), organophosphonate (A), sodium salts of phosphonic acids (B), polyacrylate (C) and unspecified copolymer (D) were tested at two concentration levels of 6 and 12 ppm on $CaSO_4$ scaling systems [9]. SHMP provided the highest induction periods. Antiscalants C and D displayed a somewhat lower inhibitory effectiveness. The least effective antiscalants were those denoted as A and B.

Doubling the antiscalants dosage had a slight effect on the extent of induction time period for the more effective antiscalants (SHMP, C, D). However, in the case of the less effective antiscalants (A and B), doubling the antiscalant dosage significantly improved the antiscalnt performance-induction time approached those of the more effective antiscalants.

Demadis [10] examined the effect of polyaminoamide dendrimers (PAMAM-1 and 2), polyethyloxazoline (Aquazol-5, 50, 200, 500) and polyethyleneimine (PEI) for silica inhibition. PAMAM-1 and 2 were more efficient inhibitors than the other additives, while PEI was more effective than the Aquazol additives.

Therefore, the main objective of this work is to study the effect of sodium hexametaphosphate (SHMP), Belgard EV 2030 and ethylenediamene-tetraacetic acid (EDTA) on the scale formation of calcium sulfate in water systems (like thermal desalination plants).

## 2. Experimental work

### 2.1. Experimental set-up

The experimental setup used in the present work is shown in Figs. 1 and 2. This setup consists of a closed circulation loop and a test section as follows:

### 2.1.1. The circulation loop

The experimental setup used in the present work is shown in Fig. 1. It consists of the feed tank with 20-l capacity for the preparation and adjusting the test solu-

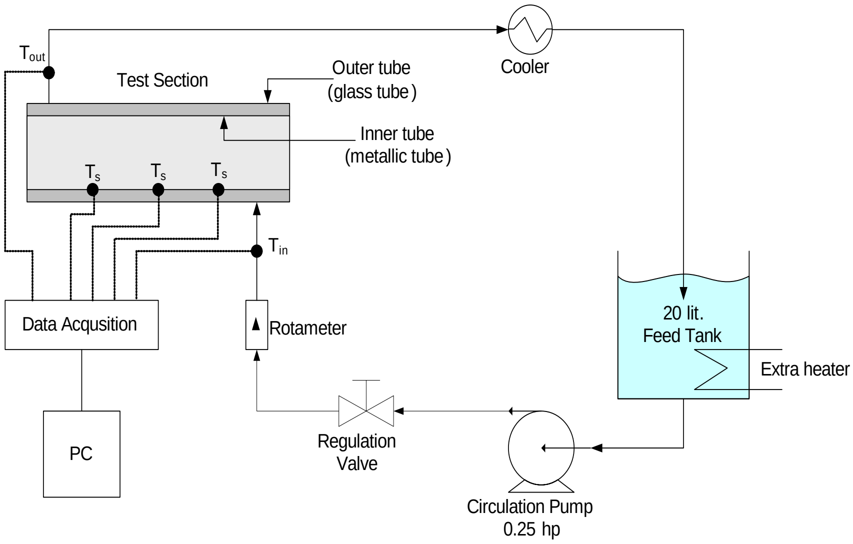

Fig. 1. The circulation test loop of the experimental setup.

tion. The tank is also connected to a level controller to compensate for any water evaporation losses during the whole period of experimental runs. The loop has a centrifugal pump of 0.25 hp for circulating the flow inside the test section according to the desired flow rate which is indicated by the flow meter reading. The loop is fitted with a cooler to adjust the temperature of the exit solution from the test section before entering into the feed tank. An extra heater is inserted in the feed tank to adjust the input temperature of the test solution. The temperature measuring devices, mainly thermocouples, are connected to the data acquisition system.

The following parameters are kept constant during each experimental run: $T_{in} = 50°C$, Re = 3000, heat flux ($q$) = 31 kW/m², time = 72 h and pH = 8.

Two levels of calcium sulfate concentration are used in the present work, i.e. 3000 and 7000 ppm. Moreover, antiscalant concentration levels used in the present experimental work are 1 and 3 ppm.

#### 2.1.2. The test section

The test section shown in Fig. 2 is an electrically heated metal tube (stainless steel) with 1.7 cm outside diameter and 60 cm length while its wall thickness is 0.25 cm. Inside this tube, an electric heater of the cartridge type (home made with a power of 1 kW) is inserted longitudinally as shown in Fig. 2. The metallic tube itself is enclosed in a wider glass tube of 4 cm inside diameter and 60 cm length while its thickness is 0.5 cm. The test fluid is forced to flow through the annuals between the metallic tube and the glass one. Visual observations are always possible with this configuration. The scale deposits with this type of test rigs are formed on the outside surface of the investigated metallic tube. Hence, for each run, the weight of the test section, the metallic tube, was obtained at the start and at the end of each run to find the weight of the fouling deposits (using an accurate mettler balance of model no. PL 1200 with readability of 0.01 and capacity of 1200 g) from which the fouling resistance $R_f$ was calculated (as will be explained later). Among the advantages of the present test unit, one can mention that it is compact in size, it can be easily removed for inspection of its deposit and also its weighting, it enables visual observation during experimental runs, two methods can be used for evaluating the fouling resistance $R_f$: weight method and heat transfer measurements method.

### 2.2. Experimental procedure

The following steps are carried out for each experimental run:

1. Preparation of 25 l solution of calcium sulfate according to the required concentration.
2. The required amount of the antiscalant is also added to the prepared solution in step (1).
3. Then starting the mixer operation and the heater of the mixing tank until the required temperature is achieved.
4. Start the circulating pump and adjust the required flow rate inside the loop.
5. Start the heater of the testing section until the required surface temperature is achieved.
6. Start the cooler of the exit water to adjust the water temperature before entering the mixing tank.
7. Leave the system running continuously for 72 h while the data acquisition system monitoring the required temperatures (surface temperatures and water temperatures). These values appear also on the screen of the PC.
8. 8 At the end of each run the metallic tube is dried and weighed to find the mass of the deposit.

Calcium sulfate solution was prepared by dissolving the required weight of $CaSO_4.2H_2O$ in distilled water. The required weight of the salt to prepare 1 l of certain concentration was calculated from the following equation:

$$\text{Weight of } CaSO_4.2H_2O \text{ (g)} = \frac{M_{wt} \cdot CaSO_4 \cdot 2H_2O}{M_{wt} \cdot CaSO_4} \cdot \frac{\text{Conc. (ppm) of } CaSO_4}{1000} \qquad (1)$$

The antiscalant was prepared by dissolving the required weight of the antiscalant in the salt solution. The weight of the antiscalant to prepare 1 l of certain concentration was calculated from the following equation:

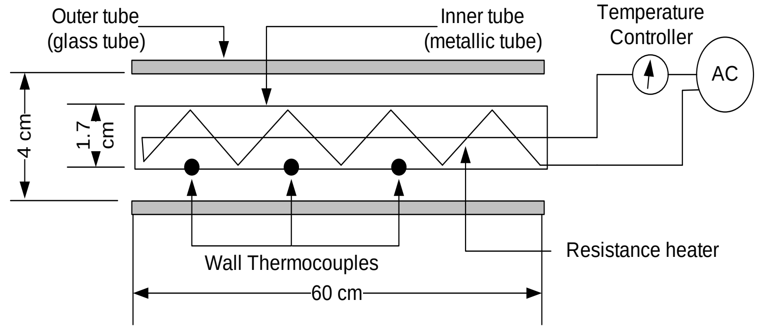

Fig. 2. The test section with its cartridge heater.

$$\text{Weight of antiscalant (g)} = \frac{\text{Conc. (ppm) of antiscalant}}{1000} \quad (2)$$

### 2.3. Fouling resistance calculation

Weight method is used to calculate the fouling resistance as follows:

$$R_f = \frac{\ln\left(D_f / D_o\right)}{2\pi k_f L} \quad (3)$$

$$w = \left[\frac{\pi}{4}\left(D_f^2 - D_o^2\right)\cdot L\right]\cdot \rho_f \quad (4)$$

where $D_f$ is average diameter of fouled tube (to be calculated), m; $D_o$ — external metallic tube diameter, m; $L$ — length of the tube, m; $k_f$ — thermal conductivity of fouling deposited salt, W/m°C; $\rho_f$ — density of fouling deposit, kg/m$^3$; $w$ — weight of fouling deposit measured in the experimental run, kg.

It is worth mentioning that the required salt properties for this procedure are $\rho_f$ and $k_f$ while the other variables like $L$, $D_o$ and $w$ are known from the experiment, hence $D_f$ is calculated from Eq. (4) and then substituted in Eq. (3) to find $R_f$. The property values of $\rho_f$ and $k_f$ for $CaSO_4.2H_2O$ salt are taken from Bott [5].

### 2.4. Sample calculation

The fouling resistance ($R_f$) was calculated from the weight of the deposit (0.31 g) as follows:

$$(w) = \left[\frac{\pi}{4}\left(D_f^2 - D_o^2\right)\cdot L\right]\cdot \rho \Rightarrow (0.00031)$$

$$= \left[\frac{\pi}{4}\left(D_f^2 - (0.017)^2\right)\cdot 0.6\right]\cdot 2418$$

$$\Rightarrow D_f = 0.017008 \text{ m}$$

$$R_f = \frac{\ln(0.017008/0.017)}{2\cdot\pi\cdot 1.34\cdot 0.6} \Rightarrow R_f = 0.0000931 \text{ m}^2\,^\circ\text{C/W}$$

## 3. Results and discussion

### 3.1. Sodium hexametaphosphate (SHMP) experiments

The collected data are reported in Table 1 and Table 2 for calcium sulfate concentration 3000 and 7000 ppm respectively and plotted in Fig. 3.

As shown in Fig. 3, the fouling resistance is reduced by about 26% and 24% when using 1 ppm of (SHMP) at 3000 ppm and 7000 ppm of calcium sulfate respectively, and about 33 and 30% when using 3 ppm of SHMP.

Table 1
Effect of SHMP concentration ($CaSO_4$ conc. = 3000 ppm, $T_{in}$ = 50°C)

| Fouling resistance (m²°C/W) | Deposit wt (g) | SHMP conc. (ppm) |
|---|---|---|
| 0.000126 | 0.42 | 0 |
| 0.0000931 | 0.31 | 1 |
| 0.0000841 | 0.28 | 3 |

Table 2
Effect of SHMP concentration ($CaSO_4$ conc. = 7000 ppm, $T_{in}$ = 50°C)

| Fouling resistance (m²°C/W) | Deposit wt (g) | SHMP conc. (ppm) |
|---|---|---|
| 0.000847 | 2.83 | 0 |
| 0.000641 | 2.14 | 1 |
| 0.000593 | 1.98 | 3 |

According to Hatch and Rice [11], «threshold treatment» using sodium hexametaphosphate (SHMP) was found to be very useful in preventing the formation of scale in many industrial applications. The term «threshold inhibition» describes the mechanism of scale inhibitor at sub-stoichiometric ratios. This threshold effect is explained by an adsorption of the inhibitor into the crystal growth site of sub-microscopic crystallites which are initially produced in the supersaturated solution, interfering with crystal growth and altering the morphology of those that grow. The additive may interfere either with the nucleation or the crystal growth process.

### 3.2. Belgard EV2030 experiments

The collected data are reported in Table 3 and Table 4 for calcium sulfate concentration 3000 and 7000 ppm respectively and plotted in Fig. 4.

From Fig. 4, the fouling resistance is reduced by about 14% and 6% when using 1 ppm of Belgard EV2030 at 3000 ppm and 7000 ppm of calcium sulfate respectively, and about 19% and 9% when using 3 ppm of Belgard EV 2030. Belgard EV2030 is an aqueous solution of an organic acid which act either as threshold inhibitor or increase the adsorption of scale so as to reduce adhesion to metal surface [12]. It is used in desalination plants to prevent or retard the precipitation of hard alkaline scale forming salts on the heat transfer surfaces [13]. Belgard EV2030 is effective in controlling scale formation at high temperatures [14–16].

### 3.3. Ethylenediamene-tetraacetic acid (EDTA) experiments

The collected data are reported in Table 5 and Table 6

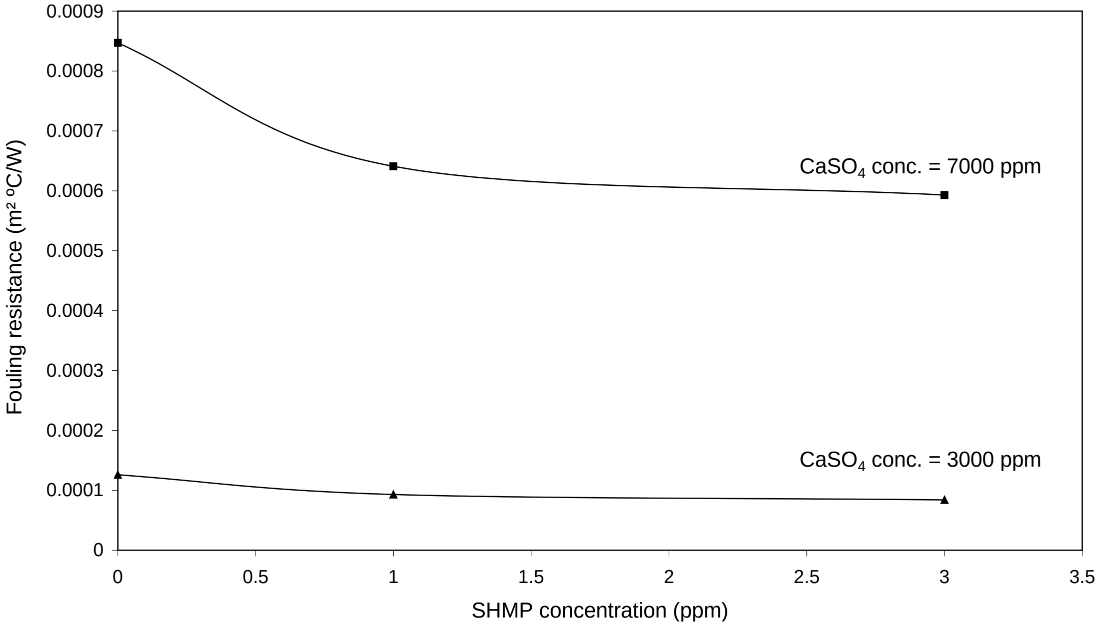

Fig. 3. Effect of SHMP on fouling resistance.

Table 3
Effect of Belgard EV2030 concentration ($CaSO_4$ conc. = 3000 ppm, $T_{in}$ = 50°C)

| Fouling resistance (m²°C/W) | Deposit wt (g) | Belgard conc. (ppm) |
|---|---|---|
| 0.000126 | 0.42 | 0 |
| 0.000108 | 0.36 | 1 |
| 0.000102 | 0.34 | 3 |

Table 4
Effect of Belgard EV2030 concentration ($CaSO_4$ conc. = 7000 ppm, $T_{in}$ = 50°C)

| Fouling resistance (m² °C/W) | Deposit wt (g) | Belgard conc. (ppm) |
|---|---|---|
| 0.000847 | 2.83 | 0 |
| 0.000796 | 2.66 | 1 |
| 0.000769 | 2.57 | 3 |

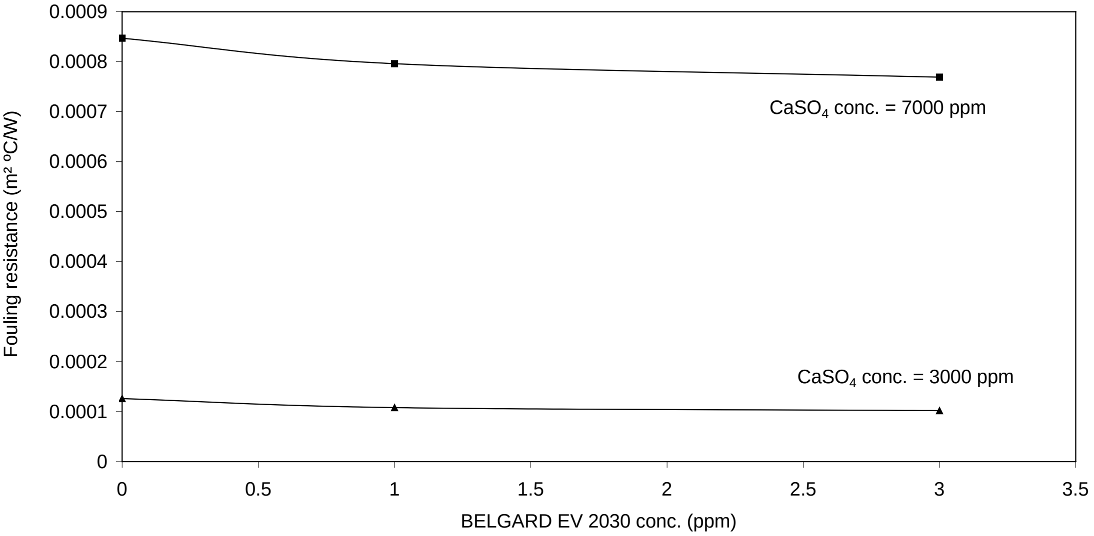

Fig. 4. Effect of Belgard EV 2030 on fouling resistance.

Table 5
Effect of EDTA concentration ($CaSO_4$ conc. = 3000 ppm, $T_{in}$ = 50°C)

| Fouling resistance (m²°C/W) | Deposit wt (g) | Conc. of EDTA (ppm) |
|---|---|---|
| 0.000126 | 0.42 | 0 |
| 0.0000841 | 0.28 | 1 |
| 0.0000751 | 0.25 | 3 |

Table 6
Effect of EDTA concentration ($CaSO_4$ conc. = 7000 ppm, $T_{in}$ = 50°C)

| Fouling resistance (m² ºC/W) | Deposit wt (g) | EDTA conc. (ppm) |
|---|---|---|
| 0.000847 | 2.83 | 0 |
| 0.00062 | 2.07 | 1 |
| 0.000542 | 1.81 | 3 |

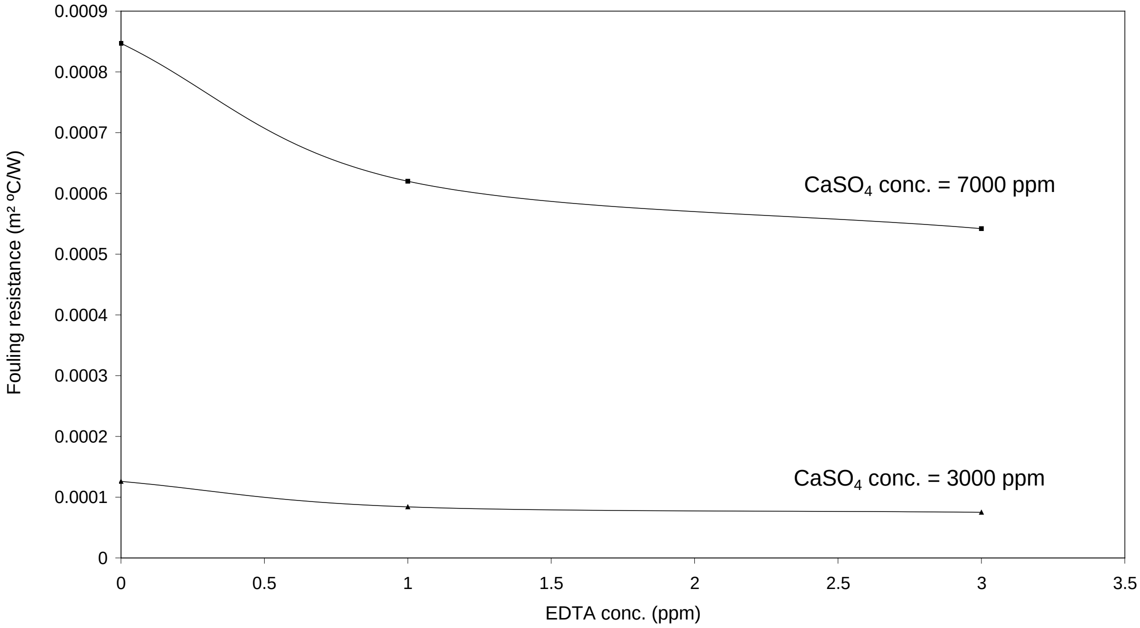

Fig. 5. Effect of EDTA on fouling resistance.

for calcium sulfate concentration 3000 and 7000 ppm respectively and plotted in Fig. 5.

From Fig. 5, the fouling resistance reduced by about 33% and 27% when using 1 ppm of EDTA at 3000 ppm and 7000 ppm of calcium sulfate respectively, and about 40 and 36% when using 3 ppm of EDTA.

The action of EDTA is similar to ion exchange, and may be described by the simplified equation [5]:

$$Ca^{2+} + Na_4EDTA \rightarrow CaNa_2EDTA + 2Na^{+} \quad (5)$$

The form of the EDTA-$Ca^{2+}$ complex according to Carini and Matell [17] is shown in Fig. 6.

Generally higher cost of EDTA compared to phosphate usually limits the use of these chealting agents to feed waters with low hardness [5].

### 3.4. Comparison

Figs. 7 and 8 show a comparison between the three antiscalants. From these figures, it can be seen that EDTA is the most effective one in controlling calcium sulfate deposition. SHMP is more effective than Belgard EV2030. From these figures, it can be seen that the effect of the antiscalants is reduced by increasing the concentration of calcium sulfate. For antiscalant concentration above 1.5 ppm, it was found that the increase in its concentration had almost no effect on fouling resistance.

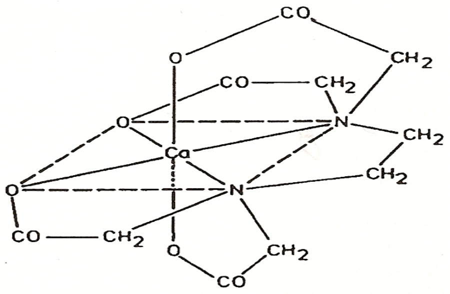

Fig. 6. EDTA-$Ca^{2+}$complex. (From [18]).

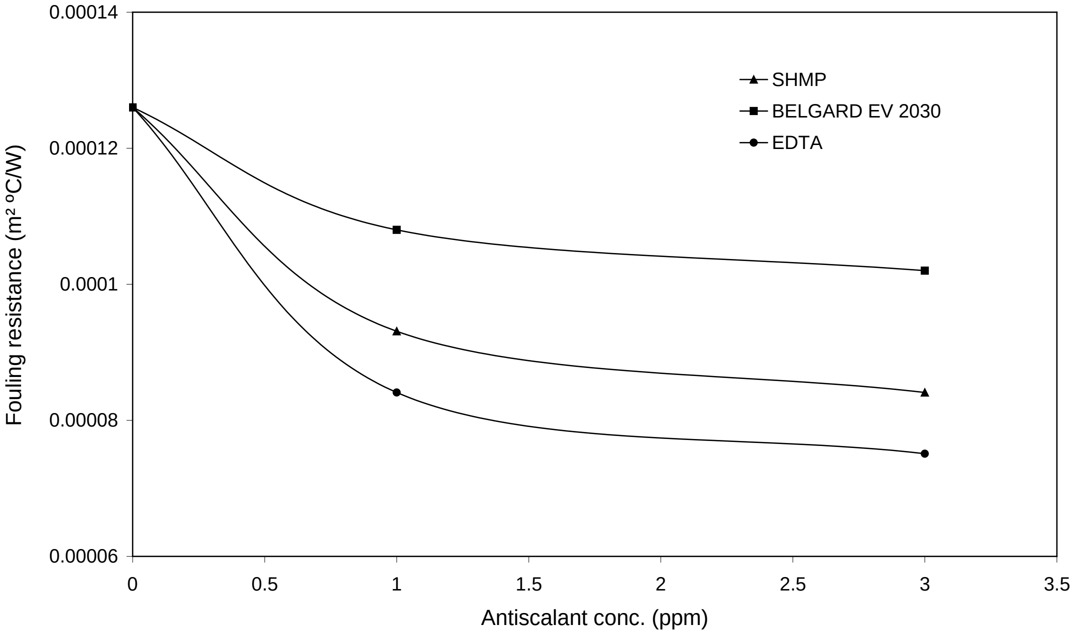

Fig. 7. Effect of antiscalants on fouling resistance ($CaSO_4$ = 3000 ppm).

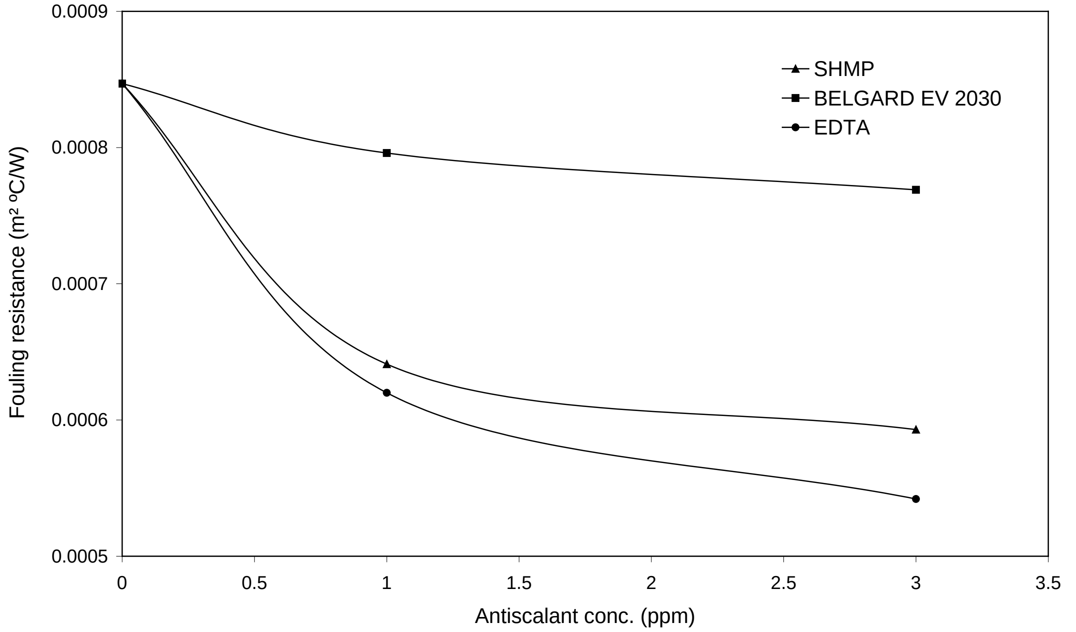

Fig. 8. Effect of antiscalants on fouling resistance ($CaSO_4$ = 7000 ppm).

## 4. Conclusions

1. Ethylenediamene-tetraacetic acid (EDTA) is the most effective inhibitor for calcium sulfate scale reduction (up to 40% reduction in fouling resistance was achieved), while sodium hexametaphosphate (SHMP) reduces the fouling resistance by about 33% and Belgard EV 2030 gives only 14% reduction in the fouling resistance.
2. No detectable effect of antiscalants on fouling resistance above the dosage of 1.5 ppm.
3. The effect of these antiscalants decreases by increasing the concentration of calcium sulfate.

## 5. Symbols

$D_f$ — Average diameter of fouled tube (to be calculated), m

| | | |
|---|---|---|
| $D_o$ | — | External metallic tube diameter, m. |
| $k_f$ | — | Thermal conductivity of fouling deposited salt, W/m°C |
| $L$ | — | Length of the tube, m |
| $R_f$ | — | Fouling resistance , W/m$^2$°C |
| $w$ | — | Weight of fouling deposit measured in the experimental run, kg |
| ρ | — | Density of fouling deposit, kg/m$^3$ |

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