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**QUANTITATIVE ANALYSIS OF AMORPHOUS CALCIUM  
 CARBONATE PRECIPITATE WITH THE PRESENCE OF  
 ALUMINA IN THE FLOW WATER**

S. Raharjo

University of Muhammadiyah Semarang, Jl. Kedungmundu Raya No.18, Semarang 50273, Central Java Indonesia

\*Corresponding author email : samraharjo2@gmail.com

**Abstract**

Scale of calcium carbonate deposited on the pipe wall was investigated in the present study. In the experimental work, the scale-forming solution was prepared by mixing equimolar solutions of CaCl<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub>. The alumina was selected to inhibit the crystal growth. The scale growth was continuously observed by measuring the conductivity of the solution coming out of the pipe. Scale formed was then evaluated using SEM/EDX analysis. The result showed that the scale has a plate like morphology and the crystalline phase of the scale was found to be mostly calcite. The presence of alumina seems to change the morphology of the crystals from calcite into vaterite and aragonite amorphous.

*Keywords: simulator scale, calcium carbonate, alumina, amorphous*

**1. Introduction**

Calcite (CaCO<sub>3</sub>) is a mineral of calcium carbonate, which is slightly soluble in water and ground water. It can be formed in certain industrial applications, namely, in the evaporator and cooling power plants. The presence of this mineral can make significant problem because it can precipitate and clog the pipe. Principally, the formation of calcium carbonate scale is influenced by many factors such as the concentration of solution, pH value, temperature, pressures, and ionic strength [1].

In general, calcium carbonate can be precipitated from the saline water upon heating and there are three polymorphs namely calcite, vaterite, aragonite. Aragonite and vaterite is the most stable phase in lower temperatures, while calcite is commonly formed at higher temperatures [2]. The scaling formation is actually the crystallization phenomenon. Bulk crystallization arises when crystal particles are formed in the bulk phase through homogeneous crystallization and deposit on membrane surfaces as sediments/particles to form a cake layer that leads to flux decline [3]. In addition, supersaturated scale forming conditions leads to scale growth and agglomeration [4]. This is due to the random collision of ions with particles and secondary crystallization occurs on the surface of these foreign bodies present in the bulk phase [5].

Further, formation of calcium carbonate scale was determined by flow rate (Bahadori, 2010). In laminar flow, the higher flow rates lead the more calcium carbonate scale mass to be deposited indicating that the increasing fluid flow raises the volume flow rates [2]. A previous study by Gourdon, [6] have shown that the scale formation can be found in fully laminar and turbulent flow. In full laminar flow, the crystal growth of deposit is found at a slow rate, while in fully turbulent the deposit was increasingly grown with the increasing mass flow rate [7]. In general, the scale growth rate does not follow linear with time, as higher velocity can sometimes lead to reduce scale deposition [8]. Moreover, crystallization due to the lateral growth of the scale deposit on the membrane surface may result in flux declining and surface blockage [9].

A method to prevent the formation of the CaCO<sub>3</sub> scale in the pipe may use chemical inhibitors, which can control the crystal growth, and change morphology [10]. The presence of inhibitors into a solution may continuously control the process of nucleation and crystal growth occurring on the surface of a growing crystal. The use of tailor-made additives may help to examine the variety of processes regarding to crystal nucleation and growth, interaction with growth environment and crystal polymorphism.

The additive used in the research with alumina is an oxide alloy which reacts with scale of calcium carbonate and form alumina foam. Alumina from is alloy with high porosity [11] and Akhyari, et.al [12] explained the calcium carbonate can transform into efficient foaming agent to produce alumina foam with closed cell. The lowest density was achieved at the addition of CaCO<sub>3</sub> within 4 %. While the energy absorption increased at the same time with the relative density.

One study Wang et al., [13] has suggested that calcite forms through nonclassical nucleation via an amorphous calcium carbonate intermediate. While another study suggested that calcite forms not through amorphous precursors but through the initial precipitation of nanocrystalline vaterite, aragonite particles that

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self-assemble into larger calcite crystals through oriented attachment.

This paper presents a study on the CaCO<sub>3</sub> scale formation on pipe with laminar flow. The variable processes investigated were: temperature (30, 40, 50, 60°C) and the concentration of alumina additives 20%. The scale deposits were then characterised by SEM/EDX for morphology and chemical elemental analysis.

## 2. Methods

### 2.1 Materials and equipment

The powder precursor used for the preparation of the crystal forming solution were CaCl<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> with the analytical grade. The alumina (Al<sub>2</sub>O<sub>3</sub>) with analytical grade was added in the solution in an amount of 5%, 10%, and 20%. The CaCO<sub>3</sub> forming scale was grown using the pilot-scale equipment shown in Figure 1.

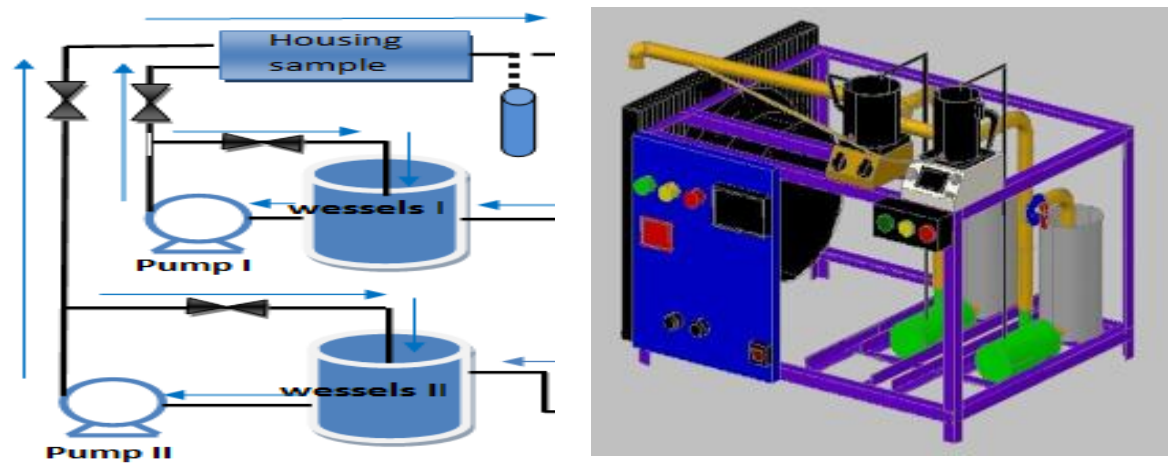


Figure 1: Experimental setup used in the CaCO<sub>3</sub> precipitation

### 2.2 Experimental method of the scale formation

For the crystallization experiment, five liters of equimolar CaCl<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> were prepared in the glass beaker. This experiment was performed in the same method which was proposed by Muryanto et al [14], by dissolving the CaCl<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> powder with the Ca<sup>2+</sup> concentration of 3000 ppm. The solutions at predetermined concentrations were separately placed in the two vessels and equilibrated until the designated temperature was reached. Subsequently, the amount of alumina additive was dissolved in a vessel containing five liters of solution CaCl<sub>2</sub>, then stirred at 200 rpm until it was well mixed.

The conductivity of the liquor exiting the test pipe section was continuously checked for up to 2 hours. The scale deposited on the surface of the coupons was carefully removed and stored in vials for subsequent characterization.

### 2.3 Characterization of precipitates

The characterization of the precipitating scales was conducted by scanning electron microscopy (SEM-analysis), equipped with EDX for morphology. For the SEM observation, the powder crystals were mounted on a circular metallic precipitate holder and finally sputtered with gold.

## 3. Results

### 3.1 Effect of temperature on the mass scale produced

The mass scale deposited in pipes during the experiment was given in Figure 2. It shows that the increasing temperature made the scale deposition rate increased. The temperatures (30, 40, 50, 60°C) have a strong effect on increasing the mass scales of CaCO<sub>3</sub>. The mass scales of CaCO<sub>3</sub> were produced respectively 13 mg, 28 mg, 49 mg and 80 mg at temperature 30°C, 40°C, 50°C and 60°C. The results were in agreement with the previous finding indicating that the increasing temperature leads to increasing mass flow rate of scale [14][15].

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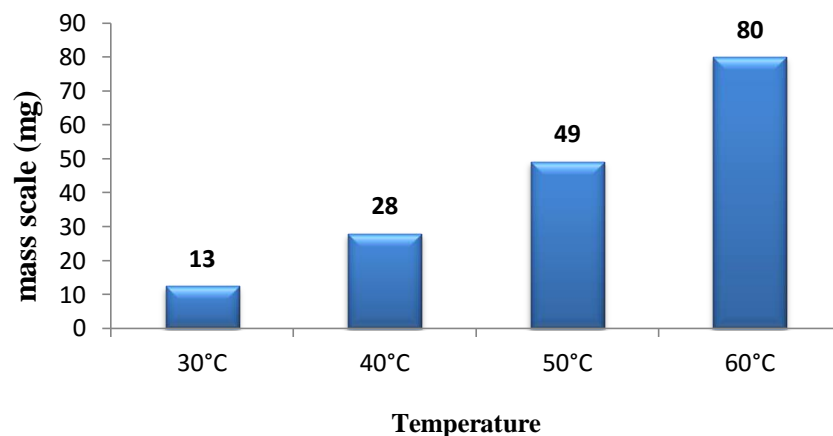


Figure 2. Effect of temperature on the resulting mass scale in pipes

### 3.2 The influence of alumina additive in the formation of CaCO<sub>3</sub> scale

The experimental result of alumina addition to the mass of scale produced are presented in Figure 3. Testing variable concentrations of alumina 20% showed a proportional decrease in the mass scales with increasing additive concentration. The mass scales obtained in the without alumina was 12.65 mg of CaCO<sub>3</sub>. Similarly provided 2.145 mg of mass scale was found in the presence of 20% Alumina. Clearly the alumina additive may be used to improve the scale produced [16][17].

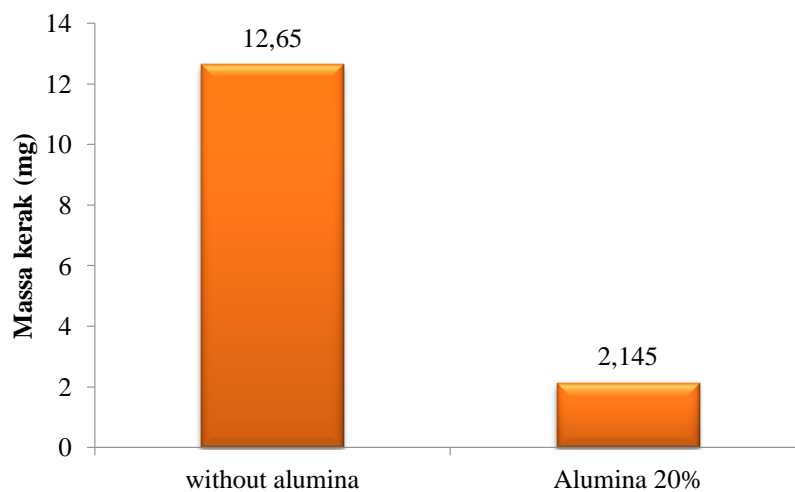


Figure 3. Effect of the alumina on the mass scale produced

### 3.3 Determination of induction time during the precipitation of calcium carbonate

The addition of alumina 20% resulted in increasing induction time of crystallization (Fig. 4). The induction time was observed in the CaCO<sub>3</sub> system in the presence of 20% alumina (32min) led to an induction time four times greater than that for in the absence of alumina system (23 min).



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concluded, its scale really crystal CaCO<sub>3</sub>.

In the presence of alumina (Fig. 5b), according to theoretical calculations on the percentage of weight of CaCO<sub>3</sub> Ca content should be 40%, while the results of the analysis of micro Ca content = 35.75% so as to have difference of 4.25%. For levels of carbon (C) shall be 12 wt % while result of analysis of micro C 39.21% of micro analysis results that have a irregular shape. micro direct 18.01 % so as to have difference of 45.99%. From the analysis of SEM-EDX test is concluded, its scale really crystal CaCO<sub>3</sub>.

Based on morphology testing it is found the scale crystal phase formulated with out alumina addition was calcite as indicated by cubical morphology ( Figure 5a). In figure 5b, it was recorded the additional of alumina influence in thin 20%. Scale crystal phase reduced into smaller size and irregular shape. The effect of scale crystal phase was the increase number of vaterite and aragonite. Those vaterite and aragonite phases was called amorphous phase. It was happened because alumina can react with calcium carbonate crystal which form alumina foam [19][20].

With the use of XRD diffractograms analysis can also prove that the scale formed is calcite. XRD results show the experiment at a rate of 30 ml/min in the absense and presence of additives citric acid. There are similarities in the position of the highest intensity at an angle 2θ. The XRD results for the difference was not significant.

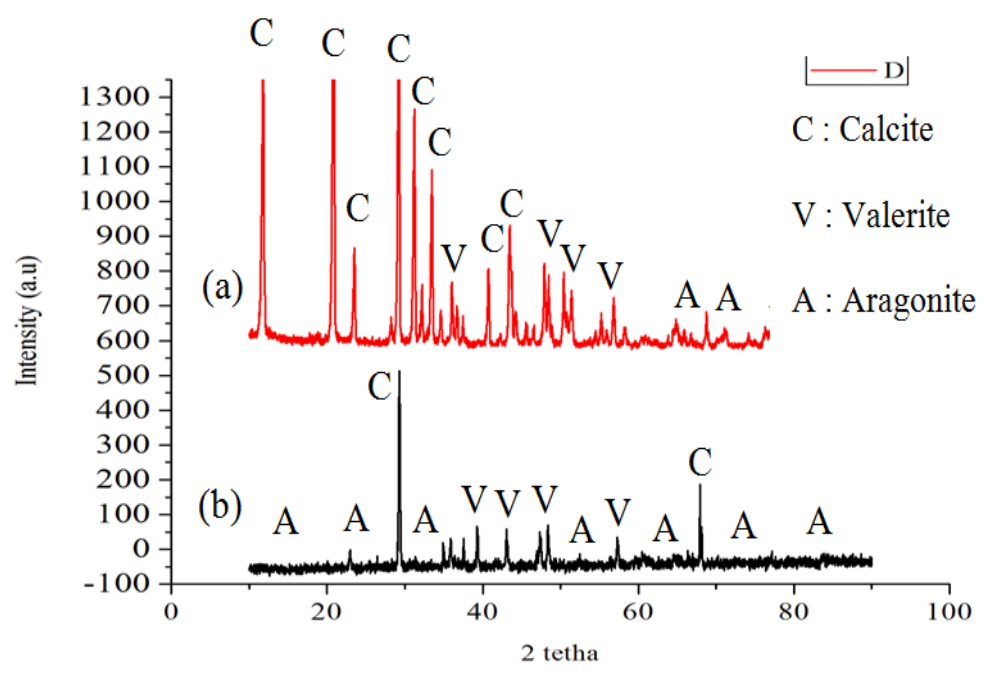


Figure 7. X-ray diffractograms of samples obtained from the scale synthesis, (a) without additive, (b) with alumina.

#### 4. Conclusions

It was found that in all experiments, the conductivity decreased abruptly after a certain induction period. The higher temperature produced, the more mass of the scale obtained indicating that the increasing temperature promoted the scale formation. SEM observation of the scale shown crystals with plate-like morphology obtained without alumina. This crystal changed to the round shaped morphology in the presence of alumina. The addition of alumina seemed to change the crystal morphology, which shows the possibility of alumina adsorption occurred on the surface of the crystal.

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