CaSO₄ Scale Inhibition by a Trace Amount of Zinc Ion in Piping System

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Abstract. Usually, a small steam generator is not complemented by equipment such as demineralization and chlorination process apparatus since the economic aspect was a precedence. Such phenomenon was uncovered in a case study of green tea industrial process in which the boiler capacity was not more than 1 ton/hour. The operation of the small boiler affected the scaling process in its piping system. In a year operation, there was already a large scale of calcium attached to the inner surface of the pipe. Such large scale formed a layer and decreased the overall heat transfer coefficient, prolonged the process time and decreased the production. The aim of the current research was to solve the problem through a laboratory research to inhibit the CaSO₄ scale formation by the addition of trace amounts of zinc ion. This research was conducted through a built in-house experimental rig which consisted of a dosing pump for controlling the flow rate and a thermocouple to control the temperature. Synthesis solution was prepared with 3,500 ppm concentration of CaCl₂ and Na₂SO₄. The concentration of zinc was set at 0.00; 5.00 and 10.00 ppm. The data found were characterized by scanning electron microscopy (SEM) to analyze crystal polymorph as the influence of zinc ion addition. The induction time was also investigated to analyze the nucleation time, and it was found on the 9th, 13th, and 19th minute of the zinc ion addition of 0.00, 5.00 and 10.00 ppm. After running for a four-hour duration, the scale grow-rate was found to be 5.799; 5.501 and 4.950 x 10⁻³ gr/min for 0.00; 5.00 and 10.00 ppm of zinc addition at 50°C.

Keywords: CaSO₄, zinc, inhibition, scale, piping system.

1. Introduction
This research was conducted based on a case study of a small steam generator operation in a green tea industry where the product decreased extremely after a year operation. The main cause of the decreased product was identified due to the scaling process occurred on the inner surface of the boiler piping system. A small steam generator usually is not completed by any equipment such as demineralization and chlorination processed apparatus since the economic aspect was precedence. That is why the calcium scale can pile up easily in the inner surface of the pipe. When the scale was analyzed through SEM EDX, the results showed that scale composition consisted of CaSO₄ and CaCO₃ in majority and MgSO₄ in the minority. In the current research, the CaSO₄ scale would be the focus of this research since this type of scale was tough to clean.

The existence of CaSO₄ scale in piping system led to a disturbance of the system such as decreased overall heat transfer coefficient, prolonged process time and increased economic cost [1, 2, 3]. Many efforts to inhibit CaSO₄ scale have been conducted on the physical and chemical factors. The flow rate...
and temperature are classified as physical factors [4,5], otherwise impurities and additive classified as
chemical factors [6,7]. Usually, the appropriate method to inhibit scale growth is performed on the
chemical factors through the addition of the trace amount of a chemical substance [1].

In order to inhibit nucleation and crystal growth, the addition of the trace amount of a chemical
substance in a supersaturated solution is a commonly employed technique [3]. Many additives have
been used to inhibit those scale, such as citric acid, nitric acid, malic acid[1,2,8] and double-
hydrophilic block copolymers [9] also phosphate component [3] and polyelectrolyte [10]. The
presence of additives could affect the structure and shape of many crystals such as CaSO₄, BaSO₄ and
ZnO [9] and also induce crystal morphology and crystal size [4].

In the current research, Zinc ion was used as the additive to inhibit the CaSO₄ scale. As an
inhibitor, zinc ion must have some affinity with the host crystal to be adsorbed on its surface and to be
able to modify its behavior [3]. The effects of zinc ion as an inhibitor of CaSO₄ scale formation from
over-saturated solutions would be the focus of this research.

2. Experimental Method

2.1. Material
CaSO₄ scaling process occurred synthetically by mixing CaCl₂ with a Na₂SO₄ solution, which was
supplied by Merck®, according to the reaction as Equation (1).

\[
\text{CaCl}_2 (aq) + \text{Na}_2\text{SO}_4 (aq) \rightarrow \text{CaSO}_4(s) + 2\text{NaCl} (aq)
\]  

(1)

The concentration of calcium solution was defined of as much as 3.500 ppm, prepared by dissolving
77.175 g of CaCl₂ to 6,000 mL of demineralized water. Sodium solution was prepared by dissolving
55.65 g of Na₂CO₃ to 6,000 mL of demineralized water, too. The straining process of the solution was
done two times by 0.22 μm microspore® paper to ensure the unwanted particles remain in the
solution. Each of the solutions was kept in each covered vessel to avoid dust and other contaminants.
Weighing, mixing and straining processes must be done carefully to ascertain that there is not a bias in
the research. The weighing process was done via Ohaus AR-2140 analytical balance in the accuracy of
0.1 mg. CHEMFEED Ca-92683 dosing pump did the mixing process.

2.2. Experimental design and characterization
As the aim of the research was to uncover the influence of zinc ion on CaSO₄ scale formation, the
research design was defined as described below. The chosen flow rate was at 35 mL/min. The selected
temperatures were 27; 40 and 50 ºC and the chosen Ca concentration was at 3,500 ppm for all
experiments. Zinc ion was found from ZnCl₂ with the zinc concentration varied of 0.00; 5.00 and
10.00 ppm. The CaSO₄ scale grow-rate was measured when the experiment was affected by the
additions of 5.00 and 10.00 ppm zinc ion and then was compared with the experiment without zinc ion.
The different scale deposition was pointed as being influenced by an additive on the deposition rate.
Induction time was also measured in the kinetic study to show the effect of the additive on the
nucleation process. Crystal polymorph was characterized via scanning electron microscopy (SEM) to
show the different crystal shape due to the zinc ion addition. Crystal component was investigated
through SEM EDX to demonstrate the alteration of crystal structure along with the zinc ion addition.

2.3. Experimental rig
To conduct the experiment, a built in-house experimental rig with the control of an electronic program
was employed. The employment is shown schematically in Figure 1. The rig consisted of two vessels,
each of which contained CaCl₂ and Na₂CO₃ solutions, respectively. A stirrer was attached in each
vessel under computer program control and automatically set at 40 rpm to establish a homogeneous
solution. All of the solutions in each vessel were pumped by CHEM-FEED Ca-92683 dosing pump (5)
similarly in the flowrate of 35 mL/min, and the solutions met in the test pipe section (6). To set the
temperature, an electrical heater (3) was immersed in the solution and controlled by a sensor (4) in order to keep stable. When the various temperatures were set,

![Figure 1. Experimental rig](image)

the computer program sent a command to the pump to delay the operation for a couple of minutes until the predetermined temperature was achieved. In the test pipe section, four pairs of coupons were inserted to the parts where the precipitation process needed to form. The pipe was attached to a table (7) vertically. The conductivity of the solution after leaving the coupon was measured by TDS meter supplied by Komatsu (8). The data were collected through the computer program (9), and the solution was then sent to the vessel (10).

2.4. Phreeqc prediction
The Phreeqc prediction on the scaling potential showed that there were not any differences in the experiments with an additive and without an additive. The data input of the solution without Zinc ion was collected as follow, temp 25; pH 7; default units g/kgW; density 1; Ca 1.75; Cl 3.105; H(0) 0.175; O(0) 0.7; S(6) 4.2; Na 2.1 and water 1 kg. Otherwise, input data with 10 ppm of Zinc ion was done such as: temp 25; pH 7; units g/kgW; density 1; Ca 1.75; Cl 3.105; H(0) 0.175; O(0) 0.7; Na 2.1; S(6) 4.2; Cu 0.01 and water 1 kg. The specific conductance of the solutions in their initial condition showed differences i.e. 14.102 μS/Cm and 14.082 μS/Cm respectively in the solutions with and without 10 ppm Zinc ion.

The phreeqc program predicted the potential of crystal phase produced through the analysis of the amount of each saturation index. The prediction showed that there were not any differences between the experiments without and with zinc ion performed thermodynamically. Thus, the presence of 10 ppm zinc ion did not have any effects on the solution in its thermodynamic.

3. Results and discussion
The results of this experiment consisted of several forms of data such as induction time, the scale grow rate, inhibition rate, crystal polymorph and crystal structure. All data were measured in the absence and in the presence of zinc ion to show the influence of the zinc ion addition. Furthermore, the data
were then compared with each other, and the differences found in those data stood as the effect of the zinc ion addition.

3.1. Induction time
The time of firstly measurable change of conductivity is called as an induction time [11]. The measurable change of conductivity showed that some ions in the solution have been reacted and precipitated as scales. Induction time also describes the time needed to produce a nucleus which is also called as nucleation time [12].

To identify the induction time, the conductivity of the solution after leaving the coupon was measured by conductivity meter and acquired by a computer program in every two seconds. After being calculated in the mean value of every one minute, the data were plotted to show the measurable change of conductivity. To describe the influence of the addition of zinc ion to the solution, a conductivity versus time was plotted in a graph of the zinc ion concentration varied to 0.00, 5.00 and 10.00 ppm as shown in Figure 2.

![Figure 2. Plot of conductivity over the time](image)

In this experiment, the induction time at 27 °C was found to be 21, 25 and 31 minutes of zinc ion addition in 0.00, 5.00 and 10.00 ppm. For the experiment at 40 °C the induction time was found in the 15th, 19th, and 23rd minute of zinc ion addition in 0.00, 5.00 and 10.00 ppm. When the temperature was set at 50 °C, the induction time was found to be at the 9th, 13th and 19th minute of zinc ion addition in 0.00; 5.00 and 10.00 ppm. These data show close agreement with other research, such as the research published by Ang [7].

The extended nucleation time showed the evidence that the addition of zinc ion in 5.00 and 10.00 ppm has successfully inhibited the nucleation process of CaSO₄ scale formation. The data also showed the influence of zinc ion addition on induction time in various temperatures which successfully inhibited the nucleation process at higher temperatures. As the nucleation time was longer than normal, the scale formed could be fewer. The following section would discuss the scale grow rate and inhibition rate section in detail.

3.2. CaSO₄ scale grow rate
CaSO₄ scale, as the product of precipitation process, was found in the coupon. The assessment of the CaSO₄ scale grow as the influence of the zinc ion addition was conducted in three temperature conditions i.e. 27; 40 and 50 °C meanwhile the zinc ion concentration varied to 0.00, 5.00 and 10.00 ppm. The result was expressed in a graph such as shown in Figure 3.
The scale grow rate was calculated as the mass of the coupon which was formed in a 4-hour duration and was then converted in the unit of gr/min. When the temperature was set at 27 °C and zinc ion was as much as 0.00; 5.00

![Figure 3. CaSO₄ scale grow rate in various zinc concentration and temperatures](image)

and 10.00 ppm, the scale grow rates were found to be as much as 0.755; 0.728 and 0.618 x 10⁻³ g/min. The experiment with the temperature at 40 °C and zinc ion of as much as 0.00, 5.00, and 10.00 ppm resulted in the scale grow rates of as much as 2.942; 2.860 and 2.687 x 10⁻³ gr/min. the scale grow rates found in the experiment at the temperature of 50 °C and zinc ion varied of 0.00, 5.00, and 10.00 ppm were 5.799, 5.501 and 4.950 x 10⁻³ g/min.

The data showed that CaSO₄ scale grow rate was decreased by the addition of trace amount of zinc ion even at the amount of 5.00 and 10.00 ppm and in various temperatures. These inventions showed the evidence that the addition of the trace amount of zinc ion has successfully inhibited the CaSO₄ scale grow rate at different temperatures. The decrease of the CaSO₄ scale growth was in conformance with the research published by Ang [7].

3.3. Inhibition rate
In this experiment, an inhibition rate was determined as the different scale growth between the experiment of 5.00 and 10.00 ppm and the experiment of 0.00 ppm of zinc ion of which result is presented in Figure 4.
Figure 4. Inhibition rate of CaSO₄ scale growth in various zinc concentrations and temperatures

As for the measurement, the inhibition rates of CaSO₄ scale growth which were developed through the experiment at 27 ºC were 0.00, 0.298 and 0.829 x10⁻³ gr/min of zinc ion addition in the amount of 0.00, 5.00 and 10.00 ppm.

The inhibition rates of CaSO₄ scale growth of the experiment at 40 ºC were 0.00, 0.082 and 0.255 x 10⁻³ g/min of zinc ion addition of as much as 0.00, 5.00 and 10.00 ppm. The inhibition rates of CaSO₄ scale growth of the experiment at 50 ºC were 0.00, 0.027 and 0.137 x 10⁻³ g/min of zinc ion addition varied to 0.00, 5.00 and 10.00 ppm.

The graph of inhibition rate as the addition of zinc ion showed that the inhibition rate increased as the rising temperature. It has been broadly understood that calcium solubility will decrease when the temperature increase [7] as solubility is defined as the maximum amount of a solution that will dissolve in a given quantity of solvent at a specific temperature [13]. Thus, the rising temperature will be followed by the decreasing solubility. That is why the CaSO₄ scale-grow rate increases as the rising of temperature could be accepted. Moreover, when the inhibition rate increases as the rising CaSO₄ scale-grow rate could also be tolerated.

3.4. Crystal polymorph

The polymorph of CaSO₄ crystal was found after a characterization by scanning electron microscopy (SEM) regarding investigating the influence of zinc ion addition to the crystal polymorph. Figure 5a) shows the CaSO₄ crystal polymorph in the experiment without zinc ion, meanwhile figure 5b) shows the CaSO₄ crystal polymorph in the experiment with the addition of 10.00 ppm of zinc ion.
Both of the crystal polymorphs showed that they were not different in their shapes and their polymorphs. Refer to crystal system, SEM images in figure 5a and 5b indicate that the crystal polymorphs are rhombohedral [14] as well as the usual. However, it could be distinguished from their dimension that the crystal polymorph in the experiment with 10.00 ppm zinc ion has shorter needles and a smaller dimension.

The data show the mechanism of zinc ion in inhibiting the CaSO$_4$ scale growth. As the growth of crystal dimension was inhibited, CaSO$_4$ scale mass was decreasing. This phenomenon has a close agreement with the phreeqc prediction. The addition of zinc ion does not have any differences in the thermodynamic as predicted by phreeqc program. So, the inhibition mechanism was not based on its thermodynamic but through another mechanism i.e. through covering the crystal surface by a zinc ion. This phenomenon explained how the crystal growth was inhibited by the presence of zinc ion [7].

3.5. Crystal composition

The crystal composition was investigated through the characterized CaSO$_4$ scale by SEM EDX. The results consisted of crystal spectrum and composition in atomic percent (at %) also in weight percent (wt %). The crystal spectrum such as shown in figure 6 shows the atomic composition and its peak.

The spectrum shows the structure of the crystal components i.e. Ca, S and O. The existence of Na and Cl ions in the crystal composition could be caused by the trapping of those ions in the inner crystal. The composition of CaSO$_4$ shows that the crystal was pure and the process was done carefully [15]. The crystal was not found in its stoichiometry, which can be caused by the presence of Na and Cl ions in the crystal.
4. Conclusions

Based on a case study on green tea production of which steam generator piping system was hampered by the presence of calcium scale, this laboratory experiment had been employed. The experiment to inhibit CaSO$_4$ scale by a trace amount of zinc ion was successfully conducted. The addition of zinc ion of 5.00 and 10.00 ppm significantly decreased the CaSO$_4$ scale grow rate from 5.799 to 5.501 and 4.950 x $10^{-3}$ g/min. As the investigation, the inhibition rates of CaSO$_4$ scale growth of the experiment at 27°C were 0.00, 0.298 and 0.829 x $10^{-3}$ g/min for zinc ion addition varied to 0.00, 5.00 and 10.00 ppm. The inhibition rates of CaSO$_4$ scale grow of the experiment at 40°C were 0.00; 0.082 and 0.255 x $10^{-3}$ g/min for zinc ion addition of 0.00, 5.00 and 10.00 ppm. The inhibition rates of CaSO$_4$ scale grow in the experiment at 50°C were 0.00, 0.027 and 0.137 x $10^{-3}$ g/min for zinc ion addition of 0.00, 5.00 and 10.00 ppm. The crystal polymorph remained in rhombohedral and showed that the zinc ion addition of 5.00 and 10.00 ppm does not have any effects on its polymorph, but their dimensions were changed. The microanalysis of the CaSO$_4$ crystal show that the crystal component was not in the stoichiometry because of the presence of Na and Cl ions in the inner part of the CaSO$_4$ crystal.

5. References

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Figure 6. Spectrum of CaSO$_4$ crystal composition in the experiment without zinc ion
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