

# The Effect of Citric Acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>) and Flow Rate to the Growth and Transformation of Crystal Phase of CaCO<sub>3</sub>

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**Abstract**— Scale formation, especially of calcium carbonate (CaCO<sub>3</sub>) is a serious problem faced by many industrial processes, such as chemical, desalination and oil industries. This paper discusses crystallization scaling of CaCO<sub>3</sub> in pipes. The crystallizing solution was made by mixing equimolar solution of CaCl<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub>. The parameters studied were the solution flow rates 40mL/min, temperature (30, 40, 50°C) and citric acid (0.00, 5.00, 10.00 ppm) as additives for the scaling inhibition. The CaCO<sub>3</sub> scale formation process has monitored the change of conductivity the solution out of coupons. The scale formed was characterized by SEM, EDS and XRD. This conductivity decline period, known as induction time varied from 30 min to 46 min depending on the parameters studied. Higher flow rates and temperature resulted in more CaCO<sub>3</sub> scale mass, indicating that these two variables may promote CaCO<sub>3</sub> crystallization. The higher citric acid concentrations resulted in less mass of the scale and could reduce the mass down to 88%. Therefore, it can be postulated that citric acid may be an effective additive for CaCO<sub>3</sub> crystallization and scaling. SEM and EDS analysis of the scale indicates that the scale was essentially CaCO<sub>3</sub>. In addition, an XRD test was applied to the scale and proved that the scale consisted of calcite, vaterite and aragonite phases. The scale formed under the influence of citric acid and temperature showed more aragonite phase, indicating that the acid could delay the transformation of CaCO<sub>3</sub> crystals into the ultimate stable phase, i.e. calcite.

**Keywords**—component; CaCO<sub>3</sub> scaling; flow rate; temperature; citric acid; induction time; crystal phase.

## I. INTRODUCTION

Scale formation especially the calcium carbonate scale (CaCO<sub>3</sub>) is a serious problem faced by many industrial processes, such as desalination, chemical industry and oil industry [1]. The scale causes serious problems such as narrowing of the diameter of pipes and reducing of heat transfer [2].

CaCO<sub>3</sub> scale consist of CaCO<sub>3</sub> crystals which exist in three polymorph: calcite (rhombohedral), vaterite (ball irregular) and aragonite (flower shape), with calcite the most stable form [3, 4]. Other two forms (vaterite and aragonite) are given a suitable condition, so they become calcite. The presence of certain compounds, e.g. antiscalants can slow down the transformation

of calcium carbonate into the more stable calcite [5,6]. This transformation will affect the growth process of the scale [7].

The study of CaCO<sub>3</sub> scale is always related to the crystallization that is affected by some factors, such as fluid flow rate, temperature, and additive [8]. Additive has been studied to identify its effect to the scale formation, for example organic acid such as malic acid [9].

This paper discusses a research of CaCO<sub>3</sub> scaling in pipes with laminar flow rates of 40 mL/min. Other variables studied were temperature (30, 40, 50°C) and citric acid (0.00, 5.00 and 10.00 ppm) as an additive.

## II. MATERIAL AND METHODS

### A. CaCO<sub>3</sub> scale formation

In this study, scale formation solution is prepared to use CaCl<sub>2</sub> (p.a.) and Na<sub>2</sub>CO<sub>3</sub> (p.a.) in equimolar. Citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>) as additive is expected to be able to inhibit the scaling. Additive is added to the solution in ppm. The crystallization reaction in calcium carbonate scale is expressed as follows (1) :



The concentration of CaCl<sub>2</sub> solution is 3500 ppm Ca<sup>2+</sup>. The CaCl<sub>2</sub> solution was made by dissolving CaCl<sub>2</sub> crystal in distilled water on room temperature. Na<sub>2</sub>CO<sub>3</sub> is prepared in the same way. Citric acid crystal as additive (5.00 and 10.00 ppm) is added to CaCl<sub>2</sub> solution.

The The experiment rig is shown in Figure 1. Five liters of CaCl<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> is added to each vessel (1) and (2). Two pumps (5) and (6) are used to deliver the solution to the vessel (3) and (4). Both solutions are put in the coupon house (7) that is filled with five copper coupons. Both solutions are expected to react in the coupons (that are specially designed for CaCO<sub>3</sub> scale formation). The conductivity of solution that goes out from the coupon is observed by the conductivity meter for three hours until the end of the experiment. In the end of experiment, coupon and ship pipe (3 and 4) is disconnected for one hour. After that, the coupon is taken out of the coupon house and dried in the oven with temperature of 80°C for one hour. After the coupon is cool, it is weighed to identify the

difference of coupon's weight before and after the experiment. The difference is the scale mass

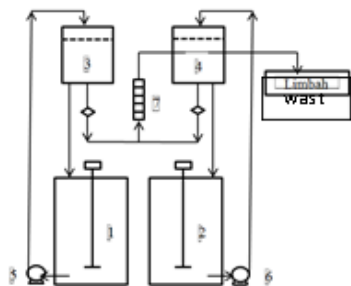


Fig. 1. Scheme Equipment of CaCO<sub>3</sub> Scale Formation

The induction time is determined by recording the solution conductivity that is out from the coupon. The solution conductivity is noted every two minutes (first hour), every six minutes (second hours) and fifteen minutes (third hours). This method has been widely applied to monitor the nucleation and organic mineral crystal growth. The end of induction period is marked by the sudden reduction of solution conductivity value. This shows that a big amount of ion forming the crystal starts leave the solution to form its first crystal.

### B. Characterization of CaCO<sub>3</sub> Scale

CaCO<sub>3</sub> scale is characterized by SEM, EDS, and XRD. SEM test machine has been integrated with EDS test, SEM and EDS tests are administered to determine crystal morphology and chemical composition of each formed scale. XRD test is done to determine the crystal phase from the formed scale. The scanning parameter that is chosen for the observation is 10-90°, 2θ, 0.020 steps, 15 s/step. The obtained data is compared to the ratio of PC-based searching data basis program. Fullpro software is employed to detect the likeliness of crystal phase in the sample. In this approach, the peak position is automatized by minima diffraction in the second derivation of diffraction tracing. The peak position and height is checked to XRD standard for CaCO<sub>3</sub>.

## III. RESULTS AND DISCUSSION

The CaCO<sub>3</sub> scale was constantly formed and stick to the coupon wall during the three-hour experiment. The mass scale result depended on the test parameter variation (temperature and citric acid concentration). It could be seen from the conductivity measure as follows.

### A. Induction time

The experiment showed the reaction between CaCl<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> solutions that could be seen from the reducing conductivity of solution coming out from the coupon. The conductivity was stable in the beginning and suddenly fell down. The time between solutions mixing to reduce the conductivity varied according to the observed parameter. This time interval was typically called induction time.

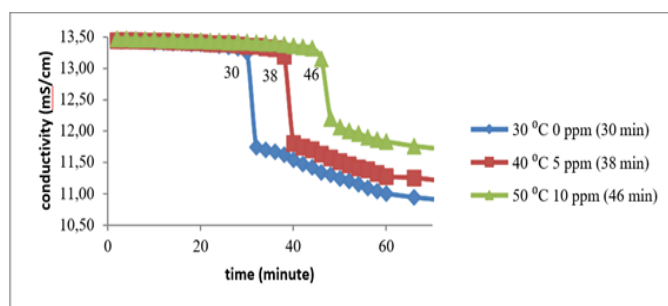


Fig. 2. Plot of conductivity versus first hour of scaling time at flow rate 40 mL/min.

### B. Temperature and Additive of Solution

This experiment used flow rate of 40 mL/min and variations of temperature (30, 40, 50°C), citric acid concentrations (0.00, 5.00, 10.00 ppm) as an additive. The stable solution concentration was maintained at 3500 ppm Ca<sub>2</sub><sup>+</sup> which meant constant stirring in all experiments. The experiment has been done with laminar flow rate (Reynolds number, NRE ± 180). CaCO<sub>3</sub> scale was formed in the surface of coupon's inner part. Table 1 showed the research parameter variation, induction time, and formed scale mass.

It was found out that the induction time and scale mass were affected by the absence of presence of citric acid. The absence of citric acid caused short induction time, and more scale mass was formed. In the other hand, he higher the citric acid concentration, the longer the induction time, and less formed scale mass. This was because of the interference activity of citric acid molecule in the formation of CaCO<sub>3</sub> crystal, so the scale formation was obstructed.

In Table 1 test parameter number 1 and 2, it was displayed that the scale mass reduced 0.0777 grams (50.49%). However, higher nitric acid concentration was added, so the formed scale mass reduced. According to Table 1 in test parameter number 2 and 3, the scale mass reduced 0.0581 grams (76.25%). This was due to the fact that more core crystal was obstructed to reach the critical measurement, so the amount of crystal mass reduced and the following mass production scale also reduced.

TABLE I. EXPERIMENT PARAMETERS

NO	Flow Rates (ml/minute)	Temperature (°C)	Citric acid (ppm)	induction time (minute)	Mass of Crystal (gram)
1	40	30	0	30	0,1539
2	40	40	5	38	0,0762
3	40	50	10	46	0,0181

Temperature also affected the morphology of CaCO<sub>3</sub> scale in the temperature of <30°C which was pure amorf CaCO<sub>3</sub> (ACC). It would transform into temporary vaterite in the temperature of ≥40°C. Pure ACC would transform into aragonite through valerite [7].

### C. Characterization of the scale

The morphology of CaCO<sub>3</sub> crystal could be examined by using SEM machine. It was displayed in Figure 3. CaCO<sub>3</sub> stage

could be seen by using XRD machine that was presented in Figure 5. In Figure 3, it was shown the clear difference of the formation of  $\text{CaCO}_3$  crystal. In the temperature of  $30^\circ\text{C}$ , there was no citric acid (Fig 3.a), crystal was formed particularly vaterite (irregular ball), and there was little calcite (rhombohedral). However, the presence of citric acid 5.00 and 10.00 ppm in the temperature of  $40^\circ\text{C}$  and  $50^\circ\text{C}$  (Fig 3.b and Fig 3.c) dominated the formed aragonite crystal (flower shape), little vaterite (irregular ball) and calcite.

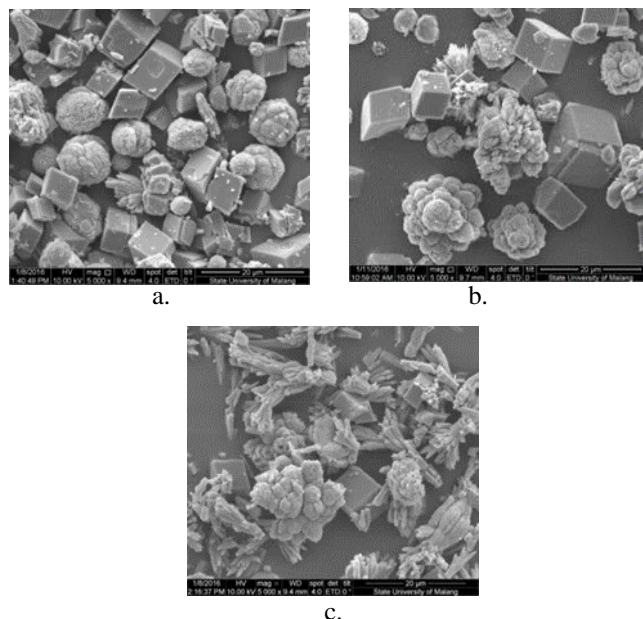


Fig. 3. Morphology  $\text{CaCO}_3$  crystals at 40 mL/min (a). absence of citric acid at  $30^\circ\text{C}$ , (b). presence of citric acid 5 ppm at  $40^\circ\text{C}$ , and (c). presence of citric acid 10 ppm  $50^\circ\text{C}$ .

The citric acid in the high temperature could be used to transform the morphology of vaterite crystal into aragonite. It could be concluded that citric acid was highly effective to transform the morphology of  $\text{CaCO}_3$  crystal.

The chemical composition of  $\text{CaCO}_3$  crystal could be examined by using EDS machine. The result of EDS for  $\text{CaCO}_3$  sample was that the presence of crystal in 10.00 pp, nitric acid. The percentage sample of weigh (% Wt) was as follows: Ca = 49.87% Wt, C = 09.24% Wt, and O = 40.17% Wt. The difference between the actual and theoretical weigh percentage (% Wt) was as follow: Ca = 8.0 – 9.0% Wt, C = 2.0 – 3.0% Wt, and O = 7.0 – 8.0% Wt. The EDS analysis could be made from the formed  $\text{CaCO}_3$  scale because the proportion of every percent of Ca, C, and O weigh showed the approach of 1:1:3.

XRD analysis was done to determine the formed crystal phase by comparing the experiment data and basis data (JCPDS). The result of XRD test was lines (peak). Figure 5 below showed the direct experiment of formed crystal phase with the absence of citric acid in the temperature of  $30^\circ\text{C}$  and presence of citric acid (5.00 and 10.00 ppm) in the temperature of (40 and  $50^\circ\text{C}$ ).

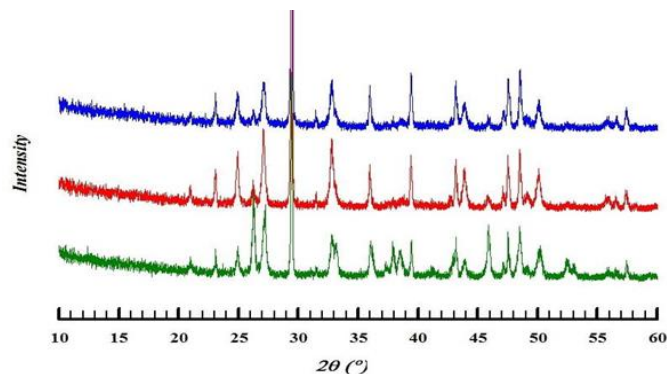


Fig. 4. XRD analysis in the absence of citric acid at  $30^\circ\text{C}$  (above), presence of citric acid 5.00 ppm at  $40^\circ\text{C}$  (middle) and presence of citric acid 10.00 ppm at  $50^\circ\text{C}$  (below). Peak given the symbol V: vaterite, C: calcite and A: aragonite.

The Absence of citric acid at  $30^\circ\text{C}$  in Figure 4 (above side) detected vaterite and calcite with the strongest peak at  $27.03^\circ 2\theta$  (PDF # 96-901-5899) and  $29.38^\circ 2\theta$  (PDF # 96-210-0993). It was in accordance with SEM analysis in Figure 3.a. The presence of citric acid 5.00 ppm at  $40^\circ\text{C}$  in Figure 4 (middle) shows the crystal phase vaterite transformed into aragonite, calcite whereas there (JCPDS - PDF # 96-500-0086). It was in accordance with SEM analysis in Figure 3.b. The presence of citric acid 10.00 ppm at  $50^\circ\text{C}$  in Figure 4 (below) shows the crystal phase vaterite transformed into aragonite, calcite whereas there (JCPDS - PDF # 96-500-0086). It was in accordance with SEM analysis in Figure 3.c.

At  $\geq 40^\circ\text{C}$  the first phase is formed by mixing the calcium chloride and sodium carbonate saline solution, the ACC results in the coupon and in just a few minutes the aragonite phase. The rapid changes similar to the findings of [10] subsequently aragonite transformed into calcite (the most thermodynamically stable polymorph) within a few hours. Overall XRD analysis of the crystals of the scale was obtained in accordance with the powder diffraction data for calcium carbonate.

#### IV. CONCLUSION

The experiment of calcium carbonate ( $\text{CaCO}_3$ ) scale formation with parameters flow rate 40 mL/min, variation of temperature (30, 40,  $50^\circ\text{C}$ ) and citric acid concentrations (0.00, 5.00, 10.00 ppm) were conducted.

The parameters of solution, temperature and citric acid greatly influence the formation of scale  $\text{CaCO}_3$  in the pipe. One of the negative effects on induction time is temperature, the induction time is affected by citric acid. Short. induction times are affected by higher temperatures. Short induction time for higher temperature is caused by more scale formation component that is able to react to form the scale. On the other hand, the higher the citric acid concentration, the longer the induction time. This is because of the interference activity of nitric acid molecule in the formation of  $\text{CaCO}_3$  crystal, thus, the scale formation is obstructed.

Citric acid in ppm amount and temperature are identified to be able to transform the crystal phase of  $\text{CaCO}_3$  (vaterite to aragonite).  $\text{CaCO}_3$  scale formation with the absence of nitric

acid in the temperature of 30°C produces vaterite phase (irregular ball) and little calcite phase (rhombic). The presence of nitric acid (5.00 and 10.00 ppm) in the temperature of 40°C and 50°C produces aragonite phase (flower shape), little vaterite and calcite.

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