Calcium Carbonate (CaCO$_3$) Scale Formation in A Piping System With Laminar Flow With Varied Temperatures and Malic Acid (C$_4$H$_6$O$_5$) As Additives

Muhammad Usamah$^1$, Muhammad Rizal$^2$

$^1$Faculty of Engineering, University of Muhammadiyah North Maluku, Ternate 97726, Indonesia
$^2$Faculty of Engineering, University of Khairun Ternate, Indonesia

email: musamah80@yahoo.co.id ; adam.rizal@yahoo.co.id

Abstract. Scale formation is a frequent problem encountered in industrial piping system. The occurrence of the scale is due to a chemical reaction between the dissolved ions in water. Calcium carbonate (CaCO$_3$) is one of the scale that is often found. Scaling will thicken the pipe walls and can affect the rate of low or heat transfer. Hence preventing to the growth of scales is necessary in pipe. In this study some experiments were conducted on the growth of the scale of calcium carbonate in a test pipes, by reacting solution of CaCl$_2$ and Na$_2$CO$_3$ each with a Ca$^{2+}$ concentration of 3500 ppm with a flow rate of 30ml/min and temperatures used were 25$^\circ$C, 30$^\circ$C and 40$^\circ$C. Malic acid(C$_4$H$_6$O$_5$) was added to the solution as additive with concentrations of 0, 3, and 5 ppm. Calcium carbonate crystals could be seen from the results omorphological studies conducted using Scanning Electron Microscopy (SEM). The SEM results indicate that at 25$^\circ$C and without additives, the scale comprises of calcite and vaterite, whereas with the additive of 5 ppm malic acid, the scale is vaterite with the larger crystal size and there is also calcite, but phase of the vaterite is dominant. At 40$^\circ$C and without additive the crystal of a aragonite resembles a pile of needles.

Keywords : CaCO$_3$, temperature, malic acid, scale

1. Introduction
The crust is a hard deposit of inorganic compounds, it mostly occurs on the surface of the heat exchanger equipment caused by deposition of the mineral particles in the water (A Bhatia, 2003). The cause of the formation of a crust of sediment in the pipes in the industry is there is crust-forming compounds in water with the amount exceeding the solubility equilibrium on the State so formed crystals. The crystals will decrease the diameter and inhibit the flow of the fluid in the pipe system. Disruption of the flow of the fluid causes the higher pressure so that the possibility of damage to pipes (Asnawati, 2001). With the rising temperatures then the calcium carbonate dissolves the less. So the rate of precipitation at temperatures 65$^\circ$C higher than the temperature 30$^\circ$C, because one of the increases of the kinetic of crystallization and the reduced solution of calcium carbon at higher temperatures (Grases et al, 2007).

The current water treatment and the prevention of the formation of the crust is generally done chemically as ion exchanger resin and the addition of an inhibitor of the crust. This chemical method
can change the chemical properties of the solution so that it is not safe enough for use in households and the food industry. In addition the investment is large enough to result in those processes is only suitable for industries that require large amounts of processed water (Kozicdkk, 2003).

Using Malic acid as an additive, where research is done from 40 mm without additives to Malic acid. Indicate that Malic acid increases affect the formation of Crystal morphology and size (Mao and Huang, 2007).

On the 500 C temperature increase rate time deposit on the solution of CaCO3, and indicates that the Crystal structure changes as a function of time at the surface. On the early existence of the observed Crystal aragonit, calcite and vaterit simultaneously on the surface of the metal. While at room temperature showed aragonit seldom formed, whereas calcite formed at any conditions (Gabrielli, 1999).

This paper aims to find out the mechanism of the formation of a crust of CaCO3 in the laminar flow with pipe, and the influence of temperature is 40°C, and the addition of Malic acid additive.

2. Methodology

Research conducted to investigate the formation of a crust on the pipe band, with a laminar reacting solution of CaCl2 and Na2CO3, and Malic acid as an additive. To make the solution of CaCl2 concentration calculation done and Na2CO3 aqueous solution with a flow rate of 30 ml/min. Then prepare a coupon or pipe test, where the amount of the coupon there are four pairs, with a length of 30 mm, outer diameter 18 mm and an inside diameter of 12.5 mm. Speed the flow leaving the coupon right fit design that is 30 ml/min. This testing is done by calculating the standard deviation of the flow, thus a tool created to have a stable flow rate. Conductivitymeter is used to measure the conductivity of the solution. The accuracy of this instrumentation can be tested by doing the measurements against the conductivity of aquades. Fig 1 is a research tool.

![Figure 1. Picture of research tools](image)

Flow speed of I and II vessels should be uniform. This can be observed through the channel level controller. When a second vessel, the level is always the same then the flow velocity are both the same. Setting the price difference in height between IE Δh surface solution on vessel III and IV against the sewage flow rate regulator as tested by trial and error. SEM test and testing can be done on one micro analysing instruments using SEM-EDX. SEM done testing to study the morphology of crystals while testing micro analyser aims to find out the composition of the Crystal and XRD test to prove that the crust of the results of the research it's downright crust Calcium Carbonat (CaCO3). Data
retrieval is done by as much as nine times that is composed of three attempts for the formation of a crust without additives, a three-time experiment for the formation of a crust with additive C4H6O5 3 ppm, a three-time experiment for the formation of a crust with additives C4H6O5 5 ppm. First solution of CaCl2 incorporated a number of five liters in the next vessel I inserted into the vessel of Na2CO3 aqueous II five litres. After that the pump is switched on and ride solution fill to the upper limit of the vessel III and IV and the vessel immediately then the pump is turned off. A few moments later the pump is switched on and the solution begins to fill in the coupon and thus the experiment has begun. Registrar at the same time also enabled where every two minutes once the measurement has to be done against the conductivity of the solution. Measurement of the conductivity of a solution to conduct sewage the solution coming out of smaller vessels on accommodated coupons made of plastic and conductivitymeter electrode may soon be included. Conductivitymeter will measure the value of the conductivity of the solution so that the digital readout starts from zero rises steadily until it finally stopped. This last figure is recorded. So this is done repeatedly restarted every two minutes. After four hours of time then the pump is stopped and a detachable coupon towards the channel. An hour later a coupon taken from home coupons and dried in an oven with a temperature of 60°C for six hours. Weighing the mass of the crust is done at the time the crust still sticking on the coupon.

3. Result and discussion

3.1. Induction Time

Induction time is the time needed by the ions in the solution to react so that forms the core of the first crystal. The methods used to determine the length of time the induction is by measuring the conductivity of the solution out of the test pipe. The end of the induction time is shown by the sudden decline of the conductivity of the solution, which means a number of Crystal-forming ions have left the solution to form crystals on the walls of the pipe. Induction time is calculated from the start ions reactions forming calcium carbonate until the conductivity of the solution down.

3.2. Induction time to experiment on temperature 25°C

Induction time on trial with temperature 25°C with three variations of additives can be seen in Fig 2. below.

![Figure 2. The relationship time and conductivity to the three additive variations on 25°C temperature](image-url)

In Fig 2, it is seen that for calcium carbonate crust formation experiments on temperature 25°C with three different variations (0, 3 and 5 ppm) indicate that to experiment with three variations of the induction time additives obtained under 45 minutes. Induction time for each time the experiment is not the same, if the additive is added with different concentration of induction time will change. Thus the third graph of induction time to room temperature (25°C), and three variations of additives indicates
that the concentration of additives can affect the time induction for the influence of temperature against time induction can be known by making the graph of the relationship between the temperature of the induction time, as shown in Fig 2.

3.3. Induction time to experiment the temperature of 40°C

Induction time on trial with temperature 40°C with three variations of the additives can be seen on the graph of the relationship between time with the conductivity as shown in Fig 3.

![Figure 3](image-url)

Figure 3. The relationship time and conductivity to the three additive variations on temperature 40°C

Fig 3 shows that the induction time to experiment the formation of calcium carbonate crust on temperature 40°C with three different additive variation shows that the induction time obtained under 30 minutes. Induction time happens on three variations of additives on temperature 40°C showed the difference between induction. Thus, the addition of the concentration of additive with different concentration can affect the conductivity. A third of the graphic above shows that rising temperatures lead to increased conductivity of reaction and going down quickly, so the free ion is reduced.

The graph happens to experiment with temperature 25°C has a similar pattern with charts on the experiment with the temperature of 30°C and graphs on an experiment with temperature 40°C. Hence, the process of crystal formation on three experiments are almost the same.

3.4. Influence of Temperature against time Induction

The influence of temperature against time induction can be known by making a graph with time-temperature relationship of induction in the produce on each experiment as shown in Picture 4.

Figure 4 shows the formation of calcium carbonate crust without additives a rise in temperature of 25°C become 30°C decreases induction time of 28.56% and the increase in temperature of 25°C became 40°C lowering induction time of 58.14%. Crust-forming experiments on calcium carbonate (CaCO3) with a temperature rise of 3 ppm additives from 25°C become 30°C decreases induction time of 22.14% and the increase in temperature of 25°C became 40°C lose time induction of 50%.

Experiment with additive 5 ppm, it increases in temperature of 25°C becoming 30°C and decreases induction time of 28.56% and the increase in temperature of 25°C became 40°C lose time induction of 42.67%.
Figure 4. The Relationship between temperature with induction time with three variations of the additive.

3.5. influence of Additive with respect to time of induction

Figure 5. Relationship between the time and the conductivity for the three variations of the additive on temperature 25°C

From Fig 5 looks that the graph happens to experiment with temperature 25°C with additives and without additives have the same shape. For the influence of additive with respect to time of induction can be known by making a graph of the relationship between the concentration of induction time as shown in Fig 6.

From Fig 6, it is seen that the experiment on temperature 25°C, in an experiment without the induction additive time is 24 hours, time of induction to experiment with additive 3 ppm is 32 minutes and experiment with additive 5 ppm induction time is 40 minutes. Induction time for each time the experiment is not the same, if the additive is added with different concentration of induction time will change. The graph of these three all showed that the higher the concentration of the additive (0 ppm – 5 ppm) the induction longer.
3.6. Influence of temperature against the masses of Crust
From experiments with temperature 25°C, 30°C and 40°C and the addition of the additive 0 ppm (without additives), 3 ppm and 5 ppm, can be made a graph of the relationship between the temperature of the mass with the crust such as picture 4.6.

3.7. The morphology of crust
The study of morphology, conducted with the aim to identify whether the Crystal experiment results actually crystals of calcium carbonate. To find out the shape of the crystals used Electron Microscopy Scanning tool (SEM) with a specific enlargement so that it can be identified if the Crystal is happening actually crystals of calcium carbonate. Scanning Electron Microscopy of results (SEM) of Crystal experiment results shown in Figure 8 and 9.
The crust of CaCO₃ alone has three different forms that will determine the type of crust formation, then these three types of CaCO₃ crystals of calcite, i.e. aragonit and vaterit. From the pictures the results of SEM in mind that forms crystals experiment results in Figure 4.8 and 4.9 was the hallmark of the Crystal forms of calcium carbonate. This is in accordance with previous studies (Qingfeng, et al., 2010).

Figure 8. The results of SEM calcium carbonate crystals experiment results of temperature 25°C, Ca²⁺ concentration of 3500 ppm, (a) without additives, enlargement 3000x enlargement, (b) 3000x, with additive 5 ppm,

Figure 8 shows the results of a test particle SEM CaCO₃ at temperature 25°C with no additive (0 ppm) and additive 5 ppm with 3000 times enlargement. Fig 8 (a) with the enlargement of the 3000x, is the result of a test particle in experiments with temperature 25°C without additives. In the picture it looks that this type of Crystal that forms is calcite and vaterit. In Fig 8 (b) with the enlargement of the 3000x is the result of a test particle with additive 5 ppm, in fig 8. (b) shows that there is a change in the form of crystals CaCO₃, at magnification 3000x, vaterit Crystal form that is visible to resemble flower (flower-like), and there is also a form of calcite crystals, but vaterit is the most widely established.

Figure 9. The results of SEM calcium carbonate Crystals experiment results of temperature 40°C, Ca²⁺ concentration of 3500 ppm, (a) without additives, enlargement of 3000x, (b) and 5 ppm 3000x magnification additive.

Fig 9 shows the results of a test particle SEM CaCO₃ temperature 40°C experiment with 3000 times. Fig 9 (a) is the result of test on temperature of 40°C without additives. In the picture it looks that this type of crystals that are formed in the form of a collection needle that is the type of aragonite. From these results it can be known that temperature can also change the shape of the crystals CaCO₃. While in Fig 9 (b) and additive 5 ppm, indicating that the changes which the Crystal magnification 3000 times seen that there is a change in Crystal form.
4. Conclusion
A strong influence of temperature against time induction, i.e. when temperature rise induction time will fall, meaning that rising temperatures will accelerate the formation of the Crystal core. Malic Acid additives (C4H6O5) was able to extend the time of the induction, which means it is able to inhibit the formation of the Crystal core. When the additive is added the more induction time also the longer, meaning that the process of the formation of the Crystal core becomes slower.

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