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Scale and Corrosion Prevention in Cooling Water Systems Part II: Calcium Sulphate

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Abstract: This paper describes an experimental study on calcium sulphate scaling and prevention by newly treated polyacrylamide in a laboratory model. In order to study the inhibiting capacity of the chemical used, experiments were performed in solutions involving treatment of synthetic sea water with different concentrations of the polymer. Polyacrylamide gave significantly lower precipitation rate compared to the treatment in absence of inhibitor. The inhibitor probably is adsorbed on the active growth sites of the initially formed crystals. The performances of scale inhibitor with different concentrations were analyzed in terms of the amount of soluble calcium ions in solution. The results showed that the amount of scale was reduced to 0.00%, with, 10-15 ppm polymer additions, after 1 day incubation at 90°C. Antiscale agents specific to calcium sulphate deposits have recently been developed and tested on a laboratory scale. The work was also extended to study the corrosion inhibition of polyacrylamide to both C-steel and copper specimens in contact with synthetic cooling water environment. Electrochemical polarization techniques reveal that the inhibitor acts as anodic type with respect to C-steel and mixed type for copper. Corrosion current j_{corr} and corrosion rate *CR* were reduced and inhibition efficiency *IE*% increases with polymer additions. The inhibition effects are due to the formation of protective film. Morphological investigation for $CaSO_4$. $2H_2O$ gypsum crystals formed in synthetic sea water indicate reduction of calcium sulphate crystals in the presence of the polymer as indicated by scanning electron microscopic (SEM) studies.

Keywords: Calcium sulphate scale, Polyacrylamide, Cooling water system, Tafel, Linear polarization, SEM.

1. INTRODUCTION

Sulphate scales in thermal desalination plants are difficult to remove and require the most stringent mechanical means. The most common sulphate scalants encountered are $CaSO_4$, $BaSO_4$, and $SrSO_4$. The best approach is prevention through the lowering of the operation temperature, reducing the concentration factor to keep brine concentration below scaling threshold or by softening of the sea water [1-3].

Precipitation of inorganic species is initiated by nucleation. Homogeneous nucleation requires a relatively high degree of supersaturation [4], whereas, heterogeneous nucleation requires much lower levels of supersaturation to initiate [4], this can possibly occur on suspended and colloidal matter in the feed [5].

Sulphate scales resulting from the direct crystallization of anhydrite ($CaSO_4$), hemi-hydrate ($CaSO_4$. 1/2 H_2O) or gypsum ($CaSO_4$. $2H_2O$) from sea water, once their solubility limits are exceeded. Precipitation age has been identified as an important criterion for consideration since older precipitates which have undergone the process of ripening have proven harder to clean [6]. Supersaturation is the main driving force for scale formation and this can be considerably augmented by the superimposed effect of concentration polarization. Other factors such as temperature, pH or feed water composition deviations, can also induce precipitation at the metal surface. Under these fluctuating conditions, the efficiency of the pretreatment system can often be undermined [1] and ineffective performance or failure of this can often induce scaling in a relatively short space of time [7].

For the control of calcium sulphate scale in cooling water systems, copolymer of acrylic acid - diphenylamine sulphonic acid was tried as the antiscalant, and show a very good antiscaling inhibitor in the sulphate brine [8]. Polymaleic acid reduces the formation of scale by acting on the nucleation and growth process namely at a concentration of 4 ppm [9].

In the present work the effect of polyacrylamide on the precipitation of calcium sulphate was investigated through laboratory scale, electrochemical and scanning electronmicroscopic studies.

2. EXPERIMENTAL

Polyacrylamide ($(CH_2 = CHCONH_2)_x$) where x is about 5,000,000, i.e. high molecular weight type [10]. Analar (USA made) was used. Experimental procedure involves dissolving 9.11 g of $CaCl_2$ per 1L of triply distilled water (brine A Ca^{2+}). On the other hand the sulphate solution (brine B) can be prepared by dissolving 7.3 g of Na_2SO_4 per 1 L of triple distilled water. Test protocol consists of mixing 50 mls of calcium solution to 50 mls of sulphate solution. The solutions are then incubated in constant thermostat at 90°C for 24 hours. At the end of test duration, the solution is filtered through a 0.22-micron filter paper and the calcium concentration is analyzed by titration using 0.01 M EDTA and Murexide as indicator. Experiments were repeated for different doses of polyacrylamide 0.5-15 ppm and test duration.

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The percentage of inhibition was calculated using the following equation:

$$\% \text{ Inhibition} = \frac{Ca_i - Ca_b}{Ca_c - Ca_b} \times 100$$

Ca_i = Calcium ion concentration with the inhibitor.

Ca_b = Calcium ion concentration in the blank.

Ca_c = Calcium ion concentration before the test.

Carbon steel containing C = 0.7%, P = 0.03%, Mn = 0.3 -0.6%, S= 0.035%, Si = 0.5 - 0.75% and iron is the remainder, and copper of 99.99% purity were used for electrochemical corrosion tests.

The material was cut into 1 × 1 × 0.3 cm in size. Each piece was attached with a brass rod using silver paste for electrical contact. Then the samples were mounted on an epoxy resin in such a way that only one side with $1cm^2$ surface area was exposed. The samples were polished successively up to 1000 grit SiC emery paper and final polishing was done with 6 and 1μm diamond paste. The samples were degreased with acetone and ultrasonically cleaned using deionized water. This served as the working electrode. Synthetic sea water was used as the electrolyte.

The polarization experiments were carried out in a conventional glass cell with platinum foil as a counter electrode and saturated calomel electrode as a reference electrode. The working electrode was immersed in the test solution and allowed to stabilize for 30 minutes. The cathodic and anodic polarization curves of both C-steel and copper specimens were carried out at a sweep rate of 5 mV/s. The polarization measurements were carried out in synthetic sea water in the absence and presence of 5 ppm polymer optimum dose. Both Tafel and linear polarization studies were carried out using EG & G potentiostat model 273/81 interfaced with a computer.

The inhibition efficiency was calculated from the following equation:

$$\text{Inhibition efficiency } (\%) = \frac{I'_{corr} - I_{corr}}{I'_{corr}} \times 100$$

I'_{corr} = Corrosion current density of uninhibited system.

I_{corr} = Corrosion current density of inhibited system.

For linear polarization studies, the scan rate was 1.66×10^{-4} mV/s.

The change of crystal habits and morphology of the calcium sulphate scale was examined through SEM studies using JOEL JSM 840 S Scanning microscope for the scales formed without and with the presence of the polymer.

3. RESULTS AND DISCUSSION

3.1. Scale Tests

Distillation of sea water and other naturally occurring saline waters gives rise to the formation of calcium sulphate scale deposits. It was found that the addition of small amounts of polyacrylamide of selected high molecular weight > 5,000,000, to the synthetic sea water had a remarkable effect in reducing the adverse effects of scale formation on the heat transfer surfaces. The present work was carried out in an attempt to establish the optimum dosage of this organic polymer for reducing calcium sulphate deposition in saline water evaporator. For laboratory type operations, using synthetic sea water of pH 7.7 and 1 day incubation at 90°C, polyacrylamide at a 0.5 ppm concentration, gives 83% scale reduction. Similar experiments with increasing doses of polymer up to 15 ppm indicated an effective scale reduction of 100%, (Fig. **1**, curve a). The absence of sulphate crystallization in synthetic sea water samples treated with polyacrylamide show some promise for control of sulphate scales at higher temperatures and an important advance may be made in desalination technology.

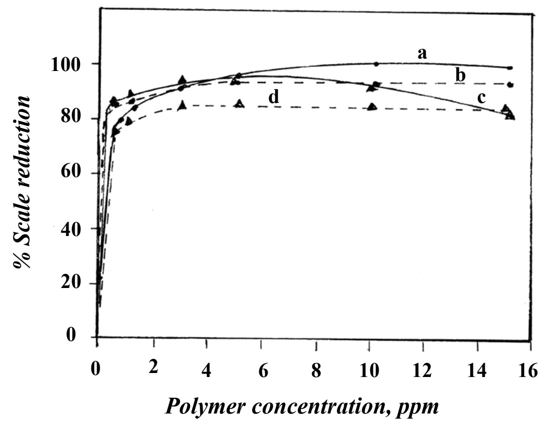

Fig. (1). Effect of polymer dosage on scale reduction at 90°C, after **a**) – 1 day incubation; **b**) – 3 days incubation; **c**) – 7 days incubation; **d**) – 10 days incubation.

One of the successful applications of polyacrylamide as a scale preventive additive was to study the incubation time 3,7,10 days, at 90°C, on the % scale reduction (Fig. **1**, curves b, c, d). In order to determine the antiscale performance on scale reduction during synthetic saline water evaporation, experimental runs were made with polymer doses ranging from 0.5-15 ppm concentrations. The reason for selecting such treatment concentrations can be obtained by operating in the range of treatment concentrations where scaling effect still persisted.

The results obtained with concentrations 0.5-15 ppm are presented in Fig. (**1**, curve b). Maximum scale reduction (93.4%) was obtained with 10 and 15 ppm polymer concentrations. After 7 days incubation at 90°C (curve c), the percent scale reduction of polyacrylamide of 0.5-3 ppm concentrations ranged from 85-93.4%. Higher doses of polyacrylamide show less effective scale reduction. In this respect the scale problems have been controlled using the technology of threshold-type scale inhibitor. Fig. (**1**, curve d) represents the variation of % scale reduction with polyacrylamide concentrations in ppm. % scale reduction increases regularly up to 3 ppm concentration, and then remains constant at 83.4% up to 15 ppm polymer dose. Fig. (**2**) represents the effect of time on the performance of 5 ppm polymer concentration as an optimum dose, the % scale reduction remains almost constant with time.

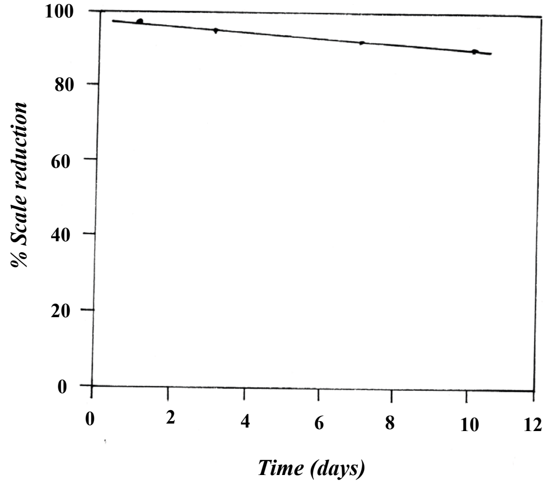

Fig. (2). Effect of time on the performance of 5 ppm polymer on calcium sulphate scale inhibition.

It is believed that polyacrylamide containing amide group can affect calcium sulphate scale reduction. The functional groups chosen for incorporation into the polymer have the ability to participate into a chemical reaction with the scale – forming minerals. This reaction causes a large, irregularly shaped body to be incorporated in the crystal lattice. This results in the distortion of a dense, uniformly structured crystalline mass on the metal surface [11]. Instead of a hard, smooth scale, irregularly shaped crystals are formed which do not adhere. There is some evidence that such distorted crystals develop internal stresses that increase as the crystals grow larger; these stresses cause the crystals to slough off the supporting surface [10].

3.2. Electrochemical Tests

Anodic and cathodic polarization curves were recorded to obtain information about the action of the polyacrylamide on the partial corrosion processes. Figs. (**3**, **4**) show Tafel polarization curves measured on C-steel and copper electrodes respectively in synthetic cooling water environment at 25°C in absence and presence of 5 ppm polyacrylamide concentration. For C-steel polarization measurement, it should be noted that, the polymer shifts Tafel polarization curve towards anodic region (anodic type inhibitor), and the corrosion current density decreases too. β_c is not affected by polymer addition, whereas, β_a is highly influenced by addition of 5 ppm polymer dose, and corrosion rate (*CR*) was reduced to 11.94 mpy. On the other hand, polarization curves for copper electrode show parallel shift of both anodic and cathodic curves towards lower current densties with 5 ppm polymer concentration, indicating that the studied compound is mixed-type inhibitor without changing the mechanism of corrosion reaction. Variation of polarization parameters for C-steel and copper in synthetic sea water environment at 25°C with addition of 5 ppm polyacrylamide dose are shown in Table **1**, including j_{corr}, E_{corr}, β_a, β_c, R_p, *CR*, and *IE*%.

The corrosion rate (*CR*) is directly related to the R_p and can be calculated from it [12]. The R_p value can help us to assess the relative ability of a material to resist corrosion. Since R_p is inversely proportional to j_{corr}, so the materials with the highest R_p (and thus the lowest j_{corr}) have the highest corrosion resistance. From all these facts, we can correlate the data obtained from the R_p and those computed from Tafel plots. It is observed that, in the presence of 5 ppm polyacrylamide concentration the value of R_p increases, while the value of j_{corr} decreases. This dose of inhibitor has a pronounced effect on the corrosion of both C-steel and copper and increases the inhibition efficiency *IE*%.

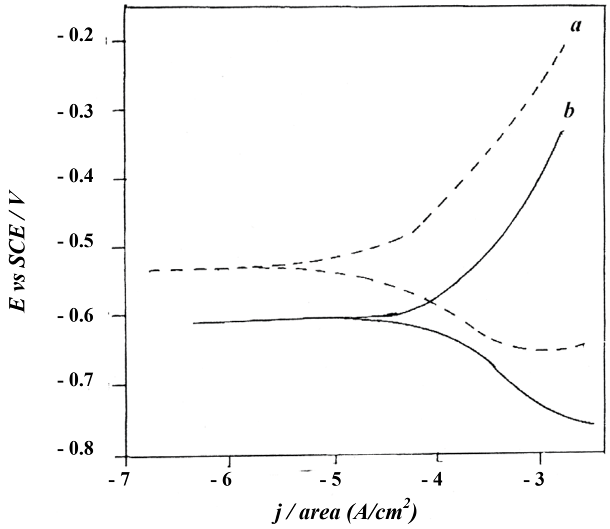

Fig. (3). Tafel polarization curves of C-steel (**a**) with and (**b**) without inhibitor.

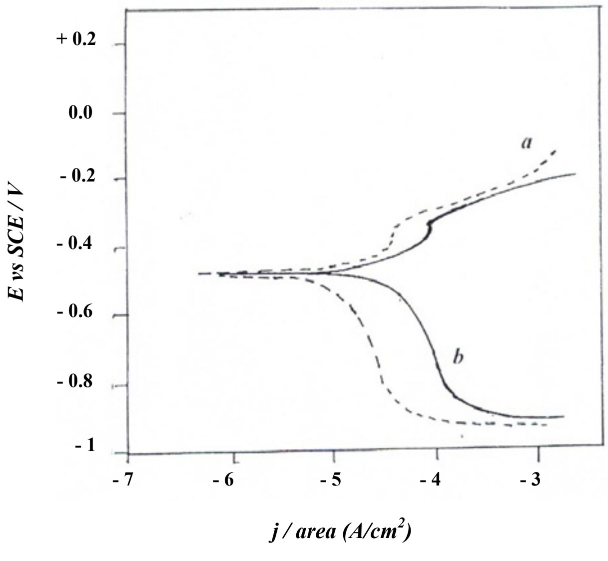

Fig. (4). Tafel polarization curves of copper (**a**) with and (**b**) without inhibitor.

Aggressive ions (Cl^-) in synthetic sea water can be adsorbed on the active sites randomly distributed on the C-steel and copper surfaces and then desorbed with the surface action. The drastic decrease in R_p and increase in j_{corr} of both C-steel and copper in additive – free solution can be ascribed to the dissolution of C-steel and copper due to the formation of corrosion products. In case of 5 ppm addition of polyacrylamide, competition of surface adsorption between the ag-

Table 1. Variation of Polarization Parameters for Both C-Steel and Copper Electrodes in Synthetic Sea Water Environment at 25°C in Absence and Presence of 5 ppm Polyacnylamide Addition

Electrode	Inh.dose	E_{corr} mV	$\beta_a \times 10^{-3}$ v/d	$\beta_c \times 10^{-3}$ v/d	j_{corr} µA/cm^2	R_p Ώ	CR mpy	IE%	
								Tafel	LP
C-Steel	Blank	-620	237.9	121.6	64.18	43.13	33.81		
	5 ppm	-535	193.7	118.4	23.05	167.23	11.94	64.05	74.2
Copper	Blank	-480	339.4	682.3	56.16	163.68	29.33		
	5 ppm	-479	234.8	648.9	12.7	1123	6.71	77.38	85.42

gressive ions and the inhibitor molecule is assumed to occur [13], but the additives have almost covered the surface of C-steel and copper, hence the process of corrosion is decreased. So, the decrease in the *CR* is associated with an increase in R_p values and a decrease in j_{corr} values with 5 ppm polymer addition. The results of this study as shown in Table **1** suggests an appreciable contribution of polymer molecules to the inhibition process by interaction with the electrode surface [14]. Moreover, this behavior may be ascribed to the facilities of adsorption of polyacrylamide to the electrode surface through coordination of oxygen atom to the vacant d-orbital of both steel and copper [15], so enhancing the corrosion inhibition efficiency *IE*%.

3.3. Morphological Investigation

The appearance of sulphate scales in thermal desalination plants is not uncommon. Their formation inside condenser tubes is a major operational problem. They are hard, adherent and unaffected by common chemicals. Unlike alkaline scales, which result from the decomposition products of HCO_3^-, sulphate scales result from the interaction of components present as such, and in great concentrations, in sea water. Scaling occurs, therefore, as a consequence of separation from saturated solution at appropriate temperatures.

Three forms of calcium sulphate are known to form in thermal desalination plants. These are the anhydrite ($CaSO_4$), hemi-hydrate ($CaSO_4.1/2\ H_2O$) and dihydrate or gypsum ($CaSO_4.2H_2O$). Both anhydrite and gypsum occur naturally, while the hemi-hydrate is a meta-stable form commercially known as plaster of Paris, obtained from gypsum by heating at approximately 125°C. The solubility of calcium sulphates in aqueous solutions is a complex process.

3.3.1. SEM Investigation

The SEM photographs of calcium sulphate scale with and without the presence of the polymer are represented in Fig. (**5**). Among the three types of the calcium sulphate crystals [8], Calcium sulphate dihydrate crystal was formed from the supersaturated solution at higher temperatures without any additives. Calcium sulphate dihydrate crystals are thin tubular cells and needles exhibiting monoclinic symmetry [16]. The influence of the polyacrylamide polymer on the morphological changes of the scales was examined extensively, the change in crystallinity and the crystal habits to be modified were reported. In the present study, SEM images show the total absence of tubular cell shaped $CaSO_4.2H_2O$ with reduced size. With the addition of polyacrylamide polymer, reduced crystallinity with spongy deposits is formed.

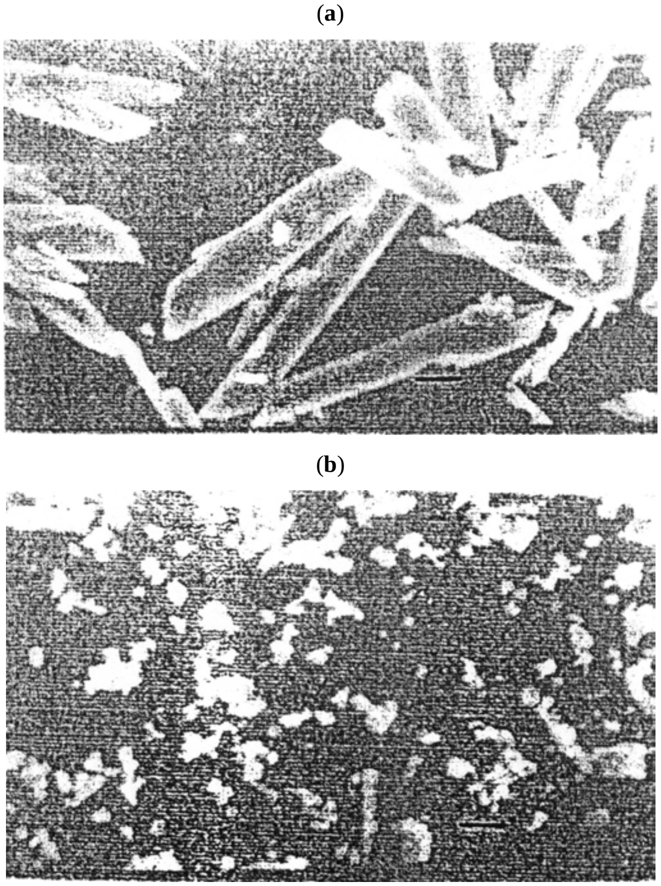

Fig. (5). SEM photographs for the $CaSO_4$ (**a**) and with the presence of polymer (**b**).

4. CONCLUSIONS

The main conclusions drawn from the studies are:

1. The efficiency of the selected polyacrylamide was tested for its ability to prevent calcium sulphate scale. Under the conditions studied, the amount of gypsum deposited was reduced and totally prevented by polymer injection.
2. Electrochemical measurements proved to be very effective means of characterizing the inhibition of corrosion of both C-steel and copper in synthetic sea water by polyacrylamide.
3. SEM images suggest reduction of calcium sulphate crystals in the presence of the polymer.

LIST OF SYMBOLS

E_{corr}(mV) : Corrosion potential
j_{corr} (μA/cm^2) : Corrosion current density
β_a (v/d) : Anodic Tafel polarization constant
β_c (v/d) : Cathodic Tafel polarization constant
R_p (Ω) : Polarization resistance
CR (mpy) : Corrosion rate
IE% : Inhibition efficiency

REFERENCES

[1] Amjad Z, Hooley J, Pugh J. Reverse osmosis failures; Causes, cases and prevention. Ultrapure Water 1991; 8: 14-21.
[2] Matthiasson E, Sivik B. Concentration polarization and fouling. Desalination 1980; 35: 59-103.
[3] Osta T, Bakheet L. Pretreatment system in reverse osmosis plants. Desalination 1987; 63: 71-80.
[4] Nielsen AE. Kinetics of Precipitation. 3rd ed. Pergamon press: London 1964.
[5] Amjad Z. Mechanistic aspects of reverse osmosis mineral scale formation and inhibition. Ultrapure Water 1988; 5: 23-8.
[6] Pervov A. Scale formation prognosis and cleaning procedure schedules in reverse osmosis system operation. Desalination 1991; 83: 77-118.
[7] Jaffer A. The application of a novel chemical treatment programme to mitigate scaling and fouling in reverse osmosis units. Desalination 1994; 96: 71-9.
[8] Shakkthivel P, Vasudevan T. Acrylic acid – diphenylamine sulphonic acid copolymer threshold inhibitor for sulphate and carbonate scales in cooling water systems. Desalination 2006; 197: 179-89.
[9] Martinod A, Euvrard M, Foissy A, Neville A. Progressing the understanding of chemical inhibition of mineral scale by green inhibitors. Desalination 2008; 220: 345-52.
[10] Shaheen E, Dixit S. Scale reduction in saline water conversion. Desalination 1973; 13: 187-206.
[11] Knudsen JG. Drew Principles of Industrial Water Treatment. 1st ed. Drew Korea: New Jersey 1988.
[12] Unling HH, Revie RW. Corrosion and Corrosion Control. 3rd ed. Wiley: New York 1985.
[13] Garrigues L, Pebere N, Dabosi F. An investigation of the corrosion inhibition of pure aluminum in neutral and acidic chloride solutions. Electrochim Acta 1996; 41: 1209-15.
[14] Metikos M, Bobic R, Grubac Z, Brinic S. Impedance spectroscopic study of aluminum and Al-alloys in acid solution: inhibitory action of nitrogen containing compounds. J Appl Electrochem 1994; 24: 772-8.
[15] Rajendran S, Apparao B, Palaniswamy N. Synergistic and antagonistic effects existing among polyacrylamide, phenyl phosphonate and Zn^{2+} on the inhibition of corrosion of mild steel in a neutral aqueous environment. Electrochim Acta 1998; 44: 533-7.
[16] Salamon JC. Polymer materials encyclopedia. CRC Press: Boca Raton 1996.

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