

# CONTROL OF CALCIUM CARBONATE SCALE FORMED ON A PIPE WITH INDUCING MAGNETIC FIELD AND TARTARIC ACID IN FLOWING WATER

## S. SUTOMO<sup>1</sup>, W. MANGESTIYONO<sup>2</sup>, S. MURYANTO<sup>3</sup>, J.JAMARI<sup>4</sup> & A.P. BAYUSENO<sup>5</sup>

<sup>1</sup>Department of Industrial Technology, Atmajaya University, Jakarta, Indonesia <sup>3</sup>Department of Chemical Engineering, UNTAG University, Semarang, Indonesia <sup>2,4,5</sup>Department of Mechanical Engineering, Diponegoro University, Semarang, Indonesia

## ABSTRACT

The polymorphic forms of calcium carbonates precipitated from water flow in a pipe at a rate of 30 ml/min in a crystal growth simulator were investigated in the study. Specifically, the calcium carbonates formed under the influence of the electromagnetic field and tartaric acid (0, 5, and 10 ppm) and varying temperatures (30, 40 and 50  $^{\circ}$ C) were analyzed by XRD, SEM and FTIR methods. As a result, the nucleation time of the first crystal form was longer, while the deposition rate decreased with the increasing tartaric acid additive. Obviously, the presence of tartaric acid at 40  $^{\circ}$ C inhibited the calcium carbonates formation and the deposition rate reduced dramatically from 0.402 to 0.211 mg/h. The resulting calcium carbonates were dominated by a high proportion of calcite with the minor vaterite. Conversely, the presence of the induced magnetic field and the tartaric acid provided the high proportion of vaterite. Morphology of the polymorphic forms of calcium carbonate showed rhombohedral calcite and vaterite like a flower structure as confirmed by the SEM method. FTIR analysis confirmed a mixture of calcite and vaterite coexisting in the precipitating solid.

KEYWORDS: Polymorphic Forms; Magnetic Field; Flow-Water Pipe; Calcium Carbonate; Tartaric Acid

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## **INTRODUCTION**

Calcium carbonates could be formed from the solution chemistry as an insoluble mineral, while their formations are undesirable because of becoming a serious problem in industrial installations. These minerals are frequently deposited and encountered as insoluble hard scale in the metal surface pipes of boilers, cooling towers, heat exchangers, geothermal processing equipment [1]. The scale formation of calcium carbonates affects decreasing in the installation efficiency, promoting energy loss, increasing the possibility of corrosion failures, which subsequently break down the operation and yield to higher operating costs. Practically, the calcium carbonates may coexist in the three different crystal structures such as vaterite, aragonite, and calcite according to the order of decreasing solubility [2]. Among these crystal structures, vaterite has high solubility and tends to change into calcite [3,4], which is the thermodynamically most stable phase. Correspondingly, understanding of kinetics of three polymorphic forms and their thermodynamic stability is required for successful controlling of calcium carbonate scale formation [5,6].

Further, the polymorphic forms of calcium carbonate could be modified in the solution chemistry adding with chemical additives; citric acid, and tartaric acid. By adding in a few of these organic acids (< 20 ppm) could control the polymorphic forms, growth mechanism, nucleation, size, and shape of calcium carbonate crystals [1, 7]. Alternatively, an induced magnetic field may influence the crystal growth of calcium carbonate. Such methodology

is commonly applied in magnetic water treatment (MWT) in which the flowing water is exposed to a magnetic field [2, 4, 8]. Moreover, no chemical additives are used in this water treatment for controlling or preventing scaling formation [3, 9, 10, 11, 13]. This magnetic field method could be effective in reducing scale deposits or removing existing scale or making a softer and less persistent scale [4, 11, 14]. However, the efficiency of this treatment for scale reduction is still arguable, and there is still an unclear explanation of the phenomenon [5, 12, 15]. Sometimes, the reported experimental works provide the opposite results [15, 16, 17].

In spite of the disputed results, the successful application of the direct current solenoid magnetic field for modifying the precipitation of calcium carbonate was reported recently [18, 19, 20, 21, 23]. For instance, the use of permanent magnet fields of MWT [1, 2, 17, 23], including a modulated electromagnetic field [6, 21] or catalytic effects [23] for mitigating scale of calcium carbonates were successfully demonstrated. Apparently, the magnetic fields have a significant effect on increasing crystal formation at the bulk fluid, whilst less crystal could be formed at the material surface, and the coagulation-flocculation processes of suspended particles increased in water [8, 18, 19, 23]. The main crystallization mechanism of the MWT may relate to bulk precipitation via heterogeneous catalysis [21]. In that way, a soft and easily-removable scale could be formed on the heat transfer surface [13]. Additionally, the use of catalytic additives of the chemistry solution could make a significant reduction of the fouling resistance by 20–38 % at a velocity range of 0.3–0.8 m/s [22].

Correspondingly, the synergetic effect of the magnetic field and chemical additives could be taken advantage for controlling of calcium carbonate formation with specific polymorph and morphology [21, 24]. For this purpose, the experimental work on the role of magnetic field and chemical additive in the solution chemistry is required along with an analytical tool capable of determining the different phases and morphology of calcium carbonates [21]. Moreover, such methodology may contribute to the quantitative analysis of the polymorphic forms of calcium carbonate found in varying industrial conditions [17, 18, 19].

Accordingly, this experimental study was conducted to explore the benefits of the combining effects of electromagnetic fields and tartaric acid on calcium carbonate precipitation in water flowing piping systems. The material characterization experiments included the x-ray diffraction (XRD), and FTIR methods for determining the polymorphic form, and SEM (scanning electron microscopy) for the morphology examination. These experimental results are expected to contribute to advanced knowledge of scale prevention and analysis.

#### MATERIALS AND METHODS

## **Calcium Carbonate Forming Solution**

Starting materials for preparing the chemistry solution included a distilled water, reagents of CaCl<sub>2</sub>·2H2O and Na<sub>2</sub>CO<sub>3</sub> (Merck, Germany) with the analytical grade, and tartaric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>). Initially, the reagents were dissolved in the distilled water (each volume of 4 liters) until the equal molar ratio (0.087 M Ca<sup>2+</sup> and CO<sub>3</sub><sup>-</sup>) was reached for yielding the solution of CaCl<sub>2</sub>·2H<sub>2</sub>O and Na<sub>2</sub>CO<sub>3</sub>, respectively. Subsequently, each solution was stirred and filtered with 0.22  $\mu$ m membrane paper. Prior to experiments, each solution was kept in a sealed container. The tartaric acid (C<sub>4</sub>H<sub>6</sub>O<sub>5</sub>) in the amount of 0, 5, and 10 ppm was added in a vessel containing CaCl<sub>2</sub>·2H<sub>2</sub>O and stirred at 30 rpm.

## **Crystallization of Calcium Carbonates**

The equipment for experiments included two solution vessels, a dosing pump (CHEM FEED) (6), a flow meter, a magnetic device, thermocouples, valves, and a data acquisition system (Figure 1). Each vessel contained  $CaCl_2 \cdot 2H_2O$  and  $Na_2CO_3$  solutions with and without tartaric acid, and each solution was then continuously pumped by the dosing pump and mixed into the system of a Teflon test pipe (7), which was wrapped around by the solenoid electromagnetic field. This system may generate the magnetic field of 2000 Gauss inside the test pipe. Experiments were performed at varying selected temperatures 30, 40, and 50  $^{\circ}C$  for each stage in the course of the study. During the experiment, the outflow of the filtrate was dispatched into the filter paper (13), where the filtrate was measured by the ion conductivity meter for subsequent kinetic analysis. Here the measurement of ion conductivity in the filtrate was conducted every five minutes and ended for four hours of testing. After a four-hour period of testing, the pump was ended, whereas the coupon was detached from the Teflon test pipe. Eventually, the coupon was dried in an oven at 60  $^{\circ}C$  for 24 hours. The removed scale was then weighted prior to microstructure analysis.



Figure 1: The Present Experimental Set-Up for Forming Calcium Carbonates.

#### Instrumentation of the Crystal Analysis

The dried powders of calcium carbonates were subjected to analysis by x-ray diffraction (XRD), scanning electron microscope (SEM) and FTIR methods. The XRD spectra were recorded with X-Ray Diffractometer (Rigaku SmartLab,), in which the  $2\theta$  of  $10^{\circ}$  - $100^{\circ}$  (0.020 steps; 15 sec/step) were set-up. The qualitative analysis of all XRD spectra was conducted by the MATCH Software to match with the entry powder diffraction data in the International Centre for Diffraction Data (ICDD). Moreover, the quantitative phase analysis with the Rietveld method (FullProf-2k, software-version 3.30) [25] performed on the spectra using the crystal structure model obtained in the literature American Mineralogist crystal structure database (AMCSD) [26]. In this way, the weight % levels of mineralogical phases were computed by the program automatically based on cell parameters and scale factors obtained from refinements. A detailed discussion of the method is presented in the literature [27].

Further, 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 measurements, a few amounts of powders were deposited by adhesive tape on the surface of the

circular aluminum holder and finally sputtered with carbon. In addition to SEM analysis, all solid was characterized by FTIR spectrometry (IR-Prestige88). All spectra in bands from 400 to 4000 cm<sup>-1</sup>, were measured at 200 scans/s with a spectral resolution of 2 cm<sup>-1</sup>.

# **RESULTS AND DISCUSSION**

#### **Nucleation Time for Precipitated Calcium Carbonate**

It is recognized that the nucleation and the crystal growth rate of calcium carbonate scale may be strongly influenced by the presence of tartaric acid in the solution. Figure 2 presents the nucleation time, which was determined from data of ionic conductivity changing firstly in the solution over time. This time refers to a crystal nucleus formed in the solution. Generally, a shorter nucleation time could be observed corresponding to the increasing temperature. The subsequent experiments with tartaric acid added (from 0 to 10 ppm) in the solution made the longer nucleation time than that without tartaric acid at varying temperatures. Obviously, the availability of tartaric acid in the solution made the lower solubility of  $Ca^{2+}$  leading to the slower heterogeneous nucleation process [6, 21, 23]. For this reason, tartaric acid could be adsorbed on the surface of the calcium carbonate crystal making it difficult for the crystal to develop. Obviously, these effects made the long heterogeneous nucleation rate of calcium carbonate. Presumably, the magnet with tartaric acid treatments was favorable for the nucleation in the bulk solution rather than in the pipe wall [23].



Figure 2: Nucleation Time at Varying Temperature Under Influence of Magnetic Field and Tartaric Acid.

## **Deposition Rate of the Calcium Carbonate on Pipe**

Figure 3 represents the deposition rate of calcium carbonates from the solution. The characteristics of scale formation in the absence of magnetic and tartaric acid were that increasing rates of scale deposition were quite fast indicating that the tartaric acid added and magnetic field in the solution contributed to the heterogeneous nucleation. These effects were also more significant when the conditioning temperature was also increased [11,16, 17]. For all deposition rates, the increasing temperatures might contribute to accelerating activation energy of these cations  $Ca^{2+}$  and anion  $CO_3^{2-}$  forming a nucleus, thereby enhancing the production of scale.

At a solution temperature of 50  $^{\text{O}\text{C}}$  without tartaric acid and magnetic field, the highest deposition rate of calcium carbonates could be observed with the increasing solution temperature. However, the deposition rate decreased continuously after adding with tartaric acid and inducing magnetic fields. The combining effects of 10 ppm tartaric acid and magnetic field made significantly reduction deposition rate of calcium carbonate at a constant flow rates. Apparently, the absence of citric acid and tartaric acid provided the highest mass of the scale; and the precipitating mass increased with the increasing temperature [16, 18]. However, for all solution temperatures, as more citric acid and tartaric acid added the less the amount of scale formed. Increased the various temperature would accelerate ions of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> reaction in

which accelerate the formation of nuclei was accelerated, but the presence of citric acid and tartaric acid have inhibited the nucleation [18].



Figure 3: Deposition Rate of Calcium Carbonate Under Influence of Magnetic Field and Tartaric Acid at Varying Temperatures.

### **Polymorphic Forms of Calcium Carbonate**

The XRD spectra of all solids were analyzed by the XRD Rietveld method revealing that calcium carbonates contained calcite and vaterite with different proportions depending on the parametric conditions. In all precipitating solid obtained at the 40 OC under influence of a magnetic field and tartaric acid, all x-ray diffraction peaks could be assigned as calcite and vaterite as the best fitting of the Rietveld diffraction plot could be observed (Figure 4). For the series of experiments, obviously calcite and vaterite were favorably formed in the solution. In particular, the experimental works at the 40 OC under the influence of the magnetic field tartaric acid yielded calcite and vaterite formed in the samples (Fig.5). Further XRD quantitative analysis by the Rietveld method supported the results that the presence of magnetic field and tartaric acid made in change of proportion for calcite and vaterite became the major amount precipitated from the solution under influence of the magnetic field and tartaric force interfered  $Ca^{2+}$  or  $CO_3^-$  ion passing through the magnetic field. Correspondingly, the combination of magnetic and tartaric effects made vaterite easily transforms into calcite when temperature solution reduced to room temperature [19, 20, 21].



Figure 4: The XRPD Rietveld Refinement Result of the Precipitating Solid Obtained from the Solution Temperature of 400 C in the Presence of Magnetic Field and Tartaric Acid.



Figure 5: XRD Spectra of the Precipitating Solid at Temperature of 40OC; (a) the Absence of Magnetic Field and Tartaric Acid; (b) Presence of Magnetic Field (c) Presence of Magnetic Field and Tartaric Acid (5 ppm) Notes: C (calcite) and V (vaterite).

Table 1: Mineral Proportion of the Calcium Carbonates based on XRD Quantitative Analysis

No	Precipitating solid	Calcite	Vaterite
		Wt.%	
1	Absence of magnetic field and tartaric acid at 40 <sup>0</sup> C	74.51 (86)	25.49 (67)*
2	Presence of magnetic field at 40 <sup>o</sup> C	62.20 (75)	37.80 (74)
3	Presence of magnetic field and tartaric acid (5 ppm) at 40 <sup>o</sup> C	37.49 (67)	62.51(56)

\* The estimated standard deviation (esd) referring to the least significant figure to left

#### Morphology of calcium carbonates

The results of XRD analyses of the precipitating solids verified that calcite and vaterite were two polymorphic forms of calcium carbonates generated during the precipitation experiments with tartaric acid and induced electromagnetically. The morphology of these calcium carbonates recorded with a scanning electron (SEM) analysis is shown in Figure 6. For this paper, the tartaric acid and induced magnetic field in the solution temperature of 40  $^{\circ}$ C are presented. Obviously, no significant change in the morphology of calcium carbonates formed in this solution could be observed. Particularly, the absent effects of tartaric acid and the induced magnetic field revealed the typical morphology for calcite with hexagonal platelets in size about 10 µm coinciding with typical vaterite spherical aggregates (framboids) (Fig.6a). Likewise, the induced electromagnetic field on the solution yielded typical morphology and spherical vaterite clusters were frequently observed in the precipitating solids with the addition of tartaric acid (5 ppm) and the induced electromagnetic field (Fig. 6c). A similar finding of this calcium carbonate morphology was also reported previously [17, 21].

The further significance of the study through SEM analysis confirmed that the morphology and size distribution of particles was influenced mostly by tartaric acid and magnetic field of the piping system. Specifically, other experimental parameters, namely the flow rate, the stirring rate, and the solution temperature did not influence the morphology development. Evidently, the magnetic field influenced on the habit of industrial calcite crystals in two aspects: on the crystal surfaces and at the crystal edges [23], whereas the tartaric acid effect is significant to change the morphology of vaterite into spherical clusters (framboids).



Figure 6: SEM Images of the Calcium Carbonates Precipitated from the Solution Temperature of 40 OC; a) The Absence of Electromagnetic Effect and Tartaric Acid; b) The Presence of Electromagnetic Field (c) The Presence of Electromagnetic Field and Tartaric Acid of 5 ppm.

#### FTIR Analysis of the Precipitating Solid

The qualitative analysis of calcium carbonate polymorph was performed by the FT-IR method. The absorption bands at ~1420, ~874, and ~712 cm-1 corresponding to the vibrations of calcite [8], could be determined in all solids (Figures 7). The absorption bands at ~1070 and ~745 cm-1 for vaterite [23, 24] were also determined in all solids with and without tartaric acid and induced magnetic field (Fig. 7b). There is a small overlap of the 700 and the 713 cm-1 bands which was observed. Moreover, the polymorphic forms of calcite and vaterite in the precipitating solids were evident under the influence of tartaric acid and the magnetic field. 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. 7c).

The further overlapping peak at 711.73 cm<sup>-1</sup> and other peaks could be observed to change due to the presence of electromagnetic fields. Consequently, the proportion of calcite precipitation might decrease. This reason is also supported by the results of XRD quantitative analysis. In this case of magnetic effect, the original absorption peaks of 875.68 cm<sup>-1</sup> with an area of 16 948 changed to 873.75 cm<sup>-1</sup> with an area of 23 878, thereby increasing it by 40.88 %. This condition may contribute to change in the proportion of calcite corresponding peaks at 876 cm<sup>-1</sup> into at 873.75 cm<sup>-1</sup>. Moreover, the absorption bands of vaterite at 744 cm<sup>-1</sup> might result in the emergence of vaterite at 744.52 cm<sup>-1</sup> in that the increased content of vaterite rather than calcite could be observed.

In the study, the absorption band at 1087.85 cm<sup>-1</sup> to 29,274 intensities might correspond to vaterite, which is commonly found in an absorption band of 1087 cm<sup>-1</sup>, so there is excess wave energy of 0.85 cm<sup>-1</sup>. The other absorption band could be observed at 744.52 cm<sup>-1</sup> for vaterite, and 874,75 cm<sup>-1</sup> for calcite. Apparently, the absorption band at 874,75 cm<sup>-1</sup> overlaps with that of the calcite at 875 cm<sup>-1</sup>. The results of the morphological analysis for vaterite and calcite indicated that crystal aggregates could be loose and spread evenly in a certain direction in the direction of the electromagnetic field. Based on the results of FTIR, XRPD, and SEM analysis, the induction of direct current

electromagnetic field with the addition of 5 ppm tartaric acid affected the formation of vaterite coinciding with calcite in the spread direction [17, 18, 23].



Figure 7: FTIR Absorption of the Calcium Carbonates Obtained at the Solution Temperature of 400C and; a) The Absence of Magnetic Field and Tartaric Acid; b) The Influence of Magnetic Field; c) Tartaric Acid Effect of 5 ppm.

## CONCLUSIONS

The precipitated of polymorph calcium carbonates in a continuous process of water flowing in the piping system with an induced direct current electromagnetic field and added with tartaric acid has been demonstrated in this study. Experiments at varying temperatures in the influence of the magnetic field, the nucleation time decreased abruptly corresponding to a certain induction period of the homogeneous nucleation of calcium carbonates. Higher solution temperature yielded a more mass scale of calcium carbonate precipitated. However, the presence of tartaric acid made a longer nucleation time with increasing solution temperature. XRD, SEM, and FTIR analysis confirmed the forming higher proportion of calcite with less vaterite affected by the electromagnetic field with varying temperatures. But the higher proportion of vaterite than that of calcite could be observed in the solution added by tartaric acid. In the study, parameters such as magnetic field, temperature, super saturation, flow rate and mass concentration of tartaric acid have significantly influenced the scale production of calcium carbonates, while the proportion of calcium carbonate phases with different characteristic morphologies such as hexagonal plate and spherical agglomerates could be produced.

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