Study of the Effect of pH and Supersaturation on the Kinetics and Rate of Solid Layer Formation at External Sides of Thermal Heat Transfer Tubes

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Abstract

The formation of scale layers at the external sides of heated tubes at situations comparable with a Multi Effect Distiller (MED) desalination processes is experimentally studied. The growth of scale layer was measured at different temperatures, pH levels and salinities. The measured scale deposition rate data were correlated to the calcium carbonate supersaturation according to a power low kinetics. It was found that the growth rate order (n) with respect to supersaturation is strongly temperature dependent. It decreases with increasing temperature. The calculated value of activation energy of scale layer growth is Ea = 33360 J/mol. The scale layer growth was found to be strongly dependent on pH. It increases in the basic medium. The salinity was found to be significant in determining the growth rate of scale layer. The scale layer composition is affected by temperature. It was found that calcium carbonate is dominant at high temperatures (80 °C). calcium sulfate deposited besides calcium carbonate at lower temperatures (60-70 °C).

Keywords: scale layer, outer tubes, MED, kinetics, growth, pH, Temperature, activation energy, tubes.

1. Introduction

Multi Effect Distiller (MED) is a well-known technology for the conversion of seawater to drinking water [1] . In this type of processes, the outer surface of the hot pipes is allowed to contact with falling seawater to reach evaporation [2]. Scale deposition of sparingly soluble compounds on outer heat transfer surfaces is one of the major challenges of the economy, operation and maintenance in MED process [3]. The solid scale layer development at the exterior side of MED tubes was investigated by several authors [4-7]. Scale layer formation leads to additional resistance to heat transfer, therefore, a reduction in the overall efficiency of desalination process [8], which contributes in increasing the energy required per one cubic meter of fresh water produced. On the other hand, formation of scale increases the risk of pipe corrosion under scaling layers with the priming of pitting. The scale layer deposited on the outer surfaces of pipes in MED plants is mainly composed of calcium carbonate [9]. The crystalline form of calcium carbonate scale layer depends on the temperature, supersaturation, salinity and pH of seawater [10]. Calcium carbonate may crystallize as calcite, vaterite or aragonite [11,12]. Also, the concentration other species existed in seawater lice magnesium ions [13], sodium ions [14] and strontium ions [15] has a significant effect on the scaling rate and crystalline form of the scaling layer. The temperature, pH and salinity of seawater affects the level of supersaturation which is the driving force for scale layer formation on the surfaces of pipes. These parameters play central roles in the carbonate system of seawater and therefore affect significantly the relative distribution of the components CO_2, HCO_3^- and CO_3^{2-} and consequently the degree of calcium carbonate supersaturation. The kinetics of crystalline layer formation of scales or fouling crystallization on the outer surfaces of heated tubes are a complex process which is poorly understood and kinetic data are limited. There are many processes occurring simultaneously and contribute either directly or indirectly to the whole fouling crystallization. Among these processes is the nucleation on the substrate and then the adherence of the particles to the surface [17].

The diffusion step of the dissolved scaling salts to the surface of the crystalline layer is an important processes which determines the kinetics of scale layer formation. After the diffusion step, the molecules or solvated ions are adsorbed and then integrated into to the surface of crystalline layer. This step is believed to be a rate determining controlling step of crystal growth. The mechanism and kinetics of growth of calcium carbonate polymorphs was studied in the literature [18,19], however little studies reported about the rate of growth and kinetics of calcium carbonate crystal layers formation on the outer surfaces of heat exchangers.

This study investigates the effect of pH, temperature and salinity on the rate and mechanism of scale layer deposition at the outer surface of the hot pipes. An experimental apparatus was designed to simulate seawater of different salinities, pH contacting hot pipe surface at different temperatures aiming at better understanding the factors influencing scale layer formation.

2. Theory

The driving force for layer growth of scales is the supersaturation, which has a direct influence on both nucleation and growth of the scale layer. The supersaturation ( ) can be defined as:

$$\Omega = \left[\frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}} \right] \tag{1}$$

Where K_{sp} is the solubility product of aragonite which is the dominating $CaCO_3$ polymorph precipitated at temperatures below 90 °C. The terms $[Ca^{2+}]$ and $[CO_3^{2-}]$ are the concentration of calcium and carbonate ions in seawater, respectively.

Crystalline scaling layers are initiated at the surface of the hot pipe whenever the amount of supersaturation exceeds a unity (>1.0). For seawaters with higher salinities, the supersaturation for aragonite is much higher than unity (5< <20), hence the deposition rate increases sharply with the substrate will undergo a severe scaling and faster growth rates of the scaling layer. The rate of mass deposition due to the crystalline deposits (Rm) on a substrate surface of area (A) can be expressed in terms of mass rate deposition by the equation:

$$R_m = \frac{1}{A} \frac{dm}{dt} \tag{2}$$

where m is the amount deposited during the time interval t.

The layer growth rate of the scales or the rate of mass deposition (R_m) can be practically related to the supersaturation ( ) by a power low relation has the form [20]:

$$R_m = K_R \, \Omega^n \tag{3}$$

Where K_R is the overall rate coefficient which includes both diffusion and surface integration steps and (n) is the overall scale layer growth order. The overall rate coefficient K_R is usually temperature dependent according to the Arrhenius equation:

$$K_R = k_0 \exp^{\frac{E_a}{RT}} \tag{4}$$

Where E is the activation energy for the growth of crystal layer and R is the universal gas constant. The value of k_0 depends on the salinity of seawater as well as the pH value and fluid dynamic conditions.

3. Experimental

In order to study the fouling at the external parts of hot tubes contacting seawater under similar conditions to MED seawater desalination processes, a simple apparatus was designed for this purpose (see Fig. 1). The apparatus consists of a small jacketed stainless steel tube of 2.5 cm diameter allowed to contact 500 mL of synthetic seawater in a closed jacketed batch vessel. A thermostat was connected to the jacketed vessel in order to adjust the seawater temperature. A second thermostat was used to circulate hot water in the internal jacket of the tube in order to control the temperature of the external side of the tube. The amount precipitated on the external part of the tube was determined as a function of time by withdrawing samples of seawater at different time intervals and analysing the samples for concentration, pH, TDS, supersaturation with respect to calcium carbonate. The level of supersaturation was adjusted by changing the pH using sodium hydroxide (NaOH) or by adding carbonate ions using sodium carbonate. The decrease in TDS of seawater was considered as the rate of deposition of scaling materials on the external part of the tube. The samples TDS were analyze using the instrument CyberScan CON 410 manufactured by EUTECH-INSTRUMENTS Pte Ltd., Singapore.

The experimental study of kinetic parameters for the calcite scale layer growth on the outer surface of heated pipes was conducted by measuring the deposition rate at different supersaturation levels.
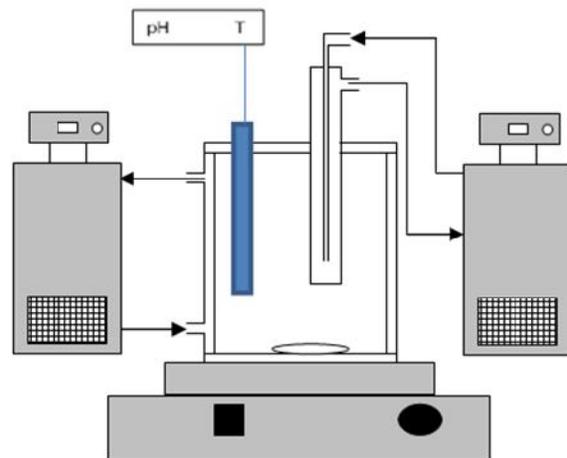
Fig. 1. The experimental apparatus used to study the solid layer deposition rate at the external side of the tube contacting seawater.

The supersaturation change with time as well as the deposition rate were determined by applying a mass balance based on the concentration and TDS analysis of seawater samples. The synthetic sea water implemented in all runs is of the same stock and was prepared from analytical grade (p.a.) salts. The chemical analysis of seawater used in all the experiments is shown in Table 1. The different salinities (S) of seawater were prepared by dilution of the prepared stock. Scale layer composition studies was conducted experimentally by scratching the deposited layer and analyzing it using XDR and optical methods.

4. Results and Discussions

4.1. Kinetics of Scale Layer Growth

The kinetic parameters of growth of scale layer were determined by measuring the TDS decrease in seawater contacted with a hot pipe in a closed vessel. It is assumed ,however, that the decrease in the TDS during the 4 hours batch cycle is attributed to the deposition of calcite, which is the dominant polymorph of calcium carbonate at temperatures below 90 °C might be deposited on the tube surface.

Table 1. The chemical analysis of the stock synthetic seawater (S = 59 g/L) used in the runs.

Component	Concentration, mg/L
Cl^-	31808
Na^+	18939
SO_4^{--}	5246
Mg^{++}	2280
K^+	751
Ca^{++}	691
CO_3^{--}	397
Total dissolved solids	60112

The measured deposited mass during the batch runs at 90 °C, 80°C, and 70°C at initial pH value of 9.25 and salt content (S = 59 g/L) are depicted in Fig. 2. It can be seen that there is a faster deposition of calcium carbonate at increased temperature. This resulted from the decrease in solubility of calcite with increasing temperature hence the supersaturation which is the driving force for the growth of scale layer will increase. This will result in a faster decay in the concentration of both carbonate and calcium ions.
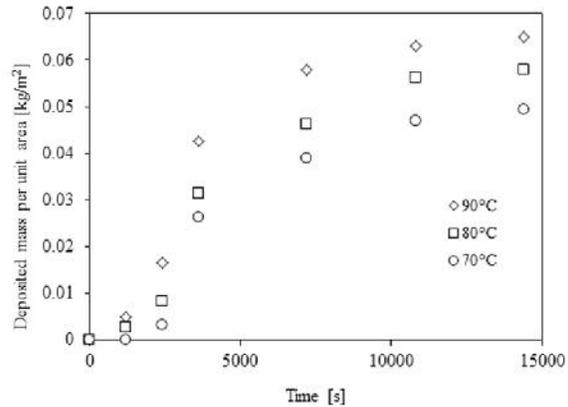
Fig. 2. The measured amount deposited of scaling components at different external tube temperatures. S = 59 g/L; Seawater temperature = 50 ºC, pH = 9.25

The kinetic parameters of growth of growth were determined by fitting the measured deposition rate (R) against supersaturation. The results are displayed in Fig. 3. As can be viewed in Fig. 3, the rate of scale layer growth of is sharply increases with increasing temperature of the tube surface.
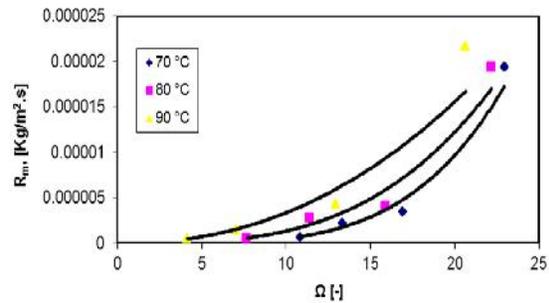
Fig. 3. The measured deposition rate of calcite against supersaturation at different surface temperatures of the pipe. S = 59 g/L; Seawater temperature =50 ºC.

The kinetic parameters which are the growth rate constant (KR) and the growth rate order (n) were determined by applying a logarithmic linear regression (according to equation 3) for the experimental data of Fig. 3. The calculated kinetic parameters at the investigated different temperatures are arranged in Table 2.

Table 2. The calculated growth rate parameters of calcite scaling layer formation.

T, K	K_R	n	R^2
343.15	3.25 E-11	4.2	0.97
353.15	8.68 E-10	3.18	0.96
363.15	2.05 E-08	2.2	0.97

It can be concluded from the calculated kinetic parameters that the order (n) for the scale layer growth rate is strongly temperature dependent. The values of n are higher at elevated temperature which means that the role of supersaturation plays a minor role at elevated temperatures.

There are two main steps involved in the growth process of the scaling layer. The first step is the diffusion step which is strongly affected by the supersaturation level and depends on temperature. The second step which is the surface reaction which depends on the mechanism by which the molecules are separated from the solvent molecules and then adsorbed to the scaled layer and are integrated to the crystal lattice. The supersaturation plays minor role in the surface reaction step.

The significant dependence of the scale layer growth process on the supersaturation at lower temperature may indicate that the diffusion step is rate determining at lower temperatures. On the other hand at elevated temperatures the diffusion step becomes very fast and the surface reaction step will be the rate determining.

The results in Table 2 indicate that the scale layer growth rate constant (K_R) is temperature dependent. It is value becomes higher at higher temperatures. Activation energy of scale layer growth can be determined by the logarithmic fitting of the values of scale layer growth rate constant (K_R) against the reciprocal of temperature (1/T) according to Eq. (4). The linear fit is displayed in Fig. 4. The estimated value of the activation energy of scale layer growth is Ea = 33360 J/mol. This high activation energy of scale layer growth indicates a significant temperature dependency of scale layer growth process.
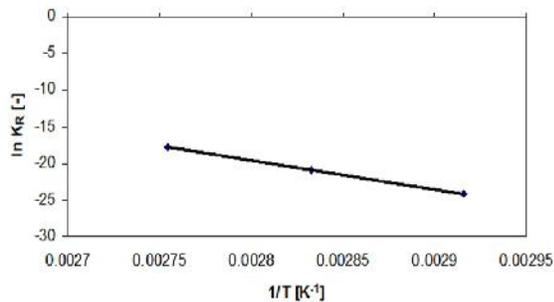
Fig. 4. A plot of the temperature dependence of growth rate constant according to Eq. (4).

4.2. Influence of seawater pH-value on the rate of scale layer formation

Figure 5 depicts the measured mass deposition rate of scaling compounds (calcium carbonate) on the exterior part of a hot tube as a function pH-value of seawater with salt content 45 g/L and at tube surface temperature of 90 °C. As shown, seawater with higher pH-values exhibits faster rate of scale formation. This can be attributed to the dependence of carbonate formation in the seawater on the pH-value.
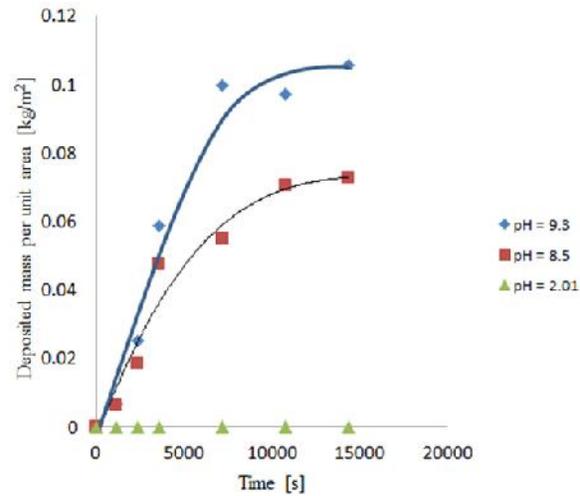
Fig. 5. The measured mass deposition rate of scaling compounds on the exterior part of a hot tube as a function pH-value of seawater. Salt content (TDS) = 45 g/L. Tube exterior temperature = 90ºC. Seawater temperature = 50ºC.

The amount of carbonate ions produced from the decomposition of bicarbonate ions is function of pH. Figure 6 shows the calculated using carbonate-water chemistry principles [21] concentrations of carbonate and bicarbonate alkalinity as a function of pH for seawater of salt contents 35 g/L and 45 g/L.

Obviously increasing the pH leads to generation of more carbonate ions in seawater and therefore the level of calcium carbonate supersaturation in seawater increases (see Eq. (1)). On the other hand, the pH value has a great influence on the scaling tendency of seawater. In order to better understand the effect of pH on the scaling tendency of seawater, the Langelier saturation index was estimated as a function of pH for seawaters of salinities 35 g/L, 45 g/L and 59 g/L using water chemistry [21] calculations. The Langelier saturation index of seawater is dependent on calcium ions concentration (salt content) and pH of seawater (carbonate concentration). Its value gives indication about the degree the seawater is supersaturated with respect to calcium carbonate ($CaCO_3$) and scale forming tendency. Values greater than zero means that the seawater is supersaturated and as the value increases the supersaturation with respect to calcium carbonate increases. Figure 7 shows the estimated variation of scaling index of seawater with pH and salt content. It can be concluded that seawater with higher salt contents at certain pH have higher scaling tendency due to the higher calcium ion concentration. The scaling tendency increases by increasing pH for certain salt content due to the higher carbonate ions concentration. Obviously increasing the pH leads to generation of more carbonate ions in seawater and therefore the level of calcium carbonate supersaturation in seawater increases (see Eq. (1)).

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Fig. 6. Calculated carbonate and bicarbonate alkalinity for seawater as a function of pH
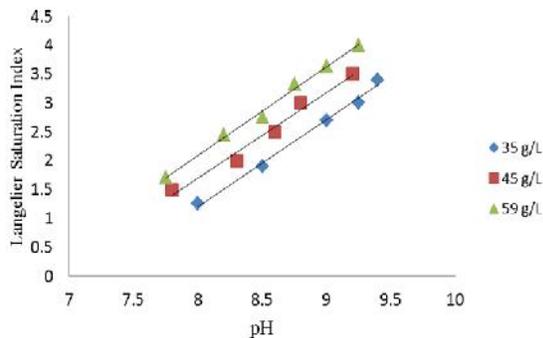
Fig. 7. Influence of pH and salt content of seawater on Langelier saturation index.

4.3. Influence of salt content (TDS) of seawater on the rate of scale layer formation

Figure 8 depicts the measured calcium carbonate deposition rates at the different salt contents: 47 g/L and 59 g/L of a seawater with pH of 9.1 and at tube surface temperature of 90 °C. The measurements indicated that the rate if scale deposition increases in seawater containing more dissolved solids at the same pH, tube exterior temperature and seawater temperature.
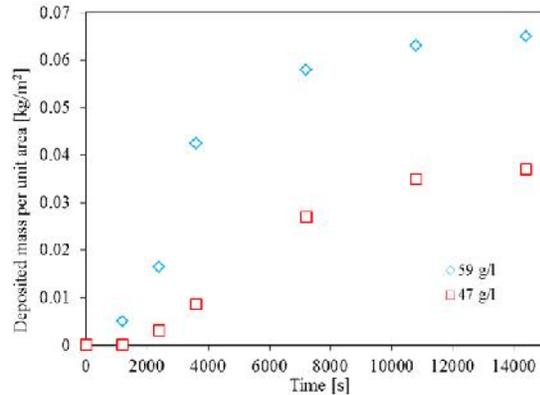
Fig. 8. The role of salt content (TDS) of seawater on the rate of scale layer formation. Tube exterior temperature = 90ºC. Seawater temperature = 50ºC. pH = 9.1

According to Figs. 6 and 7 both carbonate ions and scaling potential are enhanced at higher salts contents. Therefore higher supersaturation with respect to calcium carbonate is resulted (see Eq. (1)). The increased amounts of dissolved solids means presence of more calcium ions in seawater. Calcium ion concentration is the key parameter affecting the scale deposition rate. The supersaturation with respect to calcium carbonate increases as the concentration of dissolved calcium increases. In industrial multi effect distillers the salt content (TDS) of seawater is subjected to increasing due the loss of water while evaporating the seawater. This has a direct influence on the calcium ions concentration and therefore the rate of scale layer deposition will be influenced. In MED desalination units the lower tubes in the tube bundle is subjected to sever scaling problems more than the upper tubes due to the higher salt contents.

4.4. Effect of temperature on scale layer composition

The analysis of the deposited solid layer indicated that the calcium carbonate deposited as aragonite and the calcium sulphate precipitated as gypsum and additionally sodium chloride as halite. Gypsum and aragonite are the main scaling components that cause reduction of heat transfer rate and all the efforts focus on avoidance of its deposition on heat transfer tubes. The measured ratio of aragonite to gypsum (Wt. %) in the scale layer deposited from seawater of salt content 45 g/L at different surface tube temperatures are depicted in Fig. 9.
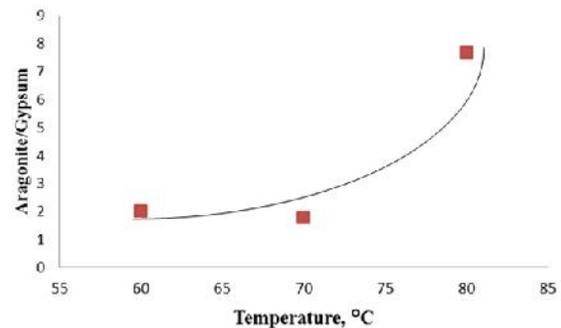
Fig. 9. Influence of Temperature on the scale layer ratio of Aragonite to Gypsum, S= 45 g/L.

As shown in Figure 9, the aragonite phase is dominant at higher temperatures, whereas. At lower temperatures, the ratio of aragonite to gypsum decreases. The results indicated that calcium carbonate is the main scaling component deposited at elevated temperatures whereas calcium sulphate deposited at lower temperatures. There are several forms of calcium carbonate scale such as calcite, vaterite, and aragonite. Each form varies The formation in its stability and solubility depending on the temperature pH, and salt composition. The precipitation of aragonite under the current conditions is attributed to the presence of magnesium ions. The ratio of magnesium to calcium has s great influence on the phase of calcium carbonate deposited. The synthetic seawater used in this study contains a Magnesium: Calcium ratio of 3.3:1 (see Table 1). It was reported [13] that a Magnesium: Calcium ratio greater than 3 will lead to the formation aragonite phase which is in good agreement with the obtained results

5. Conclusion

The way to prevent deposition of scaling materials on the exterior parts of tubes in multi effect distillers designed for seawater desalination processes is the better understanding the factors affecting the rate, type and the kinetics of scale layer formation. The results obtained indicated that the temperature, pH and salt content (TDS) of seawater are the operating conditions which required to be adjusted for controlling and minimizing the scale layer formation because these factors have a direct effect on the level of calcium carbonate supersaturation. It is recommended to conduct further kinetic studies to better recognize the role of pH and the presence of different types of ions on the kinetics of scale layer formation which may contribute in scale reduction and thus minimization the need to anti-scalants and chemicals which increase the cost of desalination and the environmental impacts of desalination industry.

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