Effects Of Magnetic Field And Citric Acid On Polymorph And Morphology Of Calcium Carbonate Crystallized In A Flow-Water Pipe

S. Sutomo, W. Mangestiyono, S. Muryanto, J.Jamari, A.P. Bayuseno

Abstract: In the study, the polymorporh and morphology of calcium carbonate scale generated in the flow-water pipe under the influence of the magnetic field with and without citric acid was investigated. Calcium carbonate was precipitated from the supersaturated solution containing 0.087 M Ca^{2+} and CO_3^{-2}. Moreover, citric acid ($C_6H_8O_7$) (5 and 10 ppm) were added to the calcium solution, whilst varying temperatures (30, 40 and 50 ^{O}C) were selected. The experiments used a batch crystallizer equipped with a flow-water pipe at a rate of 30 ml/min and direct current in the solenoid generating a magnetic field of 2000 Gauss. Nucleation time was found to be faster than that for the experiments with the citric acid additive. Simply, the deposition rate was found decreasingly in the experiments without citric acid. Phase abundances in calcium carbonate corresponding to aragonite, calcite, and vaterite were confirmed by XRPD and FTIR. Additionally, a change in the calcite/aragonite/vaterite proportions could be linked up to the treatments by inducing magnetic field and citric acid additive. The morphology of the resulting scale consisted of rhombohedral calcite, a flower structure of vaterite and a dumbbell form of aragonite. These experiments provided the knowledge of prevention scaling methods in the wastewater treatment with magnetic systems.

Index Terms: Phase abundances; Magnetic field; Flow-water pipe; Calcium carbonate; Citric acid

1. INTRODUCTION

On heat exchanger, scaling of calcium carbonate can be formed on the contact metal surface of water-flowing pipes, on which physicochemical properties of water solution (types and concentration of metal ions) and heat transfer surface properties (the surface free energy, surface roughness and so on) control the generation of scale deposits [1],[2]. In particular, the calcium carbonate becomes less soluble with increasing temperature, leading to generate adherent deposits of scale on the internal walls of the pipe. The scale deposits on pipes may hinder flowing water, often completely blocked, and influence heat-transfer performance, while removal of scale deposits could be difficult and costly [3],[4],[5],[6]. This condition could bring to an unstable operation which may result in an unscheduled shutdown. Specifically, the precipitation of calcium carbonate may be influenced by several reaction factors such as pH, temperature, the pressure resulting in the slow kinetics of the solubility process of calcium carbonate and changing the equilibrium of this salt [7]. Accordingly, understanding reaction parameters controlling the solubility of calcium carbonate in aqueous solution is required to anticipate and/or mitigate the potential scale formation of calcium carbonate. Scale formation of calcium carbonate mainly relates to equilibrium and slowing the crystallization process. This condition occurs when CO_2 release in solution following pH increases, leading to precipitation of calcium carbonate according to [8]:

$$Ca^{2+} + 2HCO_3^- \rightarrow CO_2\,(aq) + CaCO_3(s) + H_2O \quad (1)$$

Further, this reaction product of the precipitated calcium carbonate (PCC) can be used for raw materials for many industrial purposes such as in papermaking, glass, rubber, plastic, paints, pharmacy, food, cosmetics, detergent and biomaterials [9], [10], [11]. For those industrial applications, the PCC product should satisfy the requirements of chemical and physical properties such as particle size, specific surface area, morphology and chemical purity [12]. In practice, PCC may have three different crystal structures such as calcite, aragonite, and vaterite [13]. In terms of thermodynamic stability, calcite is the most stable phase than others (i.e., aragonite and vaterite). Particularly, aragonite and vaterite are less stable. Correspondingly, PCC with specific polymorph could be obtained by changing the solution chemistry with chemical additives, whilst its morphology can be altered by controlling the reaction parameters [14],[15]. Accordingly, the usage of chemical additives in the solution, especially organic acids, were reported to affect the polymorphic structure, growth mechanism, nucleation, size, and shape of PCC crystal [16], [17]. This method is often considered very costly. However, in the case of thermal power plants having high circulation flow rates, chemical additives for water conditioning are desirable to provide economically and ecologically sound treatments, in addition to good water quality that is required for the food and beverage industries or residential areas. Conversely, magnetic water treatment (MWT) has been nominated for an alternative method for preventing scale formation by supplying or circulating water exposed to a magnetic sphere. This water treatment does not use a chemical additive for controlling or preventing scaling formation [18],[19],[20],[21]. This method has been long known as controversial techniques, however, it is suggested to be used effectively for reducing scale deposit or removing existing scale or making a softer and less persistent scale [22], [23]. The mechanism of scale reduction is still not understood,

- *S. Sutomo is currently pursuing a doctoral degree program in Mechanical engineering at Diponegoro University, Semarang, Indonesia. E-mail: Sutomo_67@yahoo.com*
- *W.Mangestiyono is a senior lecturer in Mechanical Engineering, Vocational Program at Diponegoro University, Semarang, Indonesia. E-mail: rhombo_hedral@yahoo.co.id*
- *S.Muryanto is a professor of Chemical Engineering, UNTAG University in Semarang, Indonesia. E-mail: stefanusmuryanto@yahoo.com.au*
- *J.Jamari is a professor of Mechanical Egineering, Diponegoro University, Semarang, Indonesia. E-mail: j.jamari@gmail.com*
- *A.P.Bayuseno is a professor of Materials Science and Engineering, Diponegoro University, Semarang, Indonesia. E-mail: apbayuseno@gmail.com*

though MWT has been implemented for a long time. The efficiency of this treatment is shown to be questionable, and there is still an unclear explanation of the phenomenon [3],[24]. Likewise, the laboratory works sometimes provide concluding results that are opposite to each other [25], [26]. Recently, intensive studies on the effect of the magnetic field for modifying the precipitation of calcium carbonate and controlling scaling formation has still been undergoing. Furthermore, the use of MWT for the scale of calcium carbonate mitigation was reported to focus on permanent magnet fields [1], [2], [27], [20], a modulated electromagnetic field [6], [26], [22] or catalytic effects [23]. It was reported that the effect of magnetic fields on crystal formation promoted increasingly at the bulk fluid, whilst less crystal was formed at the material surface, and the coagulation-flocculation processes of suspended particles increased in water [18], [28], [29], [30]. Supposedly the main mechanism of this MWT was related to bulk precipitation via heterogeneous catalysis [31]. Subsequently, bulk precipitating solid would be accumulated to the heat transfer surface as a soft sludge coating. Importantly, the use of the catalytic materials made a significant reduction of the fouling resistance by 20–38% at a velocity range of 0.3–0.8 m/s [32]. Additionally, a soft and easily-removable scale could be formed on the heat transfer surface [33]. Despite the significant reduction of scale formation that could be achieved by using a magnetic field, a proposed combining effect of the magnetic field and chemical additives may provide benefits for controlling the crystallization of calcium carbonate with specific polymorph and morphology [34],[35],[36]. The treatment stage benefit of water by the chemical additives may be somewhat offset by generating disposal and pollution problems, handling of hazardous chemicals, and cost [6]. Hence, a degree of compromise may be involved in the selection of treatments using a magnetic field and chemical additives due to the competition between the quality benefits of the PCC for requiring industrial purpose and producing other pollutants. However, the effects of the magnetic field and chemical additives on the solution process chemistry might yield the PCC with specific mineralogy and morphology. Here, the experimental research is needed to test the validity of the chemical additive and magnetic water treatment on controlling phase abundances and morphology of PCC [27]. This could be performed through a full experimental study controlling the possible reaction conditions and material characterization being able to describe the change of mineral proportions in PCC. Also, the study of precipitation kinetics could understand the scaling process of calcium carbonate without and with chemical additive under the magnetic field [37], [38], [39]. Consequently, the aim of this work was to investigate magnetic fields influencing calcium carbonate precipitation in dynamic (circulation flow) fluid systems using aqueous solutions with and without citric acid. Here, the material characterization experiments included the x-ray powder diffraction (XRPD) method for determining the mineral proportion of PCC, and SEM (scanning electron microscopy) examination of the morphology of its crystal products, respectively.

2. Materials and Methods

2.1. Preparation of calcium carbonate forming solution Materials used for preparing the crystal-forming solution included a distilled water, powders of $CaCl_2{\cdot}2H_2O$ and Na_2CO_3 (Merck, Germany) with the analytical grade, and citric acid ($C_6H_8O_7$). Moreover, the crystals $CaCl_2{\cdot}2H_2O$ and Na_2CO_3 crystals were dissolved in the distilled water with the equal molar ratio (0.087 M Ca^{2+} and CO_3) for yielding each solution of $CaCl_2{\cdot}2H_2O$ and Na_2CO_3, accordingly. Subsequently, each solution was prepared in a vessel containing 4 (four) liters of distilled water. It was stirred for making homogenous and filtered with 0.22 µm membrane paper. The prepared solutions were then stored in a sealed container, before use for the experiment. The citric acid in the amount of 0, 5 and 10 ppm was dissolved in a vessel containing $CaCl_2{\cdot}2H_2O$, was stirred at a rotation speed of 30 rpm.

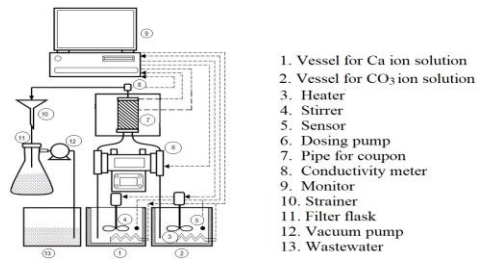

Fig. 1 *The experimental set-up for scaling of calcium carbonate on pipe*

2.2. Experimental apparatus of calcium carbonate formation

Fig. 1 shows an experimental equipment set-up used in the study. The equipment consists of two solution vessels, a dosing pump (CHEM FEED), a flow meter, a magnetic device, thermocouples, valves, and a data acquisition system. Two solutions $CaCl_2{\cdot}2H_2O$ and Na_2CO_3 were put into each vessel and continuously recirculated in the system with and without citric acid additives. A Teflon test pipe was wrapped around by the solenoid electromagnetic field. This solenoid direct current electromagnetic field produces a longitudinal electromagnetic field (2000 Gauss) inside the Teflon pipe. Solutions of each vessel were pumped by the dosing pump to the Teflon test pipe section at varying selected temperatures 30 ^{O}C to 40 ^{O}C and 50 ^{O}C for each stage of the research.

2.3 Materials characterization

The dried precipitating solids were then characterized by x-ray powder diffraction (XRPD), scanning electron microscope (SEM) and FTIR methods. The XRPD data for qualitative and quantitative phase evaluation were collected with X-Ray Diffractometer (Rigaku SmartLab,). In this way, the 2θ measured parameters of 10° -100° (0.020 steps; 15 sec/step) were selected. XRPD qualitative analysis of crystalline phases against the entry powder diffraction data in the International Centre for Diffraction Data (ICDD) was performed with the MATCH Software. The Rietveld method (FullProf-2k, software-version 3.30) [21],[25] was employed for the quantitative phase analysis with the crystal structure model obtained in the literature American Mineralogist crystal structure database (AMCSD) [23],[26]. Cell parameters and scale factors were obtained from refinements in calculating the weight % levels of mineralogical phases, which were automatically performed by the FullProf software program. A detailed discussion of the method is presented in the literature [25]. The morphology of the precipitating solids was examined by an FEI Inspect S50 scanning electron microscope with an acceleration voltage of 20 KV. Images were taken using a Mega view III digital camera (EMSIS GmbH). Prior to the SEM examination, samples were glued with adhesive tape on the surface of the circular

aluminum holder and finally sputtered with carbon. Moreover, FTIR spectrometry (IR-Prestige88) was also used to examine the influence of magnetic fields and citric acids on calcium carbonate scale formation. All spectra in bands from 400 to 4,000 cm^{-1}, were recorded at 200 scans/s with a spectral resolution of 2 cm^{-1}.

3 RESULTS AND DISCUSSION

3.1 Nucleation time for precipitated calcium carbonate

The effect of the magnetic field of water flowing in tubes was firstly examined in determining the induction time of calcium carbonate, on which the time represents both solutions of $CaCl_2 \bullet 2H_2O$ and Na_2CO_3 reacting in the electromagnetic Teflon test pipe. Here the induction time was determined from data of ionic conductivity changing firstly in the solution over time, in this way the measured ionic conductivity was firstly dropped. This condition means that a crystal nucleus is formed. A significant reduction of the conductivity of the solution corresponds to the ions forming the crystal leaving from the solution and accumulated to the wall of the pipe as a scale. Figure 2 presents the nucleation time recorded from the start reaction of ions forming calcium carbonate corresponding to the significant dropped ionic conductivity. It can be understood that the varying induction time with the homogeneous nucleation of calcium carbonate decreased with temperatures from 30 to 50 ^{O}C. Accordingly, this increase in temperature (30-50 ^{O}C) leads to the fastest homogenous nucleation. This condition is indicated that the higher temperature influenced the more Ca^{2+} reacting with CO_3^{2-} for the scale formation. This finding agreed with data in the literature that PCC is favorable at the higher temperature [1], [2], [3], [4], [5], [6].

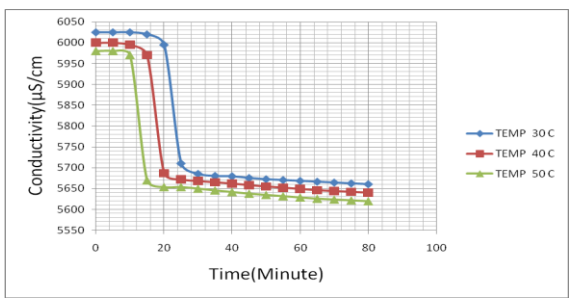

Fig. 2 *Crystallization of calcium carbonate in changing of conductivity at varying temperature (30, 40 and 500 C) in the absence of citric acid.*

Further experiments with citric acid added (from 5.00 to 10.00 ppm) in the solution made the longer induction time than that without citric acid at varying temperatures (Fig. 3). Obviously, the availability of citric acid in the chemistry solution made the lower solubility of Ca2+ that may be one of the primary causes of the slowing of the heterogeneous nucleation process [6]. Under the influence of the magnetic field and citric acid, the induction time decreased with the rising temperature (Figure 4). Obviously, these effects made the long heterogeneous nucleation rate of calcium carbonate. Consequently, magnetic and citric acid treatments were favorable for the nucleation in the bulk solution rather than in the pipe wall. These effects on nucleation type (homogeneous or heterogeneous) were significant for the lower temperatures (30 ^{O}C) [43].

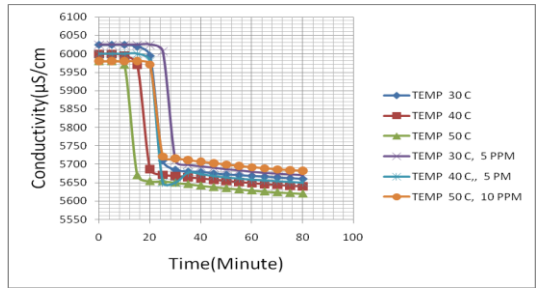

Fig. 3 *Crystallization of calcium carbonate in changing of conductivity with citric acid (0.00, 5.00, 10.00 ppm) and varying temperatures (30, 40, and 50^{0} C).*

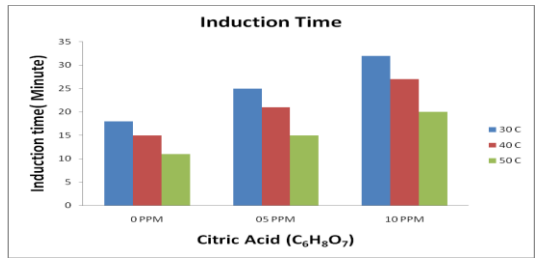

Fig. 4 *Induction time (nucleation time) in the presence of citric acid (0.00, 5.00, 10.00 ppm), and varying temperatures (30, 40, 50 ^{O}C)*

3.2 Deposition rate of calcium carbonate

In the study, the determination of calcium carbonate precipitation rate in the solution indicates that magnetically treated water supported homogeneous nucleation, while the citric acid added in the solution contributed to the heterogeneous nucleation (Fig. 5). These effects were reported to be more significance when the treatment-temperature increased [16], [17]. At a solution temperature of 50 ^{O}C without citric acid, the highest quantity rate of calcium carbonate precipitated with the magnetic field application was achieved with the increasing solution temperature. But this quantity decreased continuously after adding with citric acid. With 10 ppm citric acid added, and magnetic treatment, the quantity of calcium carbonate decreased at fixed water flow rates. Apparently, the absence of citric acid provided the highest quantity (mass) of the scale; and the precipitating mass increased with the increasing temperature. However, for all solution temperatures, as more citric acid added the less the amount of scale formed. Increased the various temperature would accelerate ions of Ca and CO_3 reaction in which accelerate the formation of nuclei was accelerated, but the presence of citric acid has inhibited the nucleation [18].

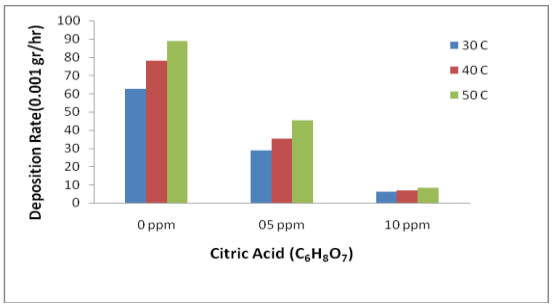

Fig. 5 *Deposition rate of calcium carbonate at various temperatures and citric acid addition (0, 5 and 10 ppm) in the influence of the electromagnetic field*

3.3 Temperature and magnetic field effects on the phase abundances of the scale

The calcium carbonate phases were supported by the XRPD Rietveld method and are subsequently exhibited in Figure 6. In the sample precipitated from the temperature solution of 40 ^{O}C and in the absence of magnetic field and citric acid, all x-ray diffraction peaks could be assigned as calcite and vaterite as the best fitting of the diffraction plot could be obtained. For these experiments, calcite and vaterite were favorably formed in the solution. Likewise, experimental works of using the temperature solution of 40 ^{O}C under the influence of the magnetic field (2000 Gauss) without citric acid yielded calcite and vaterite formed in the samples (Figure 7). However, with experimental conditions (magnetic field of 2000 Gauss; at a solution temperature of 40 ^{O}C) with citric acid (5 ppm), aragonite, calcite, and vaterite are resulting minerals that precipitated into the continuously flowing water. In this condition, aragonite favor precipitated at a higher temperature (> 30 ^{O}C), suggested in the literature that it could easily crystallize at high temperatures and high pressures [17].

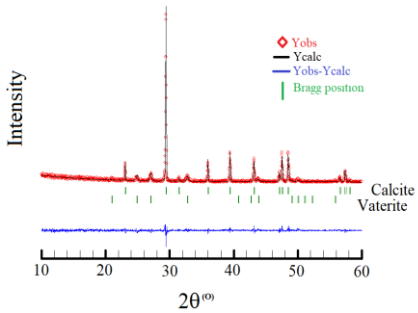

Fig.6 *The XRPD Rietveld refinement result of the precipitating solid obtained from the solution temperature of 40 ^{O} C in the absence of magnetic field and citric acid*

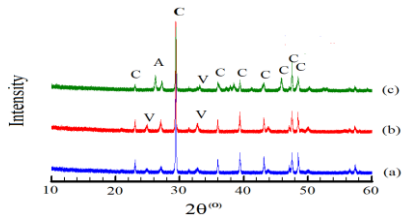

Fig 7. *X-ray spectra of the solids obtained at 40 ^{O}C; (a) in the absence of magnetic field and citric acid effects (0 ppm); (b) presence of a magnetic field; No citric acid (0 ppm) (c) presence of a magnetic field and citric acid (5 ppm) Notes: A(aragonite), C (calcite) and V (vaterite).*

Further XRPD quantitative analysis by the Rietveld method supported the results that the presence of magnetic field and citric acid made in change of proportion for calcite, in this way a high proportion of aragonite was produced at high temperature [17], while the calcite and vaterite became the minor amount precipitated from the solution (Table 1). The presence of the magnetic field in addition to citric acid changes the polymorphic crystal of calcium carbonate to facilitate the aragonite formation over calcite and vaterite. In the direct current solenoid electromagnetic, Lorentz force interfered Ca^{2+} or CO_3^{2-} ion passing through the magnetic field. In the combination of magnetic and citric acid effects, aragonite did not transform into calcite although temperature solution reduced to room temperature [19], [20], [21].

Table.*1 XRPD-based mineralogy of the crystalline solids*

Precipitating solids	Aragonite	Calcite	Vaterite
	Wt.%		
a) Absence of magnetic field and citric acid at 40^0 C		74.51 (86)	25.49 (67)
b) Only presence of magnetic field, at 40^0 C		62.20 (75)	37.80 (74)
c) Presence of magnetic field and citric acid (5 ppm) and at 40^0 C	45.91 (77)*	50.16 (75)	3.93 (59)

* Estimated standard deviation referring to the least significant figure to left

3.4 Impacts of magnetic field and citric acid on morphology of calcium carbonate

The results of mineralogical analyses of the final products show that aragonite, calcite, and vaterite were calcium carbonate scale, which could be obtained at the end of each precipitation experiment with citric acid and induced magnetic fields. Morphology of calcium carbonate scale observed with a scanning electron (SEM) analysis is presented in Figure 8. The citric acid and induced magnetic field in the solution temperature of 40 ^{O}C made a change in morphology. Without the effects of citric acid and magnetic field, typical morphology for rhombohedral calcite in size about 10 µm was clearly identified (Fig. 8a). In addition to rhombohedral calcite, a flower structure of vaterite and dumbbell form of aragonite was formed with the addition of citric acid (10 ppm) and induced magnetic field (Fig. 8c). The results are in agreement with the previous finding of calcium carbonate crystals [17], [21]. Also, SEM analysis confirmed that the morphology and size distribution of particles were influenced mostly by citric acid and magnetic field of the system. On the other hand, for the applied ranges of other parameters, i.e., the flow rate, the stirring rate and the solution temperature, no noticeable affected on the morphology. Thus, citric acid is potentially effective to change the morphology of the calcite to aragonite under the influence of the direct current solenoid electromagnetic field [36].

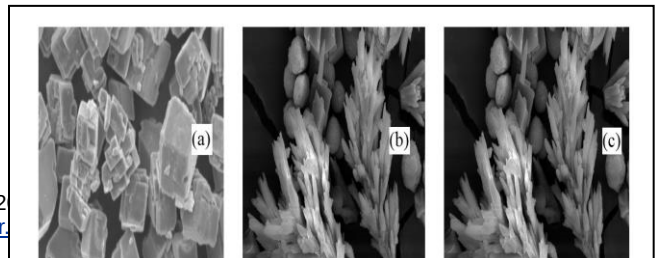

Fig. 8 *SEM images of the obtained calcium carbonate at the solution temperature of 40 OC; a) the absence of citric acid and magnetic effect; b) the presence of magnetic field and citric acid of 5 ppm; and (c) the presence of magnetic field and citric acid 5 ppm.*

3.5 FTIR analysis of the precipitating solid

The precipitating solids were also analyzed by FT-IR spectral analysis. The absorption bands identified at ~1420, ~874 and ~712 cm^{-1} could correspond to vibrations of calcite [8]. These absorption bands of calcite could be observed in all samples (Figures 9a-c). The bands at ~1070 and ~745 cm^{-1} for vaterite [44], [45] were also observed in all samples with and without citric acid and induced magnetic field (Figure 9a-c). However, the characteristic peaks of aragonite (700 and 713 cm^{-1}) [45] were only observed with the effects of citric acid and magnetic fields (Figure 9c). Accordingly, the mixture of aragonite, calcite, and vaterite could be confirmed with the effects of citric acid and the magnetic field.

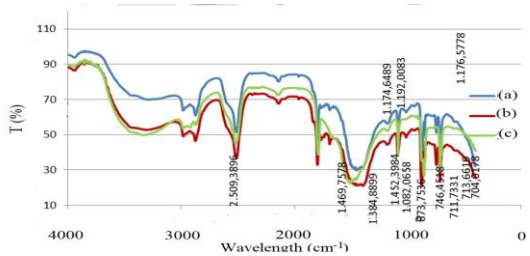

Figure 9. *FTIR absorption of the calcium carbonate scale at solution temperature of 400C; a) without citric acid and magnetic field; (b) under the influence of magnetic field; (c) under the influence of magnetic field and citric acid of 5 ppm.*

Further, FTIR analysis in the solution with the absence and presence of the magnetic field presents the absorbed band at 711.73 cm-1 for the calcite, but, their intensities decreased from 33.331 to 23.434 % (Fig. 9c). This condition indicates that there has been a change in the area of energy for the calcite formation, although the magnitude of the peak is the same at 711.73 cm^{-1} and other quantities have also changed. Apparently, the electromagnetic field made in decreases the proportion of calcite precipitation in accordance with the results of XRPD quantitative analysis. However, in the absence of induced electromagnetic field, which was originally at absorption peaks of 875.68 cm^{-1} with an area of 16 948, after the presence the electromagnetic field was changed to 873.75 cm^{-1} with an area of 23 878, thereby increasing it by 40.88 %, since for calcite at 876 cm^{-1} transformed to calcite at 873.75 cm^{-1}. Moreover, vaterite absorption occurred at 744 cm^{-1}, resulting in the emergence of vaterite at 744.52 cm-1 because only a small amount of field influence can occur, this is what shows that the field will affect the formation of precipitation resulting in the increase of vaterite and calcite. After being added by citric acid (Fig. 9c), the absorption occurred at 700.16 cm^{-1} with 38,577 intensities, while aragonite could appear or format at an absorption band of 700 cm^{-1}, so there is excess wave energy of 0.16 cm-1. The other absorption can appear at 1789.94 cm^{-1}; 2519,03 cm^{-1} for aragonite forming. The absorption at 844.82 cm^{-1} is relatively close to the absorption of the calcite formation at 849 cm^{-1}. The results of SEM analysis showed the morphology of aragonite such as flower clumps or leaves that are loose and spread evenly in a certain direction in the direction of the electromagnetic field that is formed. Based on the results of FTIR, XRPD, and SEM analysis, by giving a direct current electromagnetic field with the addition of 5 ppm citric acid affected the formation of aragonite in a regular direction [46].

4 CONCLUSION

The precipitated calcium carbonate (PCC) in a continuous process of flowing water in the batch crystallizer equipped with an induced electromagnet and added with citric acid has been demonstrated in this study. Experiments at varying temperatures under the influence of the magnetic field, the nucleation time decreased abruptly corresponding to a certain induction period of the homogeneous nucleation of calcium carbonate. Higher temperature produces a more mass scale of calcium carbonate precipitated. However, the presence of citric acid made a long time of nucleation with increasing solution temperature. XRPD, SEM, and FTIR analysis confirmed the forming of calcium carbonate polymorph affected by citric acid and the direct current solenoid electromagnetic field with variations of these temperatures. The preferred range of procedure parameters (magnetic field, temperature, supersaturation, flow rate and mass concentration of citric acid), could be identified, whilst the proportion of calcium carbonate phases with different characteristic morphologies (rhombohedral, truncated prismatic like agglomerates) could be made.

ACKNOWLEDGMENT

The authors grateful and appreciate to Diponegoro University, Semarang for providing facilities and financial support to conduct this research.

REFERENCES

[1] F. Alimi, M. Tlili, C. Gabrielli, M. Georges, and M. Ben Amor, “Effect of a magnetic water treatment on homogeneous and heterogeneous precipitation of calcium carbonate”, Water Res. Vol. 40, pp.1941–1950, 2006.

[2] F. Alimi, M.M. Tlili, M. Ben Amor, G. Maurin, and C. Gabrielli, “Effect of magnetic water treatment on calcium carbonate precipitation: influence of the pipe material”, Chemical Engineering and Processing: Process Intensification Vol. 48, pp. 1327-1332, 2009.

[3] J.S. Baker, and S.J. Judd, “Magnetic amelioration of scale formation”, Water Res. Vol. 30, pp. 247-260, 1996.

[4] Y.I. Cho, C.F. Fan, and B.G. Choi, “Use of electronic anti-fouling technology with filtration to prevent fouling in a heat exchanger”, Int. J. Heat Mass Transf. 41, pp.2961–2966, 1998.

[5] Y.I. Cho, and B.G. Choi, "Validation of an electronic anti-fouling technology in a single-tube heat exchanger", Int. J. Heat Mass Transf. Vol. 42, pp.1491–1499, 1999.
[6] S.H. Lee, and Y.I. Cho, "Velocity effect on electronic-antifouling technology to mitigate mineral fouling in enhanced-tube heat exchanger", Int. J. Heat Mass Transf. Vol. 45, pp. 4163–4174, 2002.
[7] J. Moghadasi, H. Müller-Steinhagen, M.Jamialahmadi, and A. Sharif, Theoretical and experimental study of particle movement and deposition in porous media during water injection J. Petrol. Sci. Eng. Vol. 43, pp.163-181, 2004.
[8] J. Chen, and L. Xiang, "Controllable synthesis of calcium carbonate polymorphs at different temperatures", Powder Technol. Vol. 189, pp. 64-69, 2009.
[9] C. Gabrielli, R. Jauhari, G. Maurin, and M. Keddam, "Magnetic water treatment for scale prevention", Water Res. Vol. 35, pp. 3249-3259, 2001.
[10] L. Li, A. Collis, and R. Pelton, "A new analysis of filler effects on paper strength", J. Pulp. Pap. Sci. Vol. 28, pp. 267-273, 2002.
[11] B. Stuyven, G.Vanbutsele, J.Nuyens, J. Vermant, and J.A. Martens, "Natural suspended particle fragmentation in magnetic scale prevention device", Chem. Eng. Sci. Vol. 64, pp.1904–1906, 2009.
[12] C. Martos, B. Coto, J. L. Pena, R. Rodriguez, D. Merino-Garcia, and G. Pastor, "Effect of Precipitation and detection technique on particle size distribution of $CaCO_3$", J. Cryst. Growth, Vol. 312, pp. 2756-2763, 2010.
[13] H.E.L. Madsen, "Influence of magnetic field on the precipitation of some inorganic salts", J. Cryst. Growth, Vol. 152, pp. 94–100, 1995.
[14] C. Garcia, G. Courbin, F. Ropital, and C. Fiaud, "Study of the scale inhibition by HEDP in a channel flow cell using a quartz crystal microbalance", Electrochim. Acta, Vol. 46, pp. 973-985, 2001.
[15] Y. S. Han, G. Hadiko, M. Fuji, and M. Takahashi, "Effect of flow rate and CO_2 content on the phase and morphology of $CaCO_3$ prepared by bubbling method", J. Cryst. Growth, Vol. 276, pp. 541-548, 2005.
[16] S. Muryanto, A.P. Bayuseno, H. Ma'mun, and M. Usamah, "Calcium carbonate scale formation in pipes: effect of flow rates, temperature, and malic acid as additives on the mass and morphology of the scale", Procedia Chem., Vol. 9, pp. 69-76, 2014.
[17] Y.Tang, F.Zhang, Z.Cao, W.Jing, and Y.Chen, "Crystallization of $CaCO_3$ in the presence of sulfate and additives: Experimental and molecular dynamics simulation studies", J. Colloid Interface Sci., Vol. 377, pp. 430-437, 2012.
[18] Y.I. Cho, A.F. Fridman, S.H. Lee, and W.T. Kim, "Physical water treatment for fouling prevention in heat exchangers", Adv. Heat Transf. Vol. 48, pp. 1-71, 2004.
[19] A. Szkatula, M. Balanda, and M. Kopec, "Magnetic treatment of industrial water Silica activation", Eur. Phys. J-Appl. Phys., Vol. 18, pp. 41-49, 2002.
[20] C.Y. Tai, M.C. Chang, R.J. Shieh, and T.G. Chen, "Magnetic effects on crystal growth rate of calcite in a constant-composition environment", J. Cryst. Growth, Vol. 310, pp. 3690–3697, 2008.
[21] Y. Wang, A.J. Babchin, L.T. Chernyi, R.S. Chow, and R.P. Sawatzky, "Rapid onset of calcium carbonate crystallization under the influence of a magnetic field", Water Res., Vol. 31, 346-350, 1997.
[22] A. Shahryari, M. Pakshir, "Influence of a modulated electromagnetic field on fouling in a double-pipe heat exchanger", J Mater. Process. Tech., Vol. 203, pp. 389-395, 2008.
[23] L.D. Tijing, B.C. Pak, B.J. Baek, D.H. Lee, and Y.I. Cho, "An experimental study on the bulk precipitation mechanism of physical water treatment for the mitigation of mineral fouling", Int. Commun. Heat Mass, Vol. 34, pp. 673–681, 2007.
[24] J.M.D. Coey, and S. Cass, "Magnetic water treatment", J. Magn. Magn. Mater., Vol. 209, pp. 71–74, 2000.
[25] M. Euvrard, P. Leroy, and J. Ledion, "Effects and consequences of electric treatment in reventing scaling of drinking water systems," J. Water Supply Res. T., Vol. 46, pp. 71–83, 1997.
[26] X.K. Xing, "Research on the electromagnetic anti-fouling technology for heat transfer enhancement," Appl. Therm. Eng., Vol. 28, pp. 889-894, 2008.
[27] M.C. Chang, and C.Y. Tai, Effect of the magnetic field on the growth rate of aragonite and the precipitation of $CaCO_3$, Chem. Eng. J. Vol. 164, pp. 1-9, 2010.
[28] S. Kobe, G. Drazic, P.J. McGuiness, and J. Strazisar, "The influence of the magnetic field on the crystallization form of calcium carbonate and the testing of a magnetic water-treatment device," J. Magn. Magn. Mater., Vol. 236, pp. 71–76, 2001.
[29] V.Kozic, and L.C. Lipus, "Magnetic water treatment for a less tenacious scale", J. Chem. Inf. Comput. Sci., Vol. 43, pp. 1815-1819, 2003.
[30] Z. Wu, J. H. Davidson, and L. F. Francis, "Effect of water chemistry on calcium carbonate deposition on metal and polymer surfaces," J. Colloid. Interf. Sci., Vol. 343, pp. 176-187, 2010.
[31] A.Fathi, T. Mohamed, G.Claude, G. Maurin, and B. A. Mohamed, "Effect of a magnetic water treatment on homogeneous and heterogeneous precipitation of calcium carbonate," Water Res., Vol. 40, pp. 1941-1950, 2006.
[32] G.J. Lee, L.D. Tijing, B.C. Pak, B.J. Baek, and Y.I. Cho, "Use of catalytic materials for the mitigation of mineral fouling," Int. Commun. Heat Mass., Vol. 33, pp. 14-23, 2006.
[33] J.F. Grutsch, and J.W. McClintock, "Corrosion and deposit control in alkaline cooling water using magnetic water treatment at Amoco's largest refinery," Corrosion 84 NACE, paper 330 (1984), New Orleans.
[34] N.I. Gamayunov, "Action of a static magnetic field on moving solutions and suspensions," Colloid J. Vol. 56, pp. 234–241, 1994.
[35] L.C. Lipus, J. Krope, and L. Crepinsek, "Dispersion destabilization in magnetic water treatment," J. Colloid Interface Sci., Vol. 235, pp. 60–66, 2001.
[36] T. Vermeiren, "Magnetic treatment of liquids for scale and corrosion prevention," Anti-Corros Method, Vol. M. 5, 215–219, 1958.
[37] Z. Kiaei, and A. Haghtalab, "Experimental study of using Ca-DTPMP nanoparticles in inhibition of $CaCO_3$ scaling in a bulk water process," Desalination, Vol. 33, 84-92, 2014.
[38] M. Ukrainczyk, J. Kontrec, V. Babic-Ivanic, L. Brecelic, and D. Kralj, "Experimental design approach to calcium carbonate precipitation in a semicontinuous process," Powder Technol., Vol. 171, pp. 192-199, 2007.
[39] N. Wada, K. Kanamura, and T. Umegaki, "Effects of carboxylic acids on the crystallization of calcium carbonate," J. Colloid Interface Sci. Vol. 233, pp. 65-72, 2001.
[40] J. Rodriguez-Carvajal Program Fullprof.2k, version 3.30, Laboratoire Leon Brillouin, France, June 2005.
[41] R.T. Downs, and M. Hall-Wallace, "The American mineralogist crystal structure database (AMCSD)," Am. Mineral., Vol. 88, pp. 247-250, 2003.
[42] P.-Y. Mahieux, J.-E.Aubert, M. Cyr, M. Coutand, and B. Husson,

"Quantitative mineralogical composition of complex mineral wastes–contribution of the Rietveld method," Waste Manage., Vol. 30, pp. 378-388, 2010.

[43] A.M. Lopez-Periago, R. Pacciani, C. Garcia Gonzalez, L.F. Vega, and C. Domingo, "A breakthrough technique for the preparation of high-yield precipitated calcium carbonate," J. Supercrit. Fluid., Vol. 52, pp. 298-305, 2010.

[44] C. Wang, Y. Liu, H. Bala, Y. Pan, J. Zhao, X. Zhao, and Z. Wang, "Facile preparation of $CaCO_3$ nanoparticles with self-dispersing properties in the presence of dodecyl dimethyl betaine", Colloids and Surfaces A: Physicochem. Eng. Aspects, Vol. 297, pp. 179-182, 2007.

[45] N.V. Vagenas, A. Gatsouli, and C.G. Kontoyannis, "Quantitative analysis of synthetic calcium carbonate polymorphs using FT-IR spectroscopy," Talanta, Vol. 59, pp. 831-836, 2003.

[46] L.D. Tijing, H.Y. Kim, D.H. Lee, C.S. Kim, and Y.I. Cho, "Physical water treatment using RF electric fields for the mitigation of $CaCO_3$ fouling in cooling water," Int. J. Heat Mass Transf., Vol. 53, pp. 1426–1437, 2010.