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by Samsudi Raharjo

Submission date: 01-May-2020 10:02AM (UTC+0700)

Submission ID: 1312788513

File name: 3._Controlling_of_Calcium_Carbonate_Scale_Deposition__2.pdf (1.02M)

Word count: 2506

Character count: 13405

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To cite this article: S Raharjo *et al* 2019 *J. Phys.: Conf. Ser.* **1150** 012058

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Controlling of Calcium Carbonate Scale Deposition on the Piping System with Laminar Flow and in the Presence of Citric Acids

S Raharjo^{1,3}, S Muryanto², J Jamari³, A P Bayuseno^{3*}

¹Departement of Mechanical Engineering, Muhammadiyah University in Semarang, Indonesia

²Departement of Chemical Engineering, UNTAG University in Semarang, Semarang Indonesia

³Departement of Mechanical Engineering, Diponegoro University, Semarang Indonesia

E-mail address: *samraharjo2@gmail.com; apbayuseno@gmail.com

Abstract. Scale of calcium carbonate deposited on the pipe wall was investigated in the present study. The presence of scaling inside pipes is serious problems in industries which increase maintenance cost. In the experimental work, the scale-forming solution was prepared by mixing equimolar solutions of CaCl_2 and Na_2CO_3 with a concentration of 3,000 ppm of Ca^{2+} . The solution flew in the pipe at laminar mode at temperature: 30, 40, 50 and 60°C. Other parameters selected in this experiment were the addition of additives : citric acid ($\text{C}_6\text{H}_8\text{O}_7$) with concentration of 5 ppm, 10 ppm and 20 ppm. The citric acid 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. It was found that in all the 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. Scale formed was then evaluated using SEM/EDX and XRD 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 citric acid seems to change the morphology of the crystals.

1. Introduction

Calcite (CaCO_3) 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, valerite, aragonite. Aragonite and vaterite is the most stable phase in lower temperatures, while calcite is commonly formed at higher temperatures [2]. The scaling

* A P Bayuseno

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 [6]. 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 (2011) [7] 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 [8]. In general, the scale growth rate does not follow linear with time, higher velocity can sometimes lead to reduce scale deposition [9]. Moreover, crystallization due to the lateral growth of the scale deposit on the membrane surface may result in flux declining and surface blockage [10].

A method to prevent the formation of the CaCO_3 scale in the pipe may use chemical inhibitors, which can control the crystal growth, and change morphology [11]. 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.

This paper presents a study on the CaCO_3 scale formation on pipe with laminar flow. The variable processes investigated were: temperature (30, 40, 50, 60°C) and the concentration of citric acid additives (5 ppm; 10 ppm; 20 ppm). The scale deposits were then characterised by XRD for phase composition and SEM/EDX for morphology and chemical elemental analysis.

2. Experimental Setup

2.1. Materials and equipment

The powder precursor used for the preparation of the crystal forming solution were CaCl_2 and Na_2CO_3 with the analytical grade. The citric acid ($\text{C}_6\text{H}_8\text{O}_7$) with analytical grade was added in the solution in an amount of 5 ppm, 10 ppm, and 20 ppm. The CaCO_3 forming scale was grown using the pilot-scale equipment shown in Figure 1.

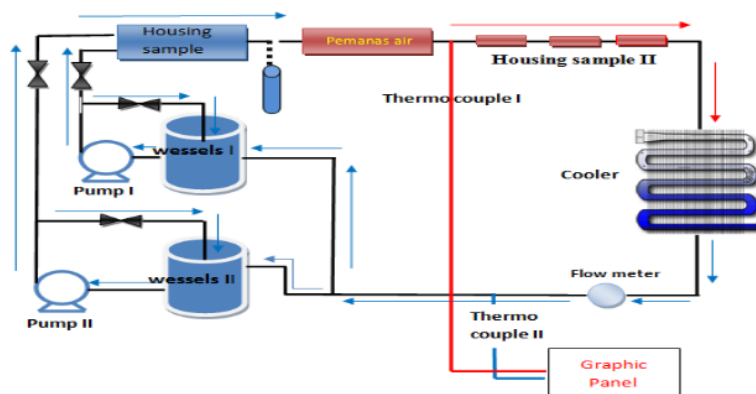


Figure 1. Experimental setup used in the CaCO_3 precipitation

2.2. Experimental method of the scale formation

For the crystallization experiment, five liters of equimolar CaCl_2 and Na_2CO_3 were prepared in the glass beaker. This experiment was performed in the same method which was proposed by Muryanto et al (2014) [2], by dissolving the CaCl_2 and Na_2CO_3 powder with the Ca^{2+} 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 citric acid additive was dissolved in to a vessel containing five liters of solution CaCl_2 , 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 and chemical elemental analysis and XRD for phase identification analysis. For the SEM observation, the powder crystals were mounted on a circular metallic precipitate holder and finally sputtered with gold.

The XRPD data collection for phase identification was performed using Cu-K α monochromated radiation in a conventional Bragg-Brentano (BB) para focusing geometry (D5005 SHIMADZU). The scan parameters (5-85 2θ , 0.020 steps, 15 s/step) were recorded. A PC-based search- match program, the MATCH Software was employed for identifying possible crystalline phases of precipitates.

3. Results and Discussion

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_3 . The mass scales of CaCO_3 were produced respective 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 [2].

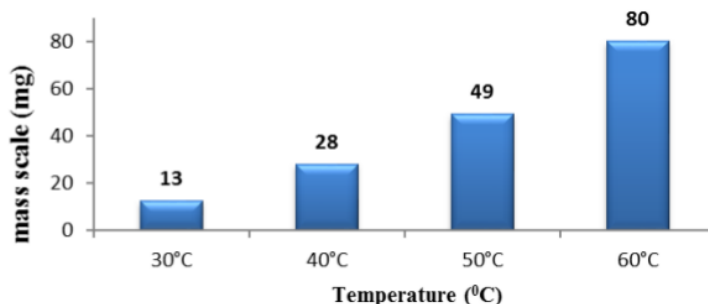


Figure 2. Effect of temperature on the resulting mass scale in pipes

3.2. The influence of citric acid additive in the formation of CaCO_3 scale.

The experimental result of citric acid addition to the mass of scale produced are presented in Figure 3. Testing variable concentrations of citric acid (5, 10, 20 ppm) showed a proportional decrease in the mass scales with increasing additive concentration. The mass scales obtained in the presence of 5 ppm

citric acid was 10 mg of CaCO_3 . Similarly provided 6 mg of mass scale was found in the presence of 10 ppm citric acid. The increasing mass scale (13 mg) was also produced at 20 ppm citric acid. Clearly the citric acid additive may be used to improve the scale produced.

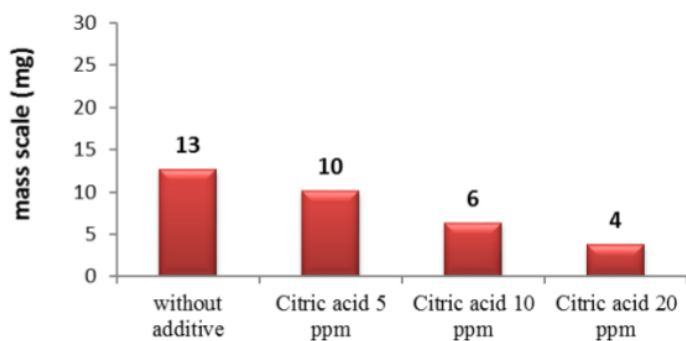


Figure 3. Effect of the citric acid on the mass scale produced

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

Measuring conductivity and estimating induction times in the absence and presence of additives is one of the most common methods of evaluating the efficiency of additives as a mechanism to delay the nucleation and growth of sparingly soluble scale minerals [4]. Additives that are biodegradable, such as the citric acids used in the study, and that delay dramatically the nucleation and or growth of a phase at low concentrations, are considered to be effective and are often referred to as ‘inhibitors’ although they do not inhibit nucleation and growth but most often just delay or change the reaction progress [2].

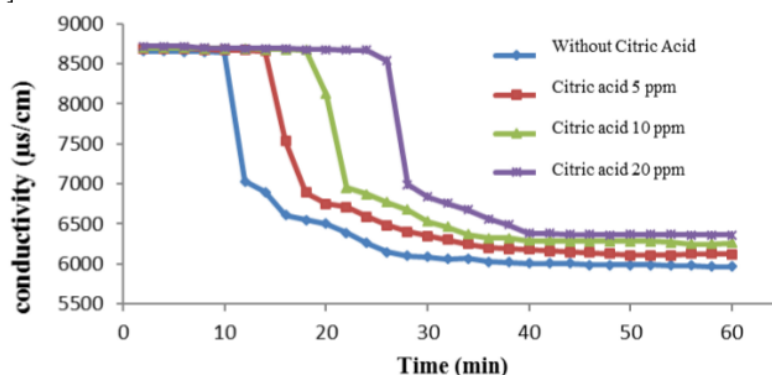


Figure 4. Induction time measured on the CaCO_3 precipitation

The addition of citric acid (5, 10, 20 ppm) resulted in increasing induction time of crystallization (Fig. 4). The induction time was observed in the CaCO_3 system almost doubled in the presence of 5 ppm citric acid (16 min), tripled with 10 ppm (20 min). Moreover, the presence of 20 ppm citric acid (26 min) led to an induction time four times greater than that for in the absence of citric acid system (12 min).

3.4. Microstructure of calcium carbonate precipitates

The addition of citric acids also affects the changes of crystal morphology as shown Figure 5. The presence of citric acid additive 5; 10; 20 ppm, resulted in the type of crystal morphology was from a prismatic to a round shaped crystal which vaterite transformed to calcite [4]. Thus, the citric acid may be potentially effective to control the morphology of the crystal calcium carbonate and the grain size.

XRD data of the experiment at a rate of 30 ml/min in the absence and presence of additives citric acid 5 ppm, 10 ppm, 20 ppm are presented in Figure 6. This can be seen in calcite phase has the intensity at an angle $2\theta^0$ according the PDF (Powder Diffraction Pattern) number # 86-2334. Vaterite has PDF#741868. The SEM/EDX analysis provided elements of Ca, C and O composing of the calcium carbonate. From the data, calcite is shown as the most stable, while vaterite is the metastable, and most likely to transform into calcite at subsequent temperature [2]. Moreover, calcite was clearly precipitated in the presence of citric acids.

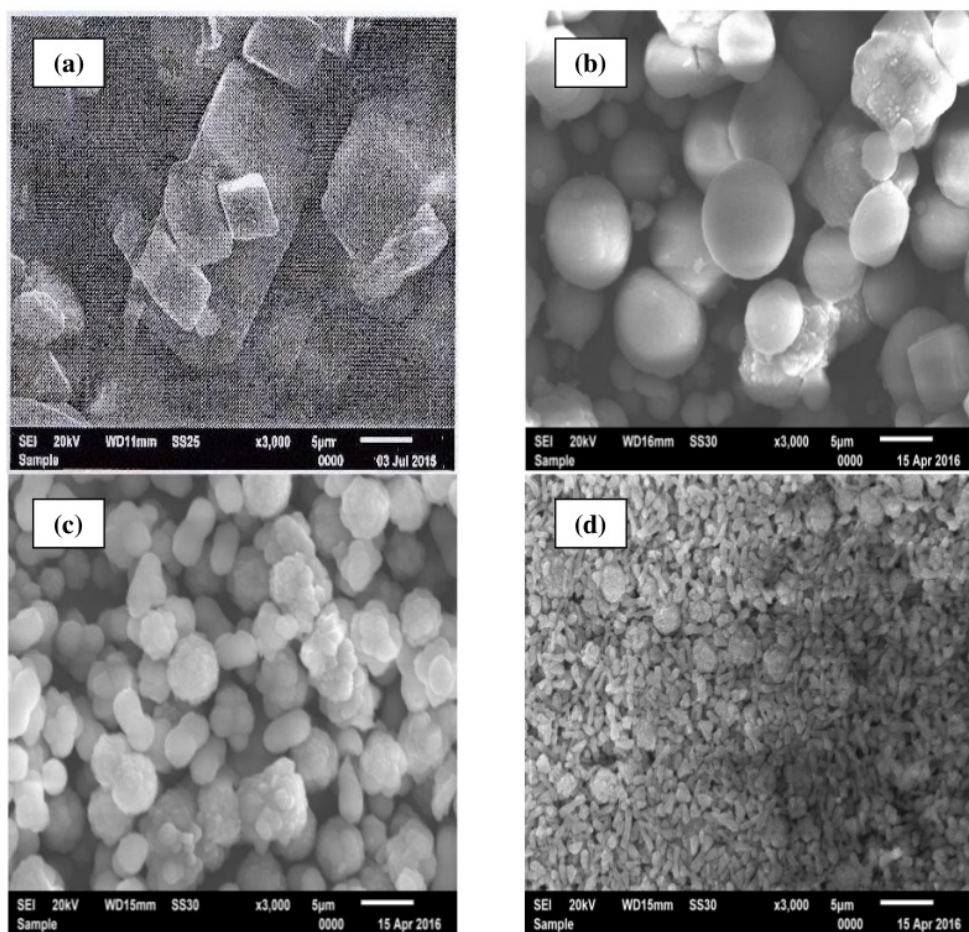


Figure 5. Morphology of the calcium carbonate scale with the citric acid (a: without additive, b: 5 ppm c: 10 ppm d. 20 ppm).

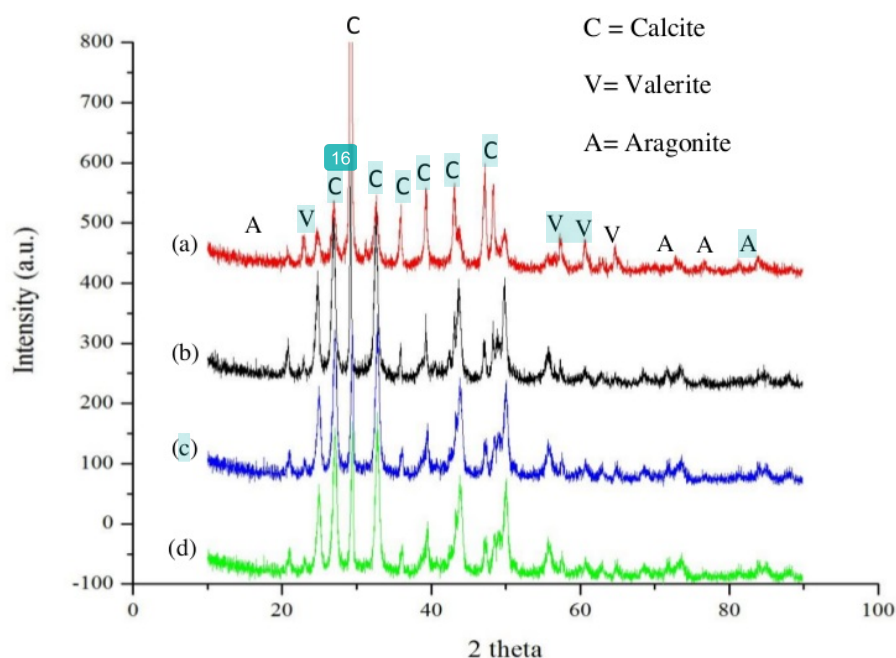


Figure 6. X-ray diffractograms of samples **12** obtained from the scale synthesis, (a) without additive, (b) with citric acid 5 ppm, (c) 10 ppm, (d) 20 ppm

4. Conclusion

It was found that in all the 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 additives. This crystal changed to the round shaped morphology in the presence of additive. The crystalline phase of the scale was found to be mostly calcite as shown by the XRD. The addition of citric acid seemed to change the crystal morphology, which shows the possibility of citric acid adsorption occurred on the surface of the crystal.

5 Acknowledgement

The authors would like to be obliged to Universiti Malaysia Pahang for providing laboratory facilities and financial assistance under project no. RDU110110.

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