EFFECTS OF pH ON CALCIUM CARBONATE PRECIPITATION UNDER MAGNETIC FIELD

Nelson Saksono1*), Yuliusman1, Setijo Bismo1, Roekmijati W. Soemantojo1, and Azwar Manaf2

1. Department of Chemical Engineering, Faculty of Engineering, University of Indonesia, Depok 16424, Indonesia
2. Department of Physics, Faculty of Mathematics and Science, University of Indonesia, Depok 16424 Indonesia

*) E-mail: nelson@che.ui.ac.id

Abstract

Magnetic field effect on CaCO3 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 CaCO3 precipitation in high and low super-saturated CaCO3 solution by varied pH CaCO3 solution using circulation flow fluid system. The observation results in the high super saturated solution (pH 8.5) showed the increase of precipitated CaCO3 in magnetized solutions compared to those in non-magnetic solution during circulation process. In the low super-saturated CaCO3 solution (pH 6.4) it was found that magnetic treatment increased CaCO3 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 CaCO3 solution, magnetic field weakens hydrate ion interaction which indicated by decreasing of the conductivity of solution. It increases the precipitation of CaCO3 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 CaCO3 precipitation process is an equilibrium and slowing process. Increase of pH due to CO2 release in solution will push precipitation of CaCO3 as follow:

$$\text{Ca}^{2+} + 2\text{HCO}_3^- \rightleftharpoons \text{CO}_2 + \text{CaCO}_3(s) + \text{H}_2\text{O}$$

(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 CaCO3 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
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.

**CaCO$_3$ 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:

$$\text{CO}_2(aq) + \text{CaCO}_3(s) + \text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^-$$ (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 Precipitation of CaCO$_3$ on Non-Magnetized Sample (NM) and Magnetized Sample (M) (Magnetic Strength: 5.2 kg, Magnet Length ($L_m$): 0.35 m, Flowrate ($v$): 0.554 m/s, Initial Concentration CaCO$_3$ ($C_{ai}$): 0.004 M, Sample Volume ($V$) 240 mL, and Temperature: 28°C).](image-url)
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, Lₘ₀ 0.35 m, v : 0.554 m/ s, Cₐ₁ : 0.004 M, Initial pH of Solution 6.4, V : 240 mL, and T : 28°C).

<table>
<thead>
<tr>
<th>Solution sample</th>
<th>Total precipitation of CaCO₃ at 120 minutes of circulation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Flow rate 0.262 m/s</td>
</tr>
<tr>
<td>Magnetized sample (M)</td>
<td>68.6</td>
</tr>
<tr>
<td>Non-magnetized sample (NM)</td>
<td>60.0</td>
</tr>
<tr>
<td>Percentage of the increase of the relative precipitation: 100 x (M- NM)/NM</td>
<td>14.3</td>
</tr>
</tbody>
</table>

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 (Lₘ₀ 0.35 m, v : 0.554 m/ s, Cₐ₁ : 0.004 M, Initial pH of Solution 6.4, V: 240 mL, and T : 28°C)

<table>
<thead>
<tr>
<th>Solution sample</th>
<th>Total precipitation of CaCO₃ at 120 minutes of circulation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 kG</td>
</tr>
<tr>
<td>Magnetized Sample (M)</td>
<td>80.1</td>
</tr>
<tr>
<td>Non-magnetized Sample (NM)</td>
<td>71.3</td>
</tr>
<tr>
<td>Percentage of the increase of the relative precipitation: 100 x (M- NM)/NM</td>
<td>12.3</td>
</tr>
</tbody>
</table>

Table 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 flow system.

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 (tₘ) is duration in which sample is exposed to magnetic field, which is a function of Circulation time (tₖ), cross sectional area of pipe (A), volume sample (V), magnet length (Lₘ). The correlation has been formulated as follows:

\[ tₘ = \frac{A Lₘ tₖ}{V} \]  (4)

The increasing of circulation time will proportionally increase the magnetized time. On this experiment, the 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 (tₘ) for 90-seconds of circulation time (tₖ), 0.35 m of the length of magnet (Lₘ), 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.
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 0.552 m/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