

Fouling Crystallization in Seawater at Heat Exchangers - Study of the Solid Layer (Incrustation) Formation Processes-

Mazen N. Al-Amaireh

Tafila Technical University, P.O. Box. 179, Tafila 66110, Jordan

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The process of formation of scale layers on the outer surfaces of hot pipes at conditions similar to a MED evaporator is experimentally studied. The composition of the scales at the surface of the pipes was determined using XRD and SEM analysis. It has been clearly recognized that the increase in pH value of seawater will result in a strongly increased scaling of the tube surface. At pH = 8.5, the pipe surface was not homogeneous due to being covered by predominantly ball formed crystals which are mainly composed of CaCO_3 and NaCl. It has been found that there are dominantly single isolated crystals formed. In contrast to that with increasing pH level of the seawater up to pH=8.8, an increased homogenized scaling layer was found. An uniform adhesion of the scaling layer on the surface of the pipe was detected. Furthermore, there is a variation in the crystal structure which is reflected in the form and size of the crystals.

I. INTRODUCTION

The Multi Effect Distiller (MED) evaporation process, which uses the idea of heat transfer within a horizontal tube bundle arrangement, is one of the most commonly used methods for producing pure water from seawater. Scaling of the exterior heat transfer surfaces is a serious issue that could affect the MED units' economy, design, operation, and maintenance. The deposition of heat resistive materials on the outer surfaces of the tube bundles of MED evaporators causes a significant reduction in the plant's thermal efficiency of 25% or more [1]. Fouling causes a decrease in heat transfer in thermal seawater desalination MED facilities, and subsequently, an additional expenditures will be incurred because to the increased steam consumption.

The creation of scale layers is influenced by the distiller's working circumstances. The temperature of the heated surface, the temperature of seawater, the amount of CO_2 emitted, the salinity of seawater, and the pH value are the most critical factors influencing the pace of scale deposition.

The pH of saltwater has a significant impact on pipe incrustation due to fouling crystallization. In the carbonate system of seawater, the pH value is crucial. It has a considerable impact on the relative distribution of the total inorganic bounded carbon components CO_2 , HCO_3^- , and CO_3^{2-} . The mole ratio of CO_2 , HCO_3^- , and CO_3^{2-} of the total carbon content in seawater as a function of pH value of an artificial seawater with a salinity of 45 g/kg at a constant temperature of 24 °C is shown in Figure 1.

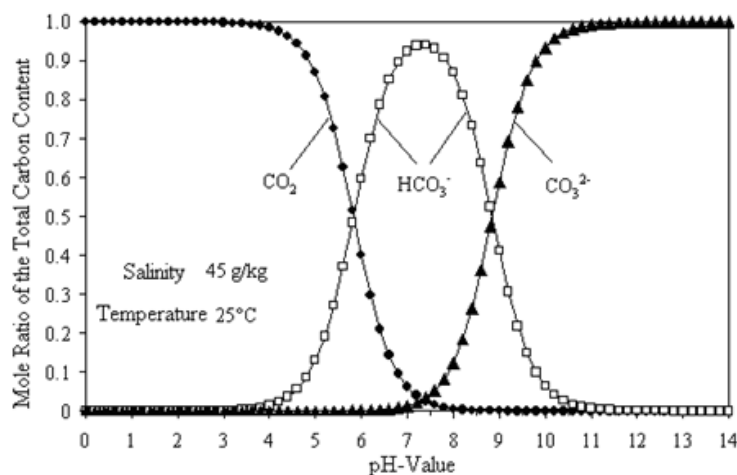


Figure 1: The mole ratio of total inorganic bounded carbon (CO_2 , HCO_3^- , and CO_3^{2-}) as a function of seawater pH [2].

Experiments on the effect of pH, temperature, and salinity on the composition of the scaling material deposited on the outer surface of hot pipes will be presented in this paper.

II. EXPERIMENTAL DETAILS

The flow chart for the rig that is used for crystallization studies using inversely soluble salts is shown in Figure 2. (e.g. CaCO₃, CaSO₄). In the experimental setup, the development of crystalline scales from falling films on horizontal tubes will be investigated. The rig's main body is made up of six horizontal tubes stacked one on top of the other (length: 250 mm, diameter: 33.7 mm). The first two tubes are used to homogenize the mixture. The first two tubes, constructed of acrylic plastic, homogenize the flow pattern, while the others, built of stainless steel, are heated by the heating fluid.

The trickling rate is controlled by the volume flow rate as the test solution is trickled onto the top tube. The solution flows back into the storage tank once it leaves the heating tube. Before being recirculates, a thermostat cools the test solution. The temperature of the heating fluid is controlled by a second thermostat. The temperature of the test solution is determined before it passes over the first tube (trickling temperature) and after leaving the heated tube (drain off temperature) (drain off temperature). The surface temperature of the heating tube is also kept track of. Throughout the studies, the heating fluid's inlet temperature, the trickling temperature of the test solution at the tube bank, and its volume flow rate are all kept constant.

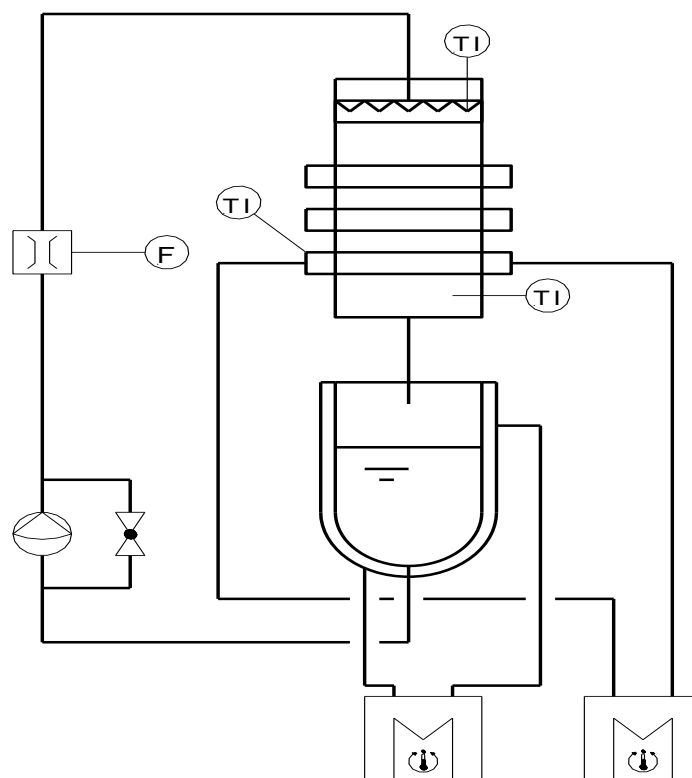


Figure 2. Schematic diagram of the experimental rig used to investigate the crystalline layer formation. (See e.g. [3])

III. RESULTS AND DISCUSSION

3.1 Effect of pH on Scale Layer Composition

In order to investigate the effect of the pH value and respectively the alkalinity of the seawater on the formation of scale layer processes, three experiments with a total duration of 50 hours in each case were carried out. A 10 wt.% Na₂CO₃ solution was used to increase the pH value of the solution. The experimental data and the respectively competed variables are summarized in table 1. In table 1 the gray colored values are related to the pH value of seawater which was adjusted before the start of the experiment. The other values in the same column represent the pH value which was measured during the runs (at 0 h, 24 h and 50 h) for the samples taken from the experimental rig. During the experiments the pH value changed only marginal. During a 50 hours run, a decrease in the total alkalinity was observed. The total alkalinity was decreased to about 35% of its initial

value in the first 24 hours of the run. On the average the alkalinity decreases about 25% of its initial value during a 50 hours run.

Table 1. Experimental data for the runs carried out in the experimental rig.

Experiment Number	t [h]	PH	Alkalinity
1		8.5	
	0	7.68	451.09
	24	7.41	183.67
	50	7.33	173.91
2		8.8	
	0	7.66	387.50
	24	7.58	125.00
	50	7.43	118.75
3		9.2	
	0	7.63	362.50
	24	7.79	118.75
	50	7.67	112.50

The outer surfaces of the pipes were analyzed using REM analysis. In the frame of this experiments the scaling layers were subjected to REM-analyses aiming to understand the scale layer formation process. This analysis was of importance in order to recognize the crystal structure and mineral composition of the scaling layer. The composition of the scales at the surface of the pipes was determined using XRD and REM analysis.

However, the measurements and the analysis results obtained are qualitative rather than quantitative. The components of scaling layer precipitated at pipes 1 to 6 of the experimental rig were analyzed by the XRD technique. The results are presented in table 2.

Table 2: A summary of the XRD-analysis results of the pipes 1 to 6

Pipe	CaSO ₄	KCl	CaCO ₃	MgCl ₂	Mg ₂ CO ₃	NaCl
1	•		•	•	•	•
2	•		•	•	•	•
3	•	•	•	•	•	•
4	•	•	•	•	•	•
5	•		•	•		•
6	•		•	•		•

In the REM analysis method which was used to analyze the outer surface of the samples of the pipes under investigation (#1 to 6), NaCl-, CaCO₃- as well as CaSO₄ was detected at all the six pipes. On the other hand, evidence was provided indicating the presence of MgCl₂ at the surface of all pipes under investigation. Furthermore, MgCl₂ and potassium incorporations as e.g. KCl were found at the pipes from #1 to 4.

At the pipes #2-4, additional traces of Iron, Chrome and Nickel were found. The appearance of this elements on the scaling layer is an evidence that corrosion of the pipe surface occurred since these elements constitute the material of construction of the pipes. A number of REM micrographs for the crystalline layer at the pipes is to be seen in figure 3. In the figure the single crystals formed as well as the crystal morphology can be identified. The number “1” in the photos in figure 3 refer to NaCl crystals. These crystals with large corners can be seen more clearly in both of the REM photos of experiment 3 (see figure 3).

It can be recognized, especially, in the REM photograph with scale 1000:1 that NaCl crystals exist in a layer of smaller crystals. A comparison among the REM photos presented in figure 3 for the runs 1-3, shows clearly that the increase in the pH value of seawater will result in a strong scaling of the pipe surface. At pH = 8.5 (experiment 1), the pipe surface is not homogeneous due to its coverage by predominantly ball formed crystals which are mainly composed of CaCO₃ and NaCl. It can also be seen that there are more single isolated crystals constructed. It can therefore be concluded from the REM micrographs that there are broken or not continuous areas within the scaling layers.

In contrast with increasing pH level of seawater up to pH=8.8 (experiment 2) an increased ratio of a homogenized scaling layer. This gives an indication of an uniform adhesion of the scaling layer on the surface of the pipe. Furthermore, there is a variation in the crystal morphology which is reflected in the form and size of the crystals.

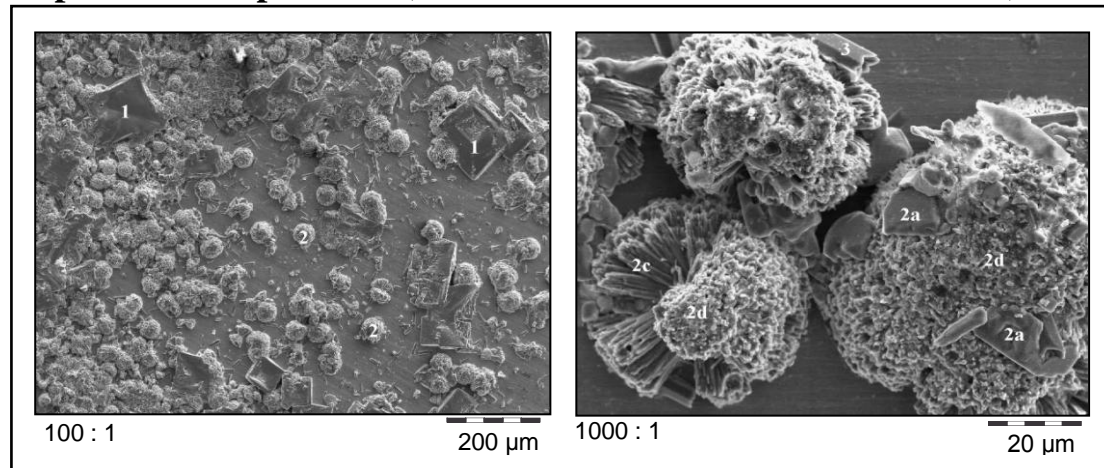
At a pH = 8.5, the surface of the pipe is predominantly covered by ball formed scaling crystals as well as scarcely rectangular scales structures, which are either large rectangular or smaller regular crystals. It is also noticeable from the REM micrographs that there is a needle form of the CaSO₄ crystals detectable. However, the area which was free from scaling materials is reduced.

An increase in the value to pH = 9.2 (experiment 3) leads to a virtually complete coverage of the surface of the pipe with small rectangular crystals.

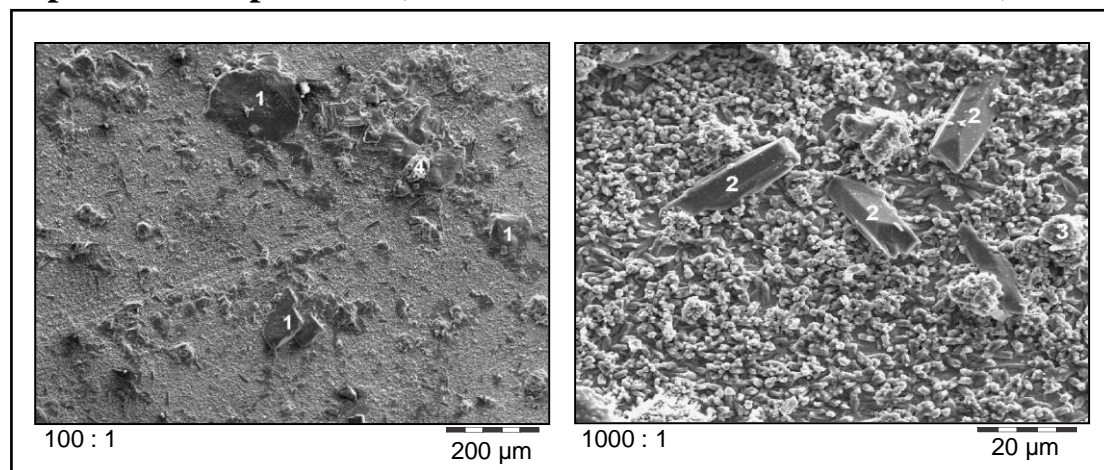
3.2 Effect of Salinity and Temperature on Solid phase Composition

Experiments with 50 hours duration were carried out using the experimental rig (see figure 2) at different temperatures and salinities. The crystalline layers were scratched off from pipe 4 at the end of each run and collected. The samples were then subjected to detailed XDR and optical analysis. The results are to be depicted in figure 4.

Experiment 1 / pH = 8.5 (Addition of 15ml 10 Wt.% Na_2CO_3 – Solution)



Experiment 2 / pH = 8.8 (Addition of 25ml 10 Wt.% Na_2CO_3 – Solution)



Experiment 3 / pH= 9.2 (Addition pf 35ml 10 Wt.% Na_2CO_3 – Solution)

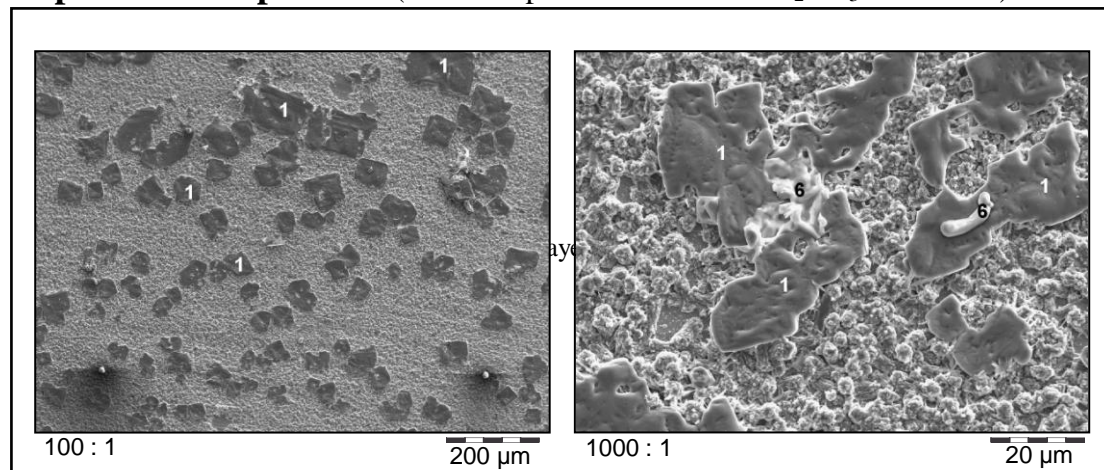


Fig. 3: REM micrographs for scaling layers deposited in the experiments 1-3.

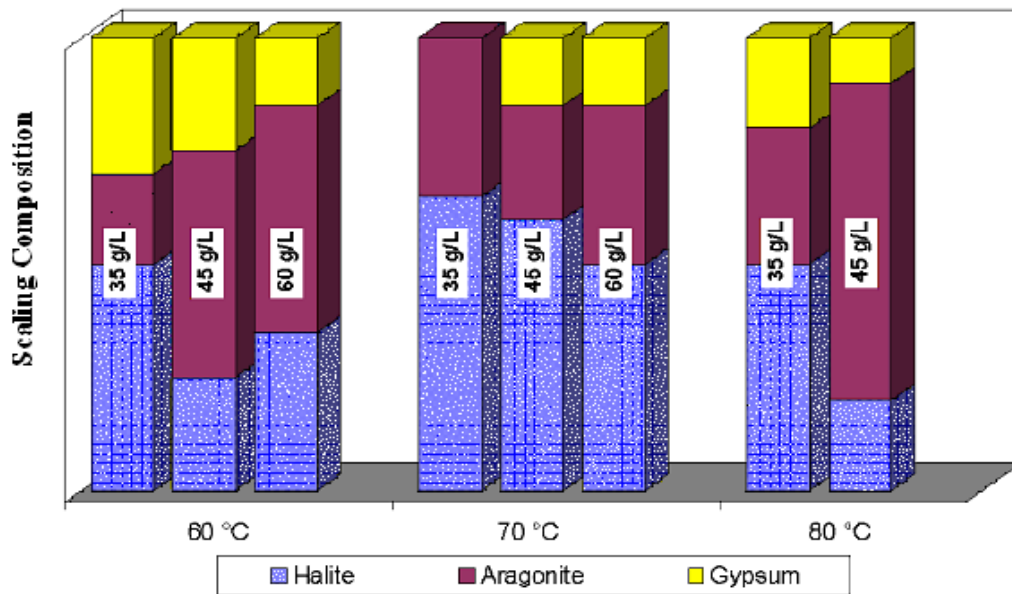


Fig. 4: The composition of the scale layer as a function of salinity and temperature.

As shown in figure 4, the aragonite phase is dominant at higher salinity and higher temperatures, whereas the halite phase is the dominant phase at intermediate temperatures and at all salinities. At lower temperatures, aragonite becomes more dominant as the salinity increases. However, gypsum phases exists in small amounts at all salinities and temperatures. The same results were reported by Hermersdorf [4].

IV. CONCLUSIONS

The XRD and REM analysis have shown that the main components of the scaling layer are calcium carbonate, calcium sulfate and sodium chloride. It can also be concluded that the addition of sodium carbonate can result in a strong accumulation of scales at the pipes. The composition of the scaling layer has not been changed by changing the pH level of seawater. As REM micrographs clearly display, there is a difference between the crystals in form and morphology. Hence, it can be concluded that the pH has a certain influence on the crystal structure in the seawater. Moreover, it can be noticed from the SEM micrographs of the scaling layers on the pipes that NaCl is not accumulated as scaling material but it is present only due to the fact of evaporation of the remaining moisture at the end of the experiment.

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