EFFECTS OF pH ON CALCIUM CARBONATE PRECIPITATION UNDER MAGNETIC FIELD

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Abstract

Magnetic field effect on $CaCO_3$ precipitation is the key parameter in evaluating the effectiveness of Anti-scale Magnetic Treatment (AMT). The purpose of this study was to investigate magnetic fields influence on $CaCO_3$ precipitation in high and low super-saturated $CaCO_3$ solution by varied pH $CaCO_3$ solution using circulation flow fluid system. The observation results in the high super saturated solution (pH 8.5) showed the increase of precipited $CaCO_3$ in magnetized solutions compared to those in non-magnetic solution during circulation process. In the low super-saturated $CaCO_3$ solution (pH 6.4) it was found that magnetic treatment increased $CaCO_3$ precipitation after circulation process. In high super-saturated solution, magnetic field strengthens ion interactions, which reduce precipitation during circulation process. However, in low super-saturated $CaCO_3$ solution, magnetic field weakens hydrate ion interaction which indicated by decreasing of the conductivity of solution. It increases the precipitation of $CaCO_3$ after the circulation of magnetization process has completed.

Keywords: calcium carbonate precipitation, circulation flow, magnetic field

1. Introduction

Scale formation on pipe walls and heat exchange equipment is a serious problem encountered in almost all water processes. Typical scale deposits are composed of minerals that become less soluble with increasing temperature. Calcium carbonate is the most common deposit. Scale deposits usually form hard-to-remove-linings, which reduce water flow capacities. When they build up on the heat exchanger surfaces, heat transfer efficiency is reduced because of their low thermal conductivity.

Scale formation in hard water as $CaCO_3$ precipitation process is an equilibrium and slowing process. Increase of pH due to CO_2 release in solution will push precipitation of $CaCO_3$ as follow:

$$Ca^{2+} + 2HCO_3^- \leftrightarrows CO_{2(aq)} + CaCO_{3(s)} + H_2O \qquad (1)$$
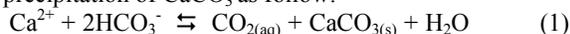
Anti-scale water treatment using chemical methods changes the solution chemistry and can be very expensive. The chemical methods for water conditioning are economically and ecologically visible especially under conditions of high circulation flow rates for large plants such as thermal power plants. In some other areas, such as food and beverage industries or residential areas, there are strict requirements for water quality.

AMT is a method, where supplied or circulated water is simply exposed to a magnetic field. This method has a long and controversial history but is reported to have been effective in numerous instances. Its main effect is to either reduce scale deposit or remove existing scale or produce a softer and less tenacious scale [1]. The mechanism is still unclear, although AMT has been practically used for over half a century. According to the review paper of Baker and Judd [2], the efficiency of this treatment is still a controversial question and clear explanation of the phenomenon does not exist yet. In the same time, conclusions drawn on the basis of laboratory works sometimes are opposite to each other. Understanding how the magnetic field of relatively low densities precisely modifies the precipitation of low magnetic minerals such as $CaCO_3$ is still being developed.

Two mechanisms have been developed to address magnetic field effects on calcium carbonate precipitation in static fluid system, viz., (1) a direct effect on dissolved ions and (2) a magnetic effect on particles [3]. They called the first mechanism as "*ionic mechanism*". Examples of ionic response to a magnetic field have been reported by Higashitani [4] who investigated the characteristics of calcium carbonate precipitation and it was found that the nucleation of calcium carbonate was

suppressed. Higashitani [4] hypothesizes that weak bounds of water molecules with the CO_3^{2-} anion are quasi-stabilized and structured by the magnetic exposure, so that they inhibit the precipitation rate of $CaCO_3$ crystals.

We call the second mechanism, which involves the magnetic effect on existing $CaCO_3$ particles present in water, as *particle mechanism*. Lundager [5], observed a faster precipitation of calcium carbonate in the presence of a magnetic field under quiescent condition than in non-magnetic treatment.

Dynamic fluid system is most commercial magnetic devices for scale control system, where treated water flows through a perpendicular magnetic field. Theoretically, in addition to the ionic and particle mechanism effect in static fluid system, Lorentz forces effect can occur in dynamic fluid. Lorentz force acts on every electrical charged particle, when it is moving through the applied magnetic field. Kozic said that Lorentz force effect on collision probability of dispersed particles causes essential local shifts of ions and particles in electric double layer, which can affect the aggregation and crystallization processes [1]. While in the same time, a conducting fluid flows through the magnetic field, an electric field is generated also according to Faraday's law and produces a potential difference that can cause a current to flow in the fluid according to Ohm's law. The presence of the induced current in the fluid and the applied magnetic field, in turn, produce a mechanical force on the fluid known as a ponderomotive force. This force flattens the profile which can ultimately result in the formation of a boundary layer near the walls. Formation of this boundary layer results in a larger velocity gradient and can trigger $CaCO_3$ precipitation. This effect is called magneto-hydrodynamic effect [1].

Gabrielli [6] found the increasing of the precipitation of $CaCO_3$ up to 25 % when the flow circulation still running, while using the same system, Fathi [7] found the increasing of the precipitation of $CaCO_3$ after the circulation has already completed. According to Fathi, the difference of the result is caused by the difference of analysis method that they used. The level of the supersaturated solution is thought to be the factor that influences the effect of magnetic field toward the precipitation while or after the circulation.

2. Experimental

Hard Water Preparation. In order to avoid any side effect by foreign ions, carbonized aqueous solutions, (water containing only Ca^{2+}, CO_3^{2-} and HCO_3^- ions) was used. It was prepared by dissolving 0.5 g dm^{-1} reagent grade $CaCO_3$ in de-ionized water, by bubbling carbon dioxide during 6 hours according to:

$$CO_{2(aq)} + CaCO_{3(s)} + H_2O \leftrightharpoons Ca^{2+} + 2HCO_3^- \qquad (2)$$
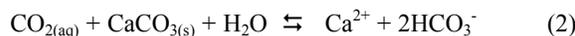
The solution was filtered and has produced ± 160 ppm hardness as Ca^{2+}. This hardness can be considered as moderate by comparison with the values used by many authors [6-9]. The pH of solution resulting from this preparation was about 6.4. Then, the carbonized aqueous solutions were displaced towards super-saturation by adjusting the pH between 6.4 and 8.5 with was added 1 M NaOH solution.

Magnetic Water Treatment. The experiment used dynamic fluid system. 400 mL of the sample solution is filled into a glass container, to the outflow of which a silicon tube is attached. The tube leads through a laboratory peristaltic pump (Master flex L/S^{TM}), employed to generate fluid flow at variable flow rates (range ca. 0.12 - 22 mL/sec), then through the treatment area of the system, and back to the container, thus forming a closed, recirculation dynamic fluid system. Neodymium permanent magnets employed to generate homogeneous Magnetic field. It consisted of a series of pairs of permanent magnets with north and south poles facing each other, which associated alternately. A Silicon tubing 2 m of total length and 0.7 cm with internal diameter was used. An average magnetic of 5200 Gauss has been produced at the gap between the poles in magnetization area. The temperature of the solution in magnetization process was not controlled, and equal to the ambient temperature of the surroundings (*i.e.*, room temperature, 28–29°C). Figure 1 shows a simplified schematic of the experimental treatment system used in the presented work.

Precipitation test. 20 ml of the solutions, which were put in precipitation glass reaction tubes (15 mm (OD) x 140 mm (H)) right after the completion of magnetic exposure. The Ca^{2+} concentration in the precipitation tube was analyzed by EDTA complexometry (accuracy ≈ 0.05 mg as $CaCO_3$), and amount of ions Ca^{2+} consumed in solution as a measure of $CaCO_3$ precipitation.
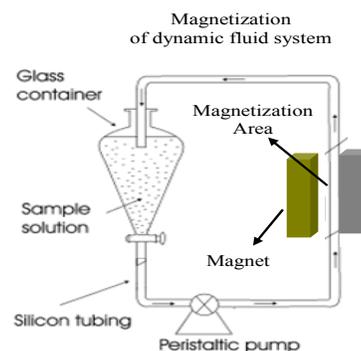
Figure 1.　Schematic of the Experimental Treatments System

3. Results and Discussion

The Results will be addressed into the following sections, *i.e.* given in two sections that is magnetization effect during circulation and after circulation process. The effects magnetic strength, flow rate, and magnetization time will also be discussed.

CaCO₃ Precipitation During Magnetization and Circulation.

Magnetization and precipitation processes have been conducted in the same tube for 180 minutes at room temperature. Figure 2 shows the characteristics of $CaCO_3$ precipitation at varied pH solution under a magnetic field. The $CaCO_3$ precipitation under magnetic treatment is higher than that non-magnetic treatment within the range of pH 6.4–8.5.

It is widely known that the pH of $CaCO_3$ solution influences the saturation and precipitation of $CaCO_3$ in the solution. Fathi [7] have found that the saturation level of 500 ppm $CaCO_3$ solution at pH 7.5 is 15 times than its solubility.

The time needed to precipitation to be started is called nucleation time (T_n). The magnetization shortens the nucleation time (T_n). It shows that the amount of the precipitation of $CaCO_3$ on the magnetized sample for all

pH of the solution at the 180th minute circulation is about 85% to 86%, while the non-magnetized sample is about 72% to 73%.

The circulation process on the $CaCO_3$ solution fastens the solute CO_2 to the gas phase so the pH solution will increase. The increasing of pH causes HCO_3^- ion to be converted into CO_3^{2-} ion and quickly create $CaCO_3$ with reaction as following:

$$CO_{2(aq)} + CaCO_{3(s)} + H_2O \; \leftrightarrows \; Ca^{2+} + 2HCO_3^- \quad (3)$$
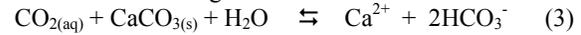
For the comparison, the circulation process of non-magnetized solution at pH 7.5 needs 10 minutes for the precipitation to be started, while the static process needs about 200 minutes [8]. It shows that the circulation process fastens the transfer of CO_2 from the hard water to the air. Figure 1.4 shows the precipitation of the $CaCO_3$ on the concentration of 0.004 M $CaCO_3$ happens at pH of 8.5 to 8.6 on this experiment.

It needs 40 minutes for the non-magnetized sample at pH of 6.4 (low super-saturation) to reach up to pH of 8.5 and precipitate, while the magnetized sample only needs 20 minutes as shown by figure 3. It shows that the magnetization fastens the nucleation time. The effect of the weakening of ion hydrate by magnetic field is thought to be cause of the faster nucleation time on the magnetized sample.
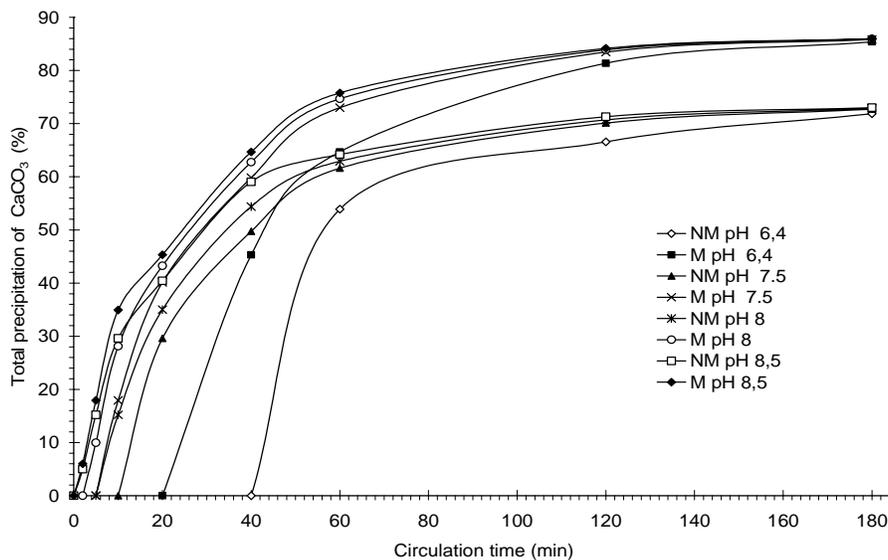
Figure 2.   The Influence of the pH of the Solution toward the Total Precipation of CaCO₃ on Non-Magnetized Sample (NM) and Magnetized Sample (M) (Magnetic Strength: 5.2 kg, Magnet Length (Lₘ): 0.35 m, Flowrate (v): 0.554 m/s, Initial Concentration CaCO₃ (Caᵢ): 0.004 M, Sample Volume (V) 240 mL, and Temperature: 28°C).
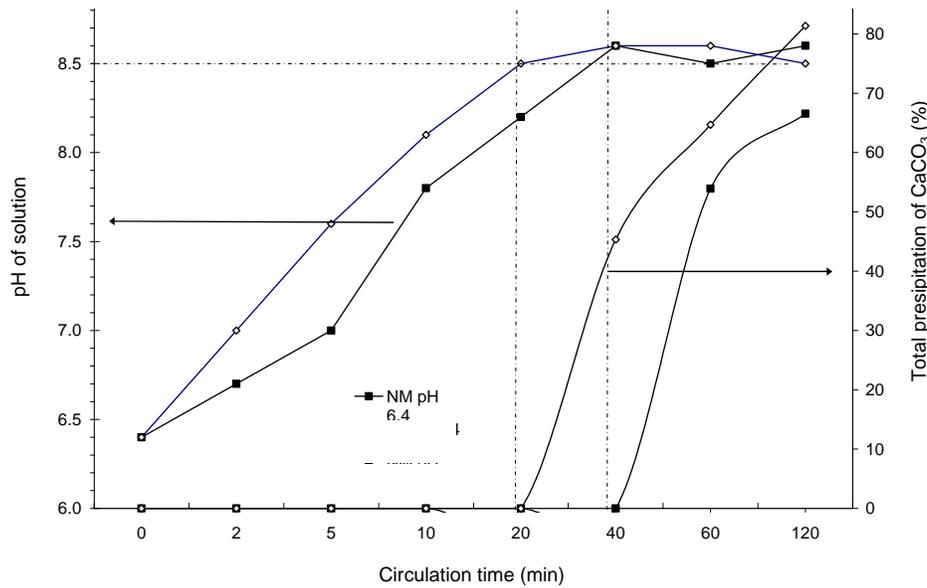
Figure 3. The Total Precipitation of CaCO₃ the pH of Solution (B : 5.2 kg, Lₘ 0.35 m. v : 0.554 m/ s, Caᵢ : 0.004 M, Initial pH of Solution: 6.4, V : 240 mL, and T : 28°C).

Flow rate. Figure 4 shows the effect of flow rate in CaCO₃ precipitation on magnetic and non magnetic treatments. CaCO₃ precipitation increases with increasing flow rate. This is due to the collision probability of ions or particles increases with increased circulation time hence raising CaCO₃ precipitation. Magnetic treatment has always gives effect of higher CaCO₃ precipitation than non-magnetic treatment for all flow rate curves as illustrated in Figure 4.

The flow rate does not influence the circulation time and the magnetization time. Figure 4 show that the increasing of flow rate increases the percentage of total precipitation of CaCO₃.

The increasing of flow rate causes the mechanical agitation to increase. Therefore the mass transfer rate of CO_2 from liquid phase to gas phase will increase with the increase of the pH of solution. The increasing of pH of solution increases the super-saturation of the solution (δ_s) which causes the increasing the amount of CO_3^{2-} ion. Therefore, the precipitation of CaCO₃ is increasing also.

Figure 4 and table 1 show that the total precipitation of CaCO₃ of the magnetized sample is higher than the non-magnetized sample's. The higher the flow rate, the higher also the percentage of the increase of the relative precipitation between magnetized sample and the non-magnetized sample; just as it shows on table 1. Lorentz's force causes the ion-shifting effect which increases the interaction between ions. The amount of the Lorentz force (F) which experienced by the particle with charge q that moves perpendicular across the
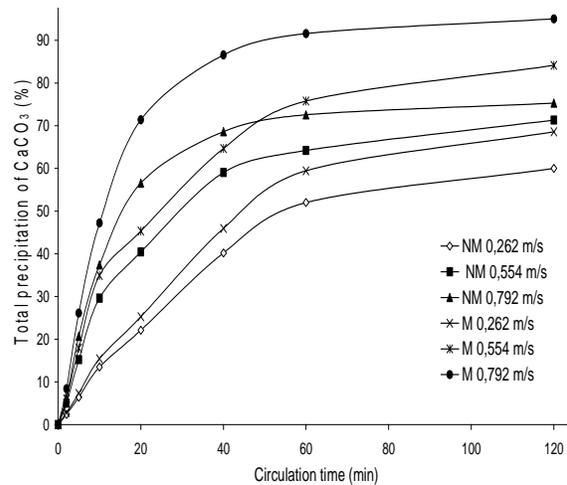
Figure 4. The Influence of Flow Rate Toward the Total Precipitation of CaCO₃ (B : 5.2 kg, Lₘ 0.35 m, Caᵢ: 0.004 M, Initial pH of Solution 64, V : 240 mL and T : 28°C).

magnetic field with magnetic strength B and velocity V is formulated as F = q .v. B. The increasing of flow rate increases the effect of Lorentz force which it shown by the increasing of the CaCO₃ precipitation.

Magnetic strength. Lorentz force effect toward the CaCO₃ precipitation is a direct function from the magnetic field strength that is given. Figure 5 shows the increasing of the percentage of total precipitation of CaCO₃ as the magnet strength increases.

Table 1. **The Percentage of the Increase of the Relative Precipitation of CaCO₃ Toward the Increase of the Flow Rate at 120 Minute of Circulation (B : 5.2 kG, L_m 0.35 m, v : 0.554 m/ s, Ca_i : 0.004 M, Initial pH of Solution 6.4, V : 240 mL, and T : 28°C).**

Solution sample	Total precipitation of CaCO₃ at 120 minutes of circulation (%)		
	Flow rate 0.262 m/s	Flow rate 0.554 m/s	Flow rate 0.792 m/s
Magnetized sample (M)	68.6	84.2	95.0
Non-magnetized sample (NM)	60.0	71.3	75.3
Percentage of the increase of the relative precipitation: 100 x (M- NM)/NM	14.3	18.1	26.2

Table 2. **The Percentage of the Increase of the Relative Precipitation of CaCO₃ Toward the Increase of the Magnetic Field Strength at 120 Minute of Circulation (L_m 0.35 m. v : 0.554 m/ s, Ca_i : 0.004 M, Initial pH of Solution 6.4, V: 240 mL and T : 28°C)**

Solution sample	Total precipitation of CaCO₃ at 120 minutes of circulation (%)		
	2 kG	4 kG	5.2 kG
Magnetized Sampel (M)	80.1	82.8	84.2
Non-magnetized sample (NM)	71.3	71.3	71.3
Percentage of the increase of the relative precipitation: 100 x (M- NM)/NM	12.3	16.1	18.1

Tabel 2 shows that there is an increasing of percentage of the increase of the relative precipitation between magnetized (M) sample and non-magnetized (NM) sample as the magnetic field strength increases. Table 1 and table 2 prove that the increasing of the velocity v and the magnetic field strength B has an impact on the increasing of precipitation of CaCO₃. It supports the hypothesis that the Lorentz force is the factor which responsible on the increasing precipitation of CaCO₃ in magnetized CaCO₃ solution at dynamic fluid circulation

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Magnetization time. Circulation time has a relation to magnetization time in which and the magnetization time will increase by longer of circulation time. Magnetization time (t_m) is duration in which sample is exposed to magnetic field, which is a function of Circulation time (T_c), cross sectional area of pipe (A), volume sample (V), magnet length (l_m). The correlation has been formulated as follows:

$$t_m = \frac{A\, L_m\, t_s}{V} \tag{4}$$

The increasing of circulation time will proportionally increase the magnetized time. On this experiment, the
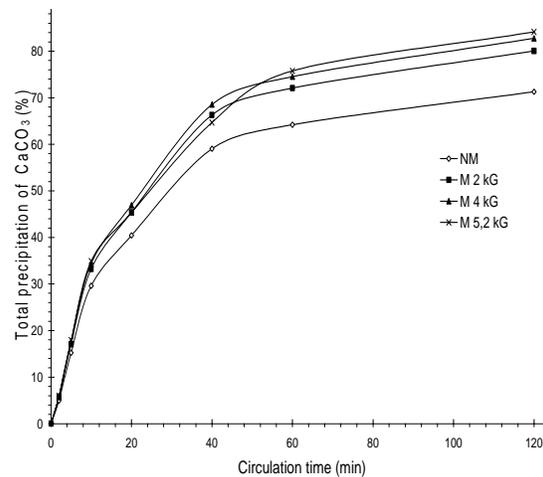
Figure 5. **The Affect of the Magnetic Field Strength Toward the Total Precipitation of CaCO₃ (L_m: 0.35 m, v: 0.554 m/s, Ca_i: 0.004 M, Initial pH of Solution: 6.4, V: 240 mL, and T: 28°C).**

magnetization process is been done at the beginning of the circulation with time variation of 30, 60, 90, 120, 150 and 7200 seconds. The circulation itself is still done for 120 minutes on each of the magnetized time variance. It is done to observe the magnetization effectiveness.

Table 3 shows that the circulation time using magnetization reach the optimum value at 1.5 minutes (90 seconds). Using the equation (1), the time for the sample to be exposed with magnetic field (t_m) for 90-seconds of circulation time (t_s), 0.35 m of the length of magnet (L_m), 240 mL of the sample volume (V), and 0.000113 m² of the pipe surface area (A), and effective magnetization time is 14.8 s.

CaCO₃ precipitation after Magnetization and circulation

The solution which is used on this stage is on the low supersaturated condition with the pH of 6.4 where the circulation magnetization process is done for just 10 minutes hence the precipitation has not occurred. The sample is moved into reaction chamber to precipitate statically, and continued with the precipitation process on the static chamber for 96 hours. Figure 6 shows that there is an increasing of the amount of precipitation of $CaCO_3$ as the strength of magnetic field increases. The magnetization suppresses the formation of the nucleus that is seen from the beginning moment of the long precipitation.

The time where precipitation starting to occurred is called nucleation time. The non-magnetized sample has longer T_n which is above 12 hours, while the magnetized sample with magnetic strength of 2 kg, 4 kG, and 5.2 kg, each of them has T_n of 12 hours, 8 hours, and 4 hours as shown in figure 6. The result shows that the solution sample that has been magnetized has an ionic character that easier to form the nucleus of $CaCO_3$.

The effectiveness of magnetization toward $CaCO_3$ from solution sample at pH 6.4 (figure. 2) is able to be observed after the magnetization process is over. The

Table 3. Effect of Magnetization Time on Total Precipitation of $CaCO_3$ (B : 5,2 kG, L_m 0,35 m. v : 0,554 m/ s, Ca_i : 0,004 M, Initial pH of Solution 6,4, V : 240 mL and T : 28 ^oC)

Circulation Time	Total precipitation of $CaCO_3$ (%) Circulation time with magnetic field						
		30 seconds	60 seconds	90 seconds	120 seconds	150 seconds	7200 seconds
	NM	M	M	M	M	M	M
0 minutes	0	0	0	0	0	0	0
2 minutes	5.0	5.6	5.8	5.9	6.0	6.1	6.0
5 minutes	15.2	17.4	17.6	17.8	17.9	18.0	17.9
10 minutes	29.6	33.8	34.4	34.7	34.8	34.8	34.9
20 minutes	40.4	43.2	44.4	45.0	45.1	45.2	45.3
40 minutes	59.1	62.2	63.7	64.5	64.6	64.7	64.7
60 minutes	64.2	72.3	74.4	75.5	75.6	75.6	75.8
120 minutes	71.3	80.2	82.7	84.0	84.2	84.3	84.2
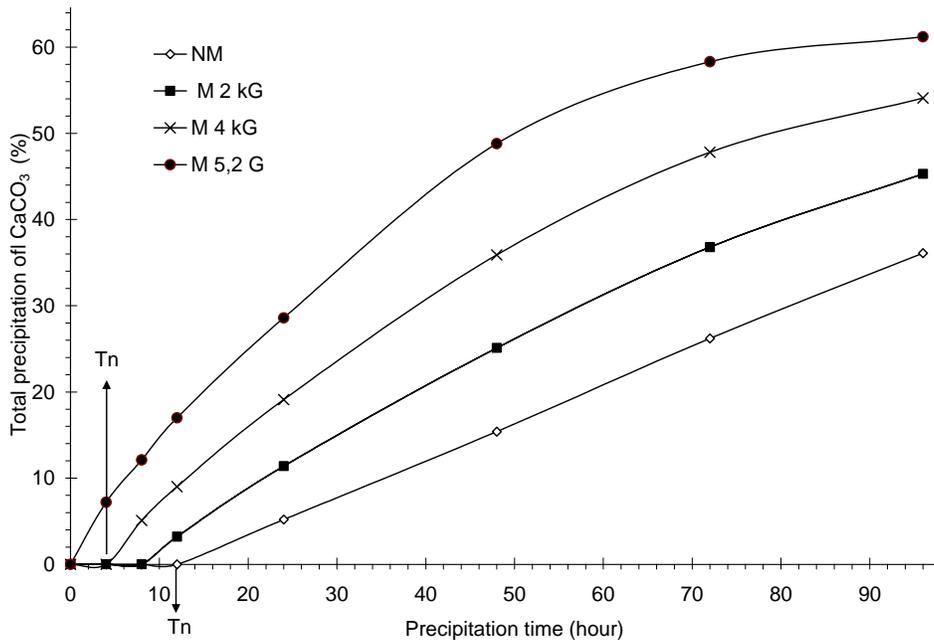
Figure 6.   The Affect of Magnetic Field Strength Toward the Toward the Total Precipitation of $CaCO_3$ (t_s: 10 Minutes, L_m: 0.35 m, v: 0.554 m/s, Ca_i: 0.004 M, Initial pH of Solution: 6.4, V: 240 mL and T: 28°C).
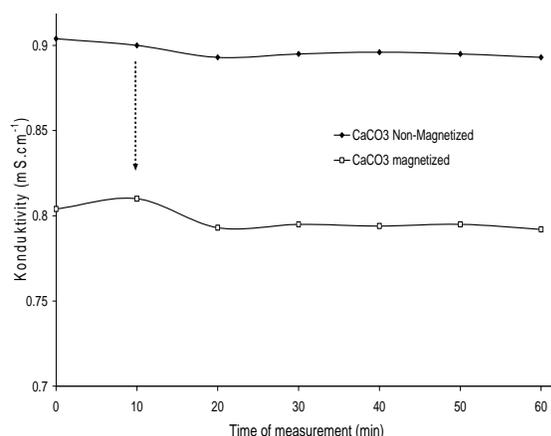
Figure 7. **The Affect of Magnetic Field on Solution Conductivity of CaCO$_3$ after 10 Minutes of Circulation (B: 5.2 kg, L$_m$: 0.35 m, v: 0.554)**

effect of magnetic field that appears after the magnetization process is known as magnetic memory effect. Fathi [7] thinks that the magnetic field causes the ion bonding process to form cluster (pre-nucleation stage) as the result of the existence of ions electrostatic that has been exposed with magnetic field. As the solute CO$_2$ looses free and the pH of solution increases, the solution super-saturation increases. Hence the clusters that have been formed will get enough energy to precipitate.

Figure 7 shows that there is a decreasing of conductivity value between magnetized sample and non-magnetized sample. It shows that the magnetization of CaCO$_3$ before precipitation occurred causes the ion hydrate interaction to decreases. The effect of ion hydrate interaction of solution as a function of solution conductivity has been completely reported of Holysz [10].

4. Conclusion

This research explains the effect of magnetic field on CaCO$_3$ precipitation on every level of solution super-saturation as pH function. At high super-saturation, (pH 8.5), magnetization will cause the ion interaction to increase which shown with the increasing of the

precipitation of CaCO$_3$ on magnetization circulation. The increasing of flow rate and the magnetic field strength will increase the magnetic field effect on increasing the precipitation of CaCO$_3$.

The effect of magnetic field occurs only on the first 90 seconds of the circulation process for the magnetic field strength of 5.2 kg, flow rate of 0.552m/s, length of magnet of 0.35 m. initial concentration of Ca^{2+} of 0.004 M, and sample volume of 240 mL, while the circulation effect is still occurs during 120 minutes of circulation process.

At low super-saturation (pH 6.4) magnetization will weaken the ion hydrate interaction. It causes the nucleation time goes faster, and increase the amount of precipitation after the magnetization process.

References

[1] V. Kozic, L.C. Lipus, Journal Chem. Inf. Comput. Sci., 43 (2003) 1815.
[2] S. Baker, S.J. Judd, Water Research, 30/2 (1996) 247.
[3] A.D. Kney, S.A. Parsons, Water Res., 40 (2006) 517.
[4] K. Higashitani, A. Kage, S. Katamura, K. Imai, S. Hatade, Journal ournal Colloid and Interface Science. 156 (1993) 90.
[5] Lundager, Madsen, Journal of Crystal Growth, 267 (2004) 251-255.
[6] C. Gabrielli, R. Jaouhari, G. Maurin, M. Keddam, Water Res. 35 (2001) 3249.
[7] A. Fathi, M. Tlili, C. Gabrelli, G. Maurin, M. Ben Amor, Water Res. 40, (2006) 1941.
[8] N. Saksono, A. Fauzi., S. Bismo, A. Manaf, R.W. Soemantojo, 14th Regional Symposium Chemical Engineering Proceeding, Yogyakarta, 2007.
[9] N. Saksono, A.S. Elisabeth, S. Bismo, R.W. Soemantojo, A. Manaf, Jurnal Sain Materi Indonesia, Edisi Khusus Oktober. (2007), p.196-201.
[10] L. Holysz, E. Chibowski, S. Aleksandra, Journal of Colloid and Interface Science, 316 (2007) 2065-2070.