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STUDY OF CALCIUM CARBONATE DEPOSITION INSIDE A PLATE HEAT EXCHANGER

Karolyna Gomes dos Santos
Jean Izidoro da Silva
Gabriel Siqueira Machado
Juliana Ferreira Gonçalves
Juliana Braga Rodrigues Loureiro
Interdisciplinary Center for Fluid Dynamics (NIDF) – Federal University of Rio de Janeiro (UFRJ)
karolyna.gomes@mecanica.coppe.ufrj.br
j.izidoro@poli.ufrj.br
gabriel.machado@mecanica.coppe.ufrj.br
juliana.goncalves@nidf.ufrj.br
jbrloureiro@mecanica.coppe.ufrj.br

Abstract. *Scaling is a phenomenon that occurs in heat exchangers used in different industrial applications. This work has investigated the calcium carbonate ($CaCO_3$) scaling inside a plate heat exchange to understand the scaling formation and the characteristics of the deposits. Experiments were conductedusing a model M3-FG heat exchanger with 27 plates operating in countercurrent flow. Calcium chloride and sodium bicarbonate solutions were prepared in two 5 m^3 tanks and then mixed to form the calcium carbonate solution (cold fluid), while the hot fluid used was water at 80 ºC from an 8 m^3 tank heated by resistances. In this study, some parameters were varied, as experiment duration, flow rate and salt solution concentration. Pressure drop, temperature variation, overall heat transfer coefficient and scaling resistance are examples of data acquired during the tests. The scanning electron microscopy revealed aragonite and calcite deposits in the entrance and exit regions where the cold fluid circulated. The deposition rate of calcium carbonate was found to be nonlinear due to the complex interaction of ionic/particle deposition and removal caused by the shear flow. These results provide an important database for validation of physical models and numerical simulations for the prediction of the scaling phenomenon.*

Keywords: *Scaling, Calcium Carbonate, Heat Exchangers, Flow Loop.*

1. INTRODUCTION

Shah and Sekulic (2003) define heat exchangers as devices used to transfer thermal energy between two or more fluids, between a solid surface and a fluid or between solid particles and a fluid, at different temperatures and in thermal contact. Therefore, they are designed based on the identification of the amount of heat required, the fluid to be used, the possibility of equipment maintenance, among other variables. Widely used by industry, the plate heat exchanger is the focus of the present work. It is usually built by a sequence of thin plates, which can be smooth or rough.

The formation of scale deposits is a frequent phenomenon in heat exchangers used on oil platforms. One of the main scaling agents is calcium carbonate ($CaCO_3$). Its solubility is inversely proportional to temperature and this characteristic makes it susceptible to precipitation as the fluid temperature increases. In heat exchangers, the solid material is precipitated and deposited on the plate's surface, promoting a decrease in heat transfer and equipment efficiency (Kakac and Liu, 2002).

Sea water is used for operations with heat exchangers on oil platforms. Yang *et al.* (2016) explained that several ions are dissolved in this water, such as Mg^{2+} and Ca^{2+}, which are prone to become scaling agents as the experiments are carried out. The authors concluded that the type of incrustation of sea water in stainless steels is ruled by crystallization.

Berce *et al.* (2021) argued that scaling induces a reduction in overall heat transfer coefficient, changes in surface roughness of plates and substantial pressure drops in heat exchangers. There are some methodologies to mitigate the effects of incrustation, as increase the heat transfer area, clean breaks, apply fluid pre-treatment. However, they are costly and time consuming. The authors also commented the causes of scale: solubility affected by pH variation, mixture of solutions with different compositions, influence of temperature on the solubility of salts in solutions.

Hoang (2022) stated that the scaling formation requires the simultaneous occurrence of three factors: supersaturation, nucleation and adequate contact time, which are responsible for the precipitation of a crystalline substance from a solution.

According to Machado *et al.* (2022), there are six polymorphs of calcium carbonate, namely amorphous calcium carbonate (consideredthe least stable form compared to the others), calcium carbonate monohydrate, calcium carbonate hexahydrate (Ikaite), inaddition to aragonite, calcite and vaterite. Calcite is the stable form; vaterite and aragonite are metastable forms, while calcitemonohydrate, ikaite and the amorphous form are unstable. The author also pointed out that, according to the experiments performed, calcite was the predominant polymorph at 23 ºC, while aragonite was thermodynamically stabilized at temperatures above 42 ºC. The results corroborated with Carteret *et al.* (2009), which suggested that under ambient conditions, calcite is the most thermodynamically stable polymorph, followed by aragonite and vaterite.

Tai and Chen (1998) investigated the $CaCO_3$ polymorphism using the constant composition method. The authors reported a trend towards aragonite formation at higher temperatures and the appearanceof calcite throughout the aging process. The experiments carried out by the authors demonstrated that high purity calcites occurred in solutions with a pH greater than 12, while high purity vaterites occurred in solutions with a pH lower than 10. The maximum yield of aragonite was observed in solutions with pH 11. In addition, the presence of magnesium and manganese ions was identified as a factor that favors the formation of both aragonite and calcite, depending on the operating conditions. The effects of supersaturation and saturation ratio were considered less significantcompared to the effects of pH and temperature of the solution, which were identified as the most important parameters.

Andritsos and Karabelas (2003) evaluated $CaCO_3$ scaling in a plate-type heat exchanger in the presence of added particulates under isothermal conditions. The presence of aragonite particles significantly increased the deposited mass and induced the appearance of scaling at low supersaturation values. Results with calcite and titanium dioxide particles (TiO_2) did not cause a significant increase in scale formation; however, these particles tended to affect the morphology of the deposit and reduced its strength.

Lee *et al.* (2014) evaluated the scaling resistance in a plate-type heat exchanger from the experiments varying the concentration of $CaSO_4$ (salt with solubility inversely proportional to temperature), plate undulation angle, flow velocity and fluid inlet temperatures. The results showed severe scaling near the gasket due to the stagnant flow in this region.The scale thickness increased in the fluid exit region. The scaling resistance curves showed an asymptotically increasing behavior over time.

It is known that the phenomenon of calcium carbonate scaling in heat exchangers is still a subject that needs further study. Therefore, experiments were conducted on a plate heat exchanger of the model Alfa Laval M3-FG that contains 27 corrugated plates with holes for the passage of the mixture of salts and heated water and gaskets that promote the sealing and direction of the fluid. This selected exchanger operates in countercurrent flow and the heat transfer process is by indirect contact. The motivation of this study is to understand the calcium carbonate scaling with the objective of providing preventive measures to mitigate the problem.

2. EXPERIMENTAL METHODOLOGY

2.1 Experimental Apparatus

Two different 5 m^3 tanks were utilized to prepare and store the 30 mM sodium bicarbonate and 11,2 mM calcium chloride. One 8 m^3 tank was used to heat water up to 353 K through electric resistances. The flow configuration performed was the countercurrent, i.e., the mixture of salts and the heated water entered in the heat exchanger through opposite inlets. The schematic representation of the experimental bench is presented in Figure 1.

The heated water was conducted to the heat exchanger through a centrifugal pump and the saline solutions by two different positive displacement pumps. The flowrate of heated water was measured by a Coriollis flow meter and for the saline solutions an electromagnetic flow meter was used. A differential pressure gauge and four PT-100 3-wire thermoresistors were used to measure pressure and temperature, respectively. Downstream of the heat exchanger, the heated water returned to the heated tank, while the calcium carbonate solution was directed for a discharge tank.

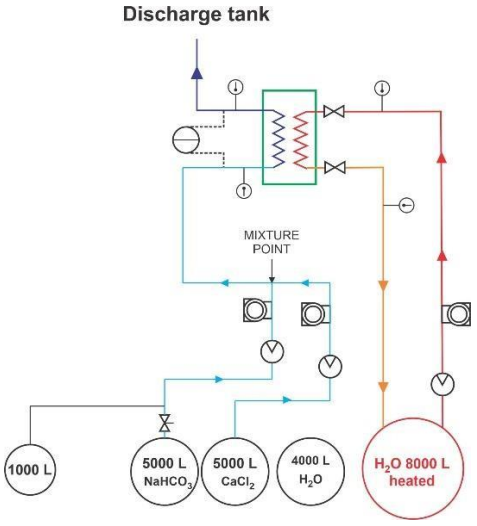

Figure 1. The experimental setup used in the tests.

2.2 Measurement techniques

Thermowells were placed in the connections used to acquire the inlet and outlet temperatures of the mixture of solutions, as can be seen at Figure 2a. Two test sections (rings) were positioned at the inlet and outlet regions of the connections, as shown in Figure 2b, with the objective of collecting solid samples for scanning electron microscopy (SEM) analysis. The equipment used was TM 4000 plus model using the backscattered image. And the material deposited over the surface of the plate was removed and analyzed in an x-ray diffractometer (XRD) model D2 PHASER. Both techniques are used to identify the crystalline structure of the calcium carbonate generated in tests.

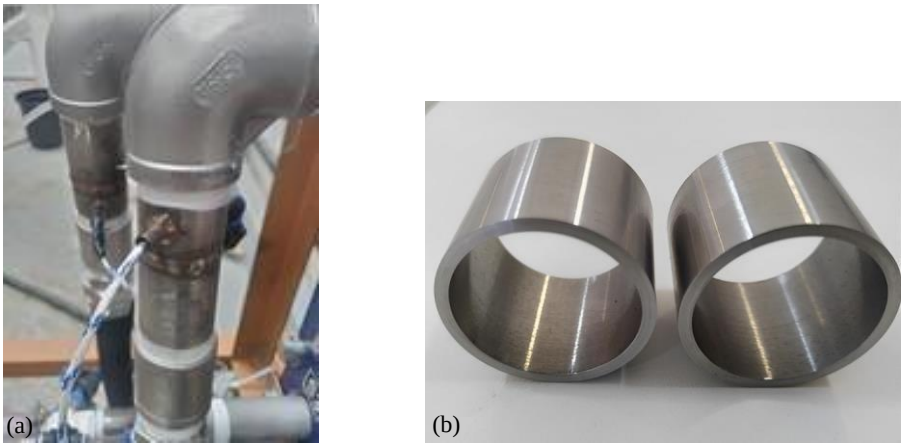

Figure 2. The thermowell configuration (a) and SEM rings (b) used in the heat exchanger.

2.3 Experimental Conditions

Four experiments were carried out using the mixture of saline solutions injected into the heat exchanger at room temperature. Experiments 1a and 1b lasted 7.200 seconds each. In both experiments, the temperature of the mixture of solutions at the time of entry was 23 ºC, with a kinematic viscosity of 9,3456 10^{-7} m^2/s. At the exit, the temperature was 73 ºC, with a kinematic viscosity of 3,98142 10^{-7} m^2/s. Experiment 2a was carried out in 14.400 seconds, with inlet, outlet and kinematic viscosity values equal to the previous experiments. For experiment 2b the temperature of the mixture of solutions in the inlet region was 28 ºC, with a kinematic viscosity value of 8,356 10^{-7} m^2/s. In the exit region, the temperature of the mixture of solutions was 66 ºC, with a kinematic viscosity value of 4,360 10^{-7} m^2/s. The Reynolds number of the experiments was calculated using the Equation 1.

$$Re = \frac{V \times D}{v} \tag{1}$$

where V is the flow velocity, D is the inlet diameter and v is the kinematic viscosity. For all experiments, the velocity and diameter values are the same: 0,444 m/s and 0,02185 m, respectively. In experiments 1a, 1b and 2a, it was observed that the Reynolds number value for a temperature of 23 ºC was 10.382, while for a temperature of 73 ºC, the value was 24.413. In experiment 2b, the Reynolds number was 11.610 at a temperature of 28 ºC and 22.249 at a temperature of 66 ºC.

The saturation ratio (SR) values were obtained through the thermodynamic commercial software called *ScaleSim*. The software was supplied with the ionic concentrations of the prepared solutions, as well as the pressure and temperature conditions, in order to derive these values. Consequently, the software returned data regarding the resulting solution derived from the mixture.

For experiment 1a, 1b, and 2a, the inlet of the exchanger yielded a SR value of 40.320, while the outlet exhibited 54.491. In experiment 2b, a SR of 41.961 was observed at the inlet and 49.086 at the outlet.

3. RESULTS

3.1 ΔP and ΔT

As the $CaCO_3$ deposited in the heat transfer area, there was a decrease in the flow passage area and, consequently, an increase in pressure value. The presence of the scaling reduced the heat transfer between the liquid and the plate surface, which also resulted in the decrease of the temperature variation during the test. Experiments 1a and 1b were carried out under identical conditions and both showed the same trend for pressure drop values and temperature variation. The experiment 2a was carried out under the same conditions, except for the duration of the experiment, which was 14.400 seconds – twice the time of the experiments 1 and 2. When comparing the experiments with different time intervals, the three tests presented the same trend, as shown in Figure 3.

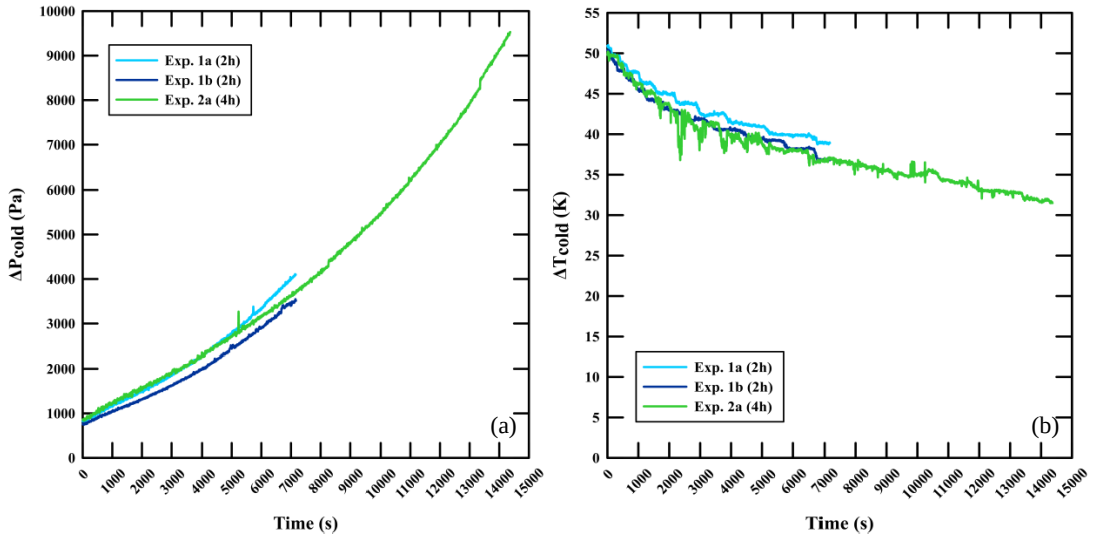

Figure 3. Temporal evolution of ΔP_{cold} (a) and ΔT_{cold} (b) for the present experiments.

3.2 Logarithmic Mean Temperature Difference (LMTD) and Overall Heat Transfer Coefficient (U)

The *LMTD* and *U* are parameters that provide information about the heat transfer between the hot and cold fluids. Figure 4 shows the decrease of both parameters along the experiments. This behavior represents the decrease in heat transfer along the experiment, due to the presence of $CaCO_3$ scaling.

3.3 Scanning Electron Microscope (SEM) and X-Ray Diffractometer (XRD)

XRD samples for the entrance region indicated predominant presence of calcite and for the exit region the predominant polymorph was aragonite. The results corroborate those obtained in the SEM analysis. Figure 5 demonstrates the polymorphs obtained in the input region (23 ºC) and output region (73 ºC).

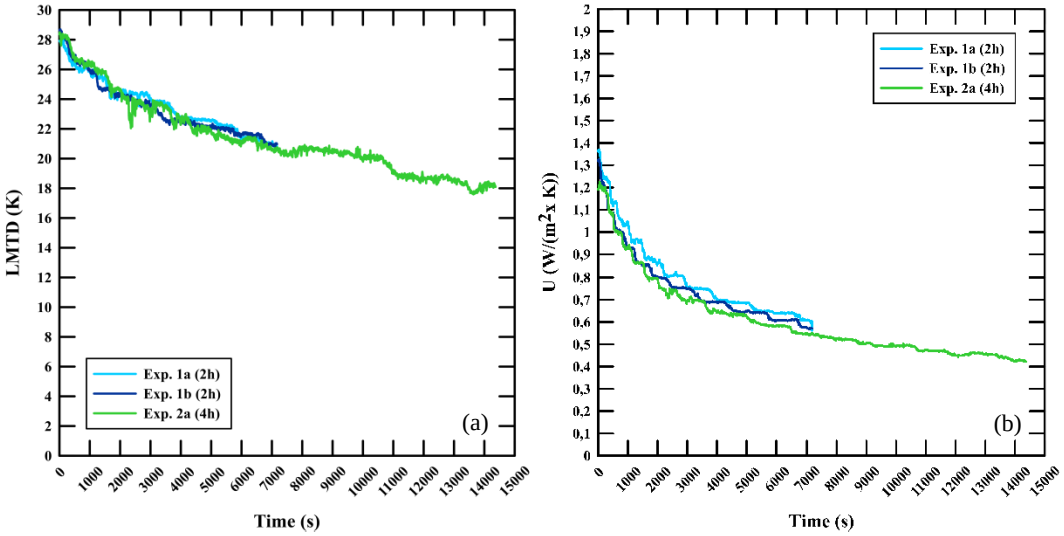

Figure 4. Graphs of time *vs.* LMTD (a) and time *vs.* U (b) obtained for the experiments.

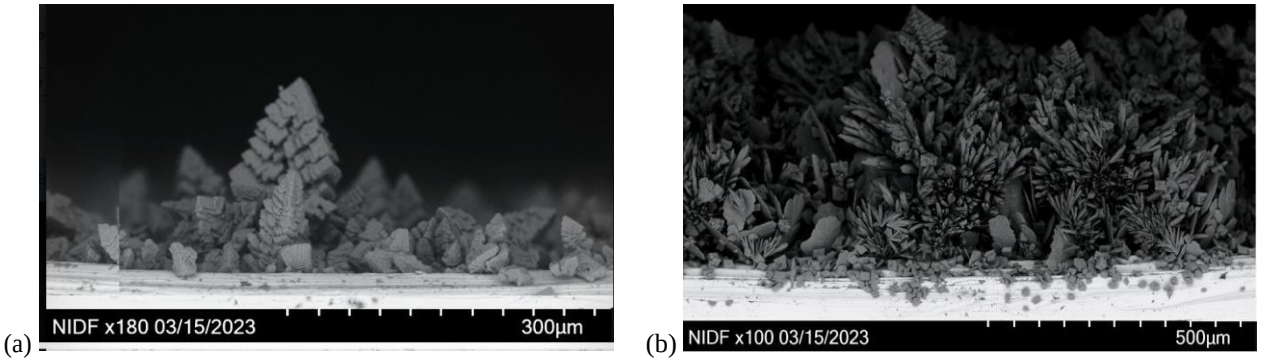

Figure 5. Crystalline structures found in the inlet (a) and outlet (b) of the heat exchanger.

As the calcium carbonate solution flowed through the plate surface, the scaling thickness increased. The difference of deposition thickness can be seen in Figure 6. The larger quantity of deposited $CaCO_3$ in the outlet of the plate is due to the entrance of the hot fluid in the neighboring plate. For XRD, samples were collected from the inlet and outlet regions of the plates, as demonstrated in the Figure. 6.

Figure 7 shows the micrography of the sample from the plate outlet and it is clear to note the presence of aragonite, the same crystalline structure shown in Figure 5b.

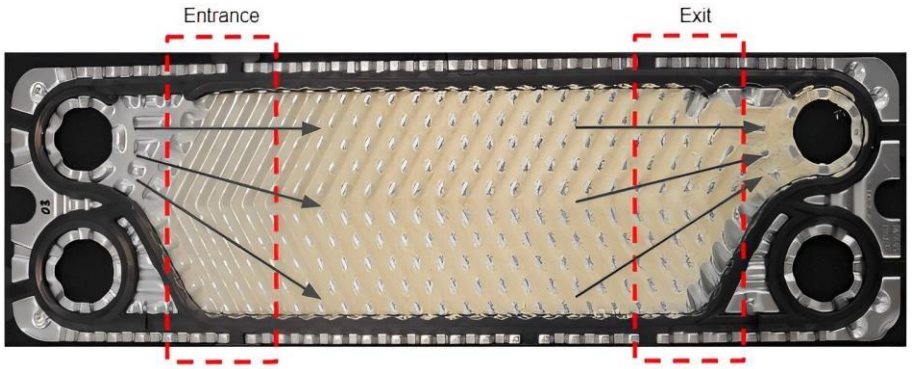

Figure 6. Regions where samples for XRD analysis were obtained through mechanical removal (scraping).

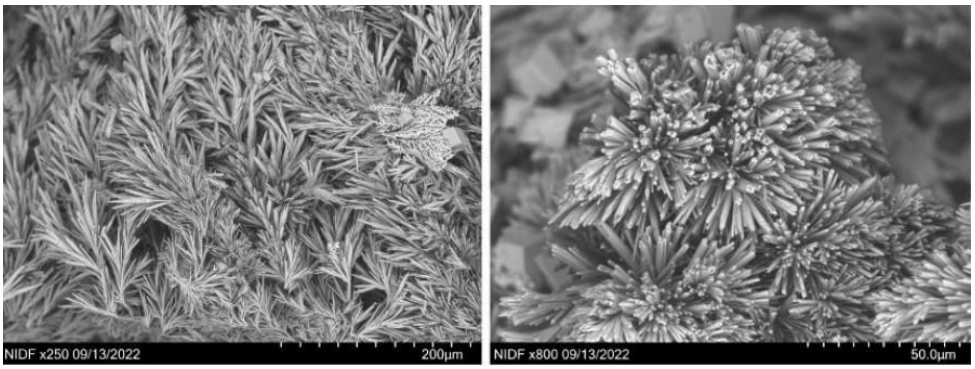

Figure 7. Aragonite obtained in the outlet region of the plates, which the temperature was 73 ºC.

The results of SEM and XRD analysis were very relevant to corroborate the influence of the temperature on crystal structure of calcium carbonate formed inside the heat exchanger.

3.4 Deposited mass and Deposition Rate

The deposited mass in each channel was obtained through gravimetric measurement. The values are indicated in Table 1.

Table 1. Value of deposited mass in each channel of heat exchanger.

	Deposited mass per channel (10^{-3} Kg)						
	Channel 1	Channel 2	Channel 3	Channel 4	Channel 5	Channel 6	Channel 7
Exp. 1a	9,436	8,894	8,653	7,377	7,03	7,011	7,341
Exp. 1b	8,880	8,727	8,826	7,262	7,151	7,471	7,028
Exp. 2a	20,175	20,278	20,259	17,551	17,538	18,043	17,869
Exp. 2b	20,224	19,912	20,222	17,435	17,389	17,64	17,38
	Channel 8	Channel 9	Channel 10	Channel 11	Channel 12	Channel 13	
Exp. 1a	7,122	6,659	6,705	6,608	6,232	2,682	
Exp. 1b	7,227	7,197	7,037	8,386	6,44	3,298	
Exp. 2a	17,274	16,739	17,056	17,008	16,417	10,546	
Exp. 2b	18,116	17,207	17,379	17,206	16,29	11,159	

From the data of Table 1, it is noted that, although the time used in experiments 2a and 2b was twice the time used in experiments 1a and 1b, the values of the deposited mass did not increase proportionately.
With the purpose of establishing the normalization of the values corresponding to the deposited mass, a parameter designated as deposition rate (δ) was evaluated, as explained by Machado (2023). The equation for the deposition rate can be seen in Equation 2.

$$\delta = \frac{m_{Ca}}{A \times \Delta t \times \dot{m}_{Ca^{2+}}} \tag{2}$$

where m_{Ca} is the calcium mass injected inside the heat exchanger [kg], A is the deposition area [m^2], Δt is the test duration [s], $\dot{m}_{Ca2+}$ is the mass flow rate of the calcium ion [kg/s].

In Figure 8, it can be observed that the experiments with the same time interval presented curves with similar behavior.

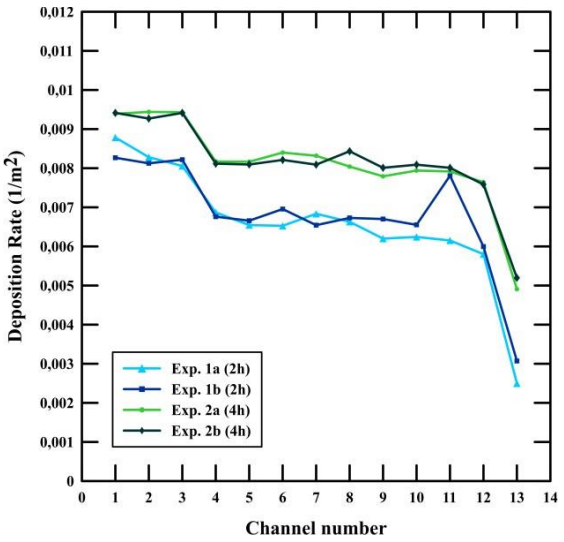

Figure 8. Deposition rate of the $CaCO_3$ per number of channel.

Comparing the values of the deposition rate between the experiments, a similarity in the deposition patterns can be observed between experiments 1a and 1b. Additionally, when comparing experiments 2a and 2b, the deposition patterns are similar, as shown in Figure 8.

As shown in Figure 8, an increase in the experiment time results in an increase of the deposition rate. This occurs because, as the deposition takes place, the characteristic flow passage area decreases and the plate roughness increases, resulting in a higher deposition rate over time.

The deposition rate is higher in the first three channels, probably due to the higher saturation index of the solution in the inlet. As the scale occurs and the deposition takes place, the saturation of the flowing fluid decreases, resulting in the constant deposition rate observed between plates 4 to 10. At the outlet, the temperature of the brine is smaller, which favors a further decrease in the saturation index and a reduced deposition rate at the outlet.

4. CONCLUSIONS

The high temperature inside the heat exchanger induced a higher amount of deposited mass of calcium carbonate and consequently, there was an increase in pressure and a decrease in heat exchange efficiency with the test duration. The SEM and XRD results showed the change of the $CaCO_3$ crystalline structure on the surface of the plates, where calcite is present in the inlet and aragonite, at the outlet. When the test duration was doubled, it was noted that both the deposited mass and the deposition rate increased, but not proportionally with the time.

5. ACKNOWLEDGEMENTS

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