Modeling and optimization of CaCO3 precipitated from laminar-flow water in the presence of citric acid at an elevated temperature

by Samsudi Raharjo

Modeling and optimization of CaCO₃ precipitated from laminar-flow water in the presence of citric acid at an elevated temperature

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Abstract

Calcium carbonate is a common mineral found in diverse industrial and technology applications and has become a subject of intensive research. In the present work, an experimental design methodology was used to optimize calcium carbonate precipitated from the laminar-flow water. The independent variables, namely temperature (50-60 ^{O}C), Ca^{2+}concentration (2000-3000 ppm), the citric acid additives (10-20 ppm) and the optimum mass of precipitate were examined using RSM (response surface methodology). The optimum results were proposed to be Ca2+ concentration of 3425.23 ppm and the 3.2 ppm of citric acid additives. In this calculation, the most influence on the mass of precipitate production was the temperature. The optimum production was 540.127 mg, which can be achieved at the temperature of 68.409 ^{O}C. SEM/EDX analysis showing that the precipitate has a blocky crystal morphology at the surface and composing of Ca, C and O element. The crystalline phase was verified by the XRPD method, supporting the formation of calcite in the precipitate. The addition of citric acid can inhibit the crystal growth from a diameter of about 5 μm to 2 μm, indicating the possibility of the citric acid adsorption occurring on the surface of the crystal.

Keywords: Calcite; Citric acid; Response surface methodology (RSM); XRPD method; SEM/EDX

INTRODUCTION

Calcium carbonate is one of the mineral scale, which can be precipitated from flowing water in industrial metal pipes. The existing of deposits may block the inside diameter pipes, leading to a reduction in heat transfer efficiency and frequently making to the shutdown of an industrial plant [1]. This mineral has been long studied as a model system of complex crystallization, because it has both great industrial importance and scientific relevance to bio-mineralization and geoscience [2, 3]. Now, precipitation of calcium carbonate is becoming a substantial issue in daily life, industry, and technology, hence using scale inhibitors are needed to control crystallization in laundry detergents, household cleaners, and in many industrial applications [4]. However, the role of calcium carbonate plays important role in drinking and waste-water treatment, including desulphurization of fuel gas, reduction of soil acidity [5, 6, 7, 8]. Moreover, calcium carbonate can be discovered in many biocompatible composites for drug delivery, bio-sensing and protein encapsulation [9]. Consequently, much effort has been devoted for understanding calcium carbonate precipitation in the water system using mineralogical approach.

Basically, calcium carbonate can exist in different crystalline phases, namely: calcite (rhombohedric structure), aragonite (orthorhombic) and varterite (hexagonal) [10]. The precipitation and stabilization of this crystal polymorph depend on the precipitation parameters: level of super-saturation, pH, ionic medium, concentration and types of impurities [11]. In general, this mineral precipitation has a relatively slow kinetic under natural conditions. Consequently, the different methods have been applied for increasing crystallization process in the laboratory. One of them is to add chemical reagents, such as strong acids, for decreasing the pH, or chelating agent to bind complex Ca^{2+} in the solution [12]. Moreover, the metal cations of Zn^+ at low contents in the solution can inhibit propagation and growth of calcium carbonate [13]. However, the method involves high operational cost and the additives is considered not environmental friendly.

Further, the use of chemical additives for water treatment has been long known for more than a century [14, 15]. It has been demonstrated that the crystal growth of scale can be controlled by "threshold inhibition" method through dosing trace amounts of chemical additives, which make the scale layer inhibited, while adhering them to crystal surface may weaken it [1]. Consequently, chemical additives as "threshold inhibitors" have been proposed to reduce or eliminate scale formation [16]. Here, many commercial additive formulations are now available in the industry, namely polyphosphates, polyphosphonates and polycarboxylic acids. Considerable research has been devoted to the prospect of scaling inhibitor and methods to detect and test the scale formation on metal surfaces [16, 17, 18, 19]. A study of the efficiency of scale inhibitors on the scale formation was also demonstrated by monitoring the heat transfer alteration [20]. The resulted study revealed that only a relative estimate of the thickness of the scale can control the heat-transfer change. Additionally, calcium concentration and temperature are important variables of calcium carbonate crystal growth. Here, certain amounts of calcium cations will interact with anions of additives, which subsequently play important role as nucleation sites for initiation of precipitation.

The use of traditional statistical methods for finding the most important factors and the optimum conditions of additive

concentration and temperature responses for calcium carbonate precipitation may be difficult and tiresome. Although the traditional methods can predict the importance of individual factors, they frequently reject their synergistic and opposed effects [21]. Correspondingly, response surface methodology (RSM) has been proposed an effective statistical method which can be applied for defining the individual character of each factor, as well as their antagonistic and opposed effects among the factors [22]. Additionally, RSM can be adopted for the experimental design to minimize the number of experiments to be performed. This methodology has been widely known to optimize conditions, such as bacterial growth, enzymatic reactions, and chemical processes [21, 23, 24, 25]. However, only limited study has been conducted by RSM to determine the optimal conditions for carbonate precipitation in the presence of additives and an elevated temperature. Therefore, in this work, the central composite design (CCD) of the RSM component, was derived to determine the concentrations of critic acid, temperature and calcium absorption and to maximize calcium carbonate precipitated. A second order transferred polynomial model (as an inverse model) was also generated, which defines calcium carbonate precipitation rate as a function of critic acid, and Ca^{2+} absorption. The crystal morphology of precipitate was then examined by scanning electron microscopy (SEM). The main element was identified by energy dispersive spectroscopy (EDS) technique. The phase composition analysis using XRPD method was applied in the characterization study of the scale.

MATERIALS AND METHODS
Crystallization experiments:
Crystallization experiments were conducted using a laboratory model of scale formation in the pipe and the schematic experiment was set-up in Figure 1. The equipment was designed having three main parts: i) two stainless steel vessels (I and II) encapsulated by wool jacket containing the $CaCl_2$ and Na_2CO_3 solutions; ii) two pumps (I and II); and iii) a housing sample unit (I and II). The housing sample unit includes three pieces of coupons made of stainless steel on which the scale is precipitated.

The crystal forming solution was run from each of stock solutions of 0.75 M $CaCl_2$ and 0.75 M Na_2CO_3, which was mixed in the housing sample. In the preparation of $CaCl_2$ solution, an analytical grade of $CaCl_2 \cdot 2H_2O$ powder (Merck™) was diluted according to the proposed concentration in the distilled water at room temperature, and followed by filtration it using 0.22 μm filter paper (Millipore™). Likewise, the sodium carbonate stock solution was made by diluting an analytical grade powder of Na_2CO_3 (Merck™) in the water. The two stock solutions were then stored in the separated vessel and the solutions were kept free from dust and insoluble matter for subsequent experiment.
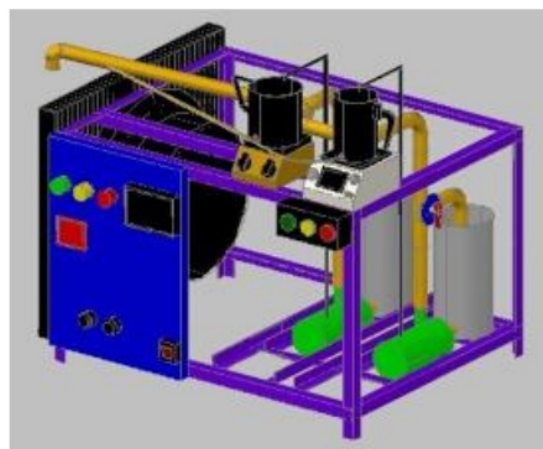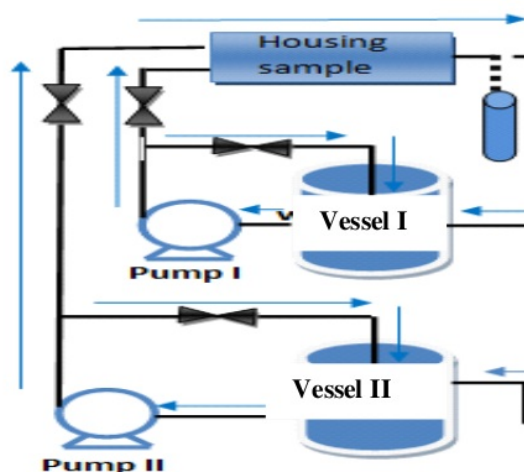

Figure 1: The pilot model of scale formation in pipe flow water

The citric acid ($C_6H_8O_7$) with the analytical grade powder (Merck™) was added in a ppm amount (0.00 to 5.00), and subsequently was dissolved in the Na_2CO_3 solution. The dilution of the citric acid was supposed to the unchanged property of Na_2CO_3 solution, because the citric acid concentration was less than one gram for each dilution, while the full bulk of the solution was ten liters (five liters in each vessel I and II). Equimolar of $CaCl_2$ and Na_2CO_3 solution was defined at a pre-determined concentration of 2000-3000 ppm of Ca^{2+}. The conductivity of the solution, leaving out the test pipe section at a flow rate of 30 ml/min was continuously monitored for up to 2 hours. Ca^{2+} concentration, citric acid concentrations, and temperature were set up as the independent variables. At the end of the experiment, the test pipe was loosened from the house unit and was drained. Subsequently, th coupons were removed from the house sample and dried in an oven overnight at 60 °C. The dried coupons were taken and weighed. The difference in the

weight of the coupons before and after the experiment was considered as the weight of the scale mass. The scale deposited on the surface of the coupons was carefully detached and stored in a plastic container for subsequent characterization.

Experimental design:
In this work, the optimization of the interaction of the three variables (temperature, concentration, and citric acid) was performed using RSM within the full experimental design (Table 1). Optimization of the experimental design was done by RSM using the software STATISTICA 6. With this method, equations of the mathematical model were fitted with the data of the calculation, and the independent variables of optimal conditions.

Table 1: Range and level of independent variable

Independent Variable	Range and level		
	Low level (-1)	Center level (0)	High level (+1)
Temperature (^{0}C)	50	55	60
Concentration Ca^{2+} (ppm)	2000	2500	3000
Citric acid (ppm)	10	15	20

In this present study, the optimum condition was analyzed using independent variables; namely X_1 = temperature, X_2 = Ca^{2+} concentration and X_3 = the citric acid against the mass of calcium carbonate precipitated (Table 1). Determination of optimum results was this mass of scale (mg) using the data from Table 1, while response variable of central composite experimental design was presented in Table 2. Variables for response optimization contained a central composite design, in which there are 3 factorial design 2 (3), central composite, and N_C = 8, N_S = 6, N_O = 2, Runs = 16, Here the low level (-1) = 50; 2000; 10. High level (+1) = 60; 3000; 20 and the center point (0) = 55; 2500; 15 were selected for an approach for the maximizing the experimental variable response for mass of scales.

Table 2: Experimental design for 2$^{(3)}$; central composite; N_C=8, N_S=6, N_O=2, Runs=16

RUN	Variable			Response
	Temperature X_1 (^{0}C)	Concentration X_2 Ca^{2+} (ppm)	Citric acid X_3 (ppm)	Mass scales (mg)
1	50.00	2000.00	10.00	92.4
2	50.00	2000.00	20.00	73.5
3	50.00	3000.00	10.00	184
4	50.00	3000.00	20.00	52.5
5	60.00	2000.00	10.00	134.4
6	60.00	2000.00	20.00	157.5
7	60.00	3000.00	10.00	180.6
8	60.00	3000.00	20.00	214.2
9	46.59	1500.00	15.00	31.5
10	63.41	1500.00	15.00	247.8
11	55.00	659.10	15.00	23.1
12	55.00	2340.90	15.00	182.7

13	55.00	1500.00	6.59	184.8
14	55.00	1500.00	23.41	27.3
15 (C)	55.00	1500.00	15.00	172.2
16 (C)	55.00	1500.00	15.00	172.2

Material characterization:
All samples of the precipitate were carbon-coated prior to examination by scanning electron microscopy (SEM) (FEI Inspect 230) with energy dispersive spectroscopy (EDS) system fitted with a field emission source and operating at an accelerating voltage of 15 kV. Phase identification of precipitates was performed by XRPD (X-ray powder diffraction) analysis. XRPD data were obtained using a conventional Bragg-Brentano (BB) diffractometry (D5005 SHIMADZU) with parafocusing geometry and Cu-Kα monochromated radiation. The scan parameters (5-90 2θ, 0.020 steps, 15 s/step) were set-up as a required for observation. A PC-based search match program, the Philips X'Pert Software (Philips Electronics N.V) was used to identify possible crystalline phases in the XRPD diffractograms. In this approach, the peak positions and peak heights were judged against the entries in the ICDD (International Centre for Diffraction Data) Powder Diffraction File (PDF).

RESULTS AND DISCUSSION
Determination of the mass scales:
The SRM analysis shows that optimization results of the mass scale response as a function of temperature (68.409 ^{0}C); Ca^{2+} concentration (3425.23 ppm) and citric acid (3.2 ppm) resulted in the optimum mass scale of 540.305 mg. Moreover, the resulting equation of the optimization with the experimental design can be presented as below:

Mass scales (Y) = -951.052 + 17.022X_1-0.065X_1^2 + 0.018X_2 + 0.0001X_2^2-44.56X_3-0.765X_3^2-0.003X_1X_2 + 1.04X_1X_3 + 0.002X_2X_3

$$(1)$$

Where X_1: temperature; and X_1^2: quadratic temperature; X_2: Ca^{2+}concentration; X_2^2: quadratic Ca^{2+}concentration; X_3: citric acid; X_3^2: quadratic citric acid; X_1X_2: interaction of temperature and concentration; X_1X_3: interaction of temperature and citric acid; X_2X_3: interaction concentration and citric acid.

Analysis of variance (ANOVA) for the mass scale produced is presented in Table 22. The significant effect of a factor can be seen from F and p-value. Here p-value is the probability of rejecting for the null hypothesis of the study. If the null hypothesis can be categorized as the fact true, the value of p-value less than 0.05 with an accuracy of 95% is obtained indicating that variable has a significant effect. The F-value is the ratio between MSF (Mean Squares of Factor) of the MSE (Mean Squares of Error). A factor can be said to have a significant effect, if the F-value is greater than the F-table.

Table 3: ANOVA (*Analysis of Variance*) optimized variables and the scale mass response.

Source	Sum of Squares	Degree of Freedom	Mean Square	F-value	F-table	R^2
S.S. Regression	62,611.53	9	62,611.53	23.2174	4.1	0.952
S.S. Error	16,153.61	6	2693.27			
S.S. Total	78,771.14	15				

The suitability of the model equations for the mass scales response can be judged by multiple criteria. The ANOVA analysis results show the mass scale response has the coefficient of determination ($R^2 = 0.952$). It shows only 4.8% of the total variation that did not fit with the model of equality, while the suitability of the model equations with crust mass response tested with static Fisher (F). The value of the F-value models is compared with the F-table, providing that F-value (23.2174) for each effect and for the F-table (9; 6; 0,05) of 4.1 was obtained. Based on the results for the response the mass scales of ANOVA analysis, F-value is greater than F-table. This proves that a significant effect on the response variable is the mass scales. The similar estimate can be seen in Chart Pareto, as shown in Figure 3.
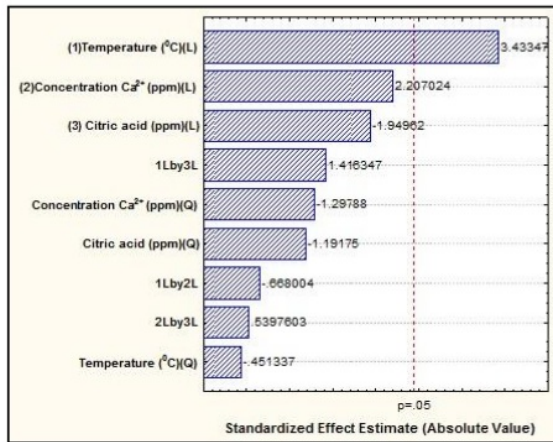
Figure 3: Graph of Pareto optimization variables on the response of the mass scales (mg)

From the graph, p-value less than 0.05 indicates that variable has a significant effect. Pareto chart shows the optimization variables on the response of the mass scale (mg), with the most influential effect goes to linear temperature (X_1). Moreover, the significant influence of mass response extend to linear concentration (X_2), linear of citric acid (X_2), the interaction between temperature and citric acid (X_1X_3), quadratic concentration (X_2^2), quadratic of citric acid (X_3^2), the interaction between temperature and concentration (X_1X_2), the interaction and the concentration of citric acid (X_1X_2). Here, the quadratic temperature (X_1^2) can be ignored because it does not provide a significant effect on the response

of the mass scales. Figure 4 present the curvature having the relationship between the model equations with the response of mass scales (mg).
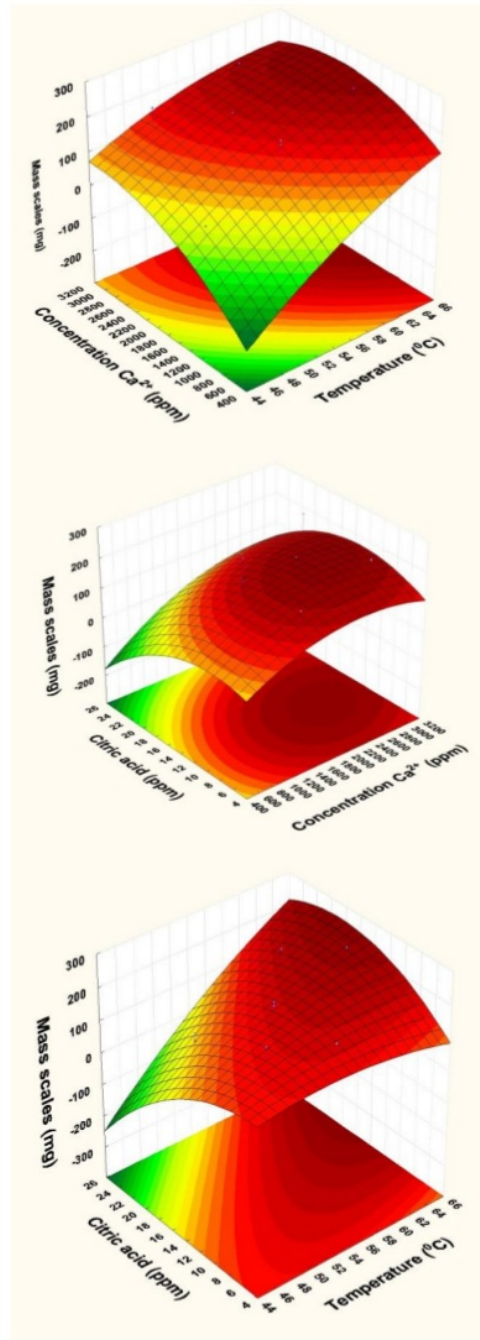
Figure 4: Surface response plot of the mass scales showing dependence of temperature, Ca^{2+} concentrations and citric acid additive

It shows that the increase in temperature resulted in the increased mass scales (mg). Increasing concentration leaded to the increasing mass scales, while the increase in citric acid concentration influenced on the mass scale reduction. Although the X_2 (concentrations) and X_3 (citric acid) are factors influencing the mass scales, X_1 (temperature) has a significant effect on the mass scales. This occurs because the increase in temperature leads to increase reaction speed and interaction between molecules more quickly. Thus the mass scales formed may also increase. By entering values into the equation for the optimum ratio of the mass response variable resulted in the optimization of the mass scale presented in Table 4.

Table 4: Optimum mass scales obtained from the calculation

Factor	Optimum state	Optimum mass scales (mg)
Temperatures (^{0}C)	68.409	540.305
Concentration Ca^{2+} (ppm)	3425.23	
Citric acid (ppm)	3.2	

Validation of value prediction on the optimum variable:
Verification was conducted by comparing the results of RSM optimization with the results of laboratory experiments. The comparison was to acquire % error of verification optimum variable. Value of % error verification resulted in the predictive value of optimum variables as presented in Table 5.

Table 5: Validation of value prediction on the optimum variable.

Optimum variable		Optimum result of RSM	Experimental result	% Relative Error
Mass scales		540.305	532.61	1.42%
Temperatures (^{O}C)	68.409			
Concentration Ca^{2+}(ppm)	3425.23			
Citric acid (ppm)	3.2			

Note: Relative error (%) = [(Experimental result-Optimum result of RSM)/Experimental result] × 100%.

Result of experiments show that the optimum ratio RSM for analysis using the mass scale response was 532.61 mg. The % error for the mass scales response was 1.42%. It means that the mass scales response has an accuracy of 98.58%. Therefore, the result of RSM for optimization analysis of the mass scales can be accepted.

Microstructure of calcium carbonate precipitated:
The crystal morphology of scale precipitated was verified using SEM and presented in Figure 5. SEM/EDX analysis confirmed that the precipitate was calcium carbonate having a blocky-shape morphology with the size order of 5 μm [10]. Moreover, the particle was composed of major ions of Ca, C and O (Fig. 5a). The presence of citric acid additive resulted in the crystal size reduction (Fig. 5b). The resulted crystals with size of about 1-2 μm were noted. Apparently, the citric

acid may be potentially effective to inhibit the crystal size of calcium carbonate.
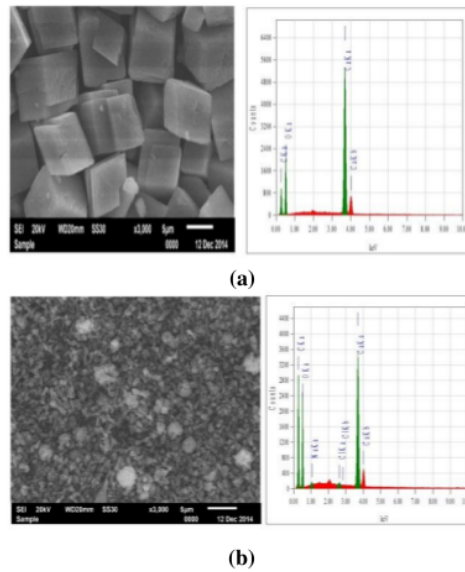

(a)

(b)

Figure 5: Morphology and ions of the precipitated calcium carbonate scale with the optimized medium a) in the absence of additive; b) in the present of citric acid.

XRPD analysis of the experimental data in the absence and presence of optimized additive is presented in Figure 6. In the absence of the additive, the precipitated particles consisted of calcite (PDF # 86-2334), [26], vaterite (PDF#741868), aragonite (PDF#76-0606), which can be identified by the search-match procedure. The presence of additives provided the precipitated particles containing calcite minerals. From the data, calcite is shown to be the most stable, while vaterite and aragonite are the metastable ones, and these minerals are more likely to transform into calcite as subsequent additives [3].
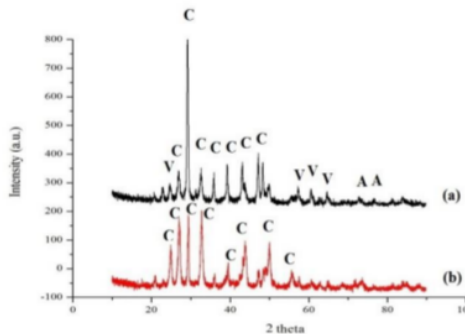

Figure 7: XRPD diffractograms of the precipitated particle from the solution (a) without additive, (b) with citric acid. Note: A: aragonite, C: calcite and V: vaterite.

CONCLUSIONS

The optimum conditions were investigated by RSM providing that most influence on mass of the scale was the temperature. The optimum result of the mass response (256.127 mg) was significantly influenced by temperature (68.409 $^{\circ}$C), Ca^{2+}concentration (3425.23 ppm) and citric acid (3.2 ppm). The higher temperature produced, the more mass of the scale obtained indicating that the increasing temperature promoted the scale formation. SEM analysis showed that the precipitated particles has a blocky-like morphology. The crystalline phase of the scale was found to be mostly calcite as shown by the XRPD method. The addition of the citric acid seemed to change the crystal size, which shows the possibility of citric acid adsorption occurred on the surface of the crystal.

ACKNOWLEDGEMENT

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