The Scale Formation of Barite (BaSO₄) from Laminar Flowing Water in The Presence of Tartaric Acid and Ba²⁺ Concentration Variation of Solution

F Fatra¹, G Ivanto¹, N S Dera¹, S Muryanto¹,² and A P Bayuseno¹

¹ Department of Mechanical Engineering, University of Diponegoro, Tembalang Campus, Semarang, 50275, Indonesia
² Department of Chemical Engineering, UNTAG University, Bendhan Dhuwur Campus, Semarang, 50233, Indonesia

Email: Fathrafahmi@gmail.com

Abstract. The barite (BaSO₄) scale is a mineral deposit that can be precipitated during the process of drilling oil and gas in the offshore. Deposit scale in pipes can cause a narrowing of the diameter of pipes, and can reduce water flowing in the pipe. The aim of this study is to investigate the effect of tartaric acid additive and Ba²⁺ concentration on the growth of the scale formation of barite in the laminar flow of the piping system. Solution forming barite crystal was prepared by mixing equimolar solutions of barium chloride (BaCl₂) and sodium sulfate (Na₂SO₄) with concentration variations of Ba²⁺ of 3000, 3500, 4000, 4500, and 5000 ppm. The flow rate of solution is 40 ml/min at temperature of 50 °C. Various concentrations of tartaric acid (C₄H₆O₆) of 0 ppm, 5 ppm and 10 ppm were added to the solutions. The formation of barite from the solution was observed by ion conductivity measurement. The obtained barite crystals before and after adding tartaric acid were dried and characterized by using SEM/EDX for morphology and elemental analysis, and XRD for phase identification. The SEM results show that the morphology of the crystals are star-like particles, while XRD analysis confirmed that the barite crystals were produced during the experiments are high purity. Moreover, the tartaric acid can inhibit the crystal growth of barite.

Keywords: Barite, tartaric acid, laminar flowing water, morphology crystal

1. Introduction

Barium sulphate (barite) has been known as a scale deposit that is particularly prevalent in the pipeline of oil and gas industry [1, 2]. Scaling of barite in oil fields may be due to the presence of insoluble barium compounds in water. Once the soluble barium compounds exceed its solubility limit, they will crystallize from the solution. The precipitate and crystal growth may consequently reduce the diameter of the pipe and hence result in inhibition of fluid flow in the pipe system. The blocking flow of water may lead to increase temperature and pressure so that the pipeline may rupture [3]. Therefore, the scale formation may be prevented by softening and acquisition of mineral water. However, the use of demineralized water in the industry may improve the operating costs [4].

In general, the scale formation can be prevented by using acid as an inhibitor to lower the solution pH, control the inorganic compounds as well as the composition and the crystal morphology. Barite crystal growth can be controlled by the process of nucleation through the presence of chemical...
additives. Moreover, the removal of barite from the surface of pipes using high concentrations of acid may be not effective because the acid can increase the corrosion rate. Also, the use of chemical inhibitors containing phosphonate and carboxylate is quite dangerous, because these inhibitors will change the quality of water [5, 6]. Additionally, phosphonates are not environmentally friendly. This present research proposes a new scale inhibitor to prevent the barite scale formation, which is more effective and environmentally friendly such as the tartaric acid [7]. The addition of this additive concentration has shown to be a significant influence on the growth of the barite crystals [8, 9].

This is to investigate the effect of the tartaric acid additive on the growth of the scale barite by using a pilot scale of laboratory rig. Here, the flow rate of water in the pipe and temperature were fixed constant. In this study, parameter variations of the solution and additive concentration were examined. The barite crystal products were then characterized by using SEM/EDX for morphology and elemental analysis, and XRD analysis for confirming the mineral. Inhibiting growth rate of the barite scale by the tartaric acid may be applied to the piping systems in the petroleum and gas industries.

2. Experimental and Method

2.1. Raw materials for preparing crystalline forming solutions

Materials, all with grade analytic powder (Merck TM), were selected in this experimental research consisting of BaCl2 and Na2SO4 crystals, distilled water and the tartaric acid (C4H6O6) with the analytical grade as an additive.

2.2. Experimental method for barite crystallization and materials characterization

In this present study, the mixing solution of BaCl2 and Na2SO4 as scale formation was diluted in the water to form barite scale. Barite crystals stick to the wall of the pipe to form a crust, while the NaCl crystals are dissolved in water. The barite formation may be presented as follows:

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

(1)

The experimental work was conducted according to the flow-chart diagram given in Figure 1. Variation of the Ba^{2+} concentration in the amount of 3000, 3500, 4000, 4500, and 5000 ppm was prepared in the solution. The flow rate and temperature were fixed during the work (40 ml/min and 50 °C). The tartaric acid in the amount of 0 ppm, 5 ppm, and 10 ppm was added in the solution during the experiments. The experiment was run by using the laboratory rig for scale formation described in elsewhere [10]. Barium scale formed in the absence and presence of additives was then examined by using XRD and SEM/EDX analysis.

XRD data were acquired by using a Bragg-Brentano diffractometer (D5005 SHIMATZU) operated on Cu-Kα radiation, and equipped by a graphite diffracted beam monochromatic, and a scintillation detector. The scan parameters (10-90 2θ°, 0.020 steps, 15 seconds/step) were recorded. The x-ray source was conventional sealed by X-ray tube operated at 50 kV and 40 mA. For selecting high intensity, incident and diffracted beam slits were fixed at 1.0 and 0.2 ° respectively. A PC-based search- match program (X’Pert plus Philips software) was used for identifying the mineral phases of precipitates through matching to the crystalline data included in the International Centre for Diffraction Data (ICDD)-PDF (powder diffraction file) database.

Furthermore, scanning electron microscopy (SEM) analysis on a JEOL DSM apparatus equipped with an EDX was conducted on the microstructure and morphology. The powder crystals were mounted on a circular metallic sample holder and subsequently sputtered with carbon for collecting imaging data.
3. Result and Discussion

3.1. Induction Time
The solution of BaCl₂ and Na₂SO₄ was met in the coupons to form barite scale. Once barite scale was formed, and then deposited on the wall of the coupon continuously for two hours. The scale mass results were obtained depending on the variation of testing parameters. This phenomenon can be seen from the measurement of conductivity for concentration variation of Ba²⁺ in the presence of 10 ppm additive (Figure 2). At Ba²⁺ concentration (5000 ppm), it shows that the crystallization reaction between BaCl₂ and Na₂SO₄ occurred for about 30 minutes. At this stage, drop in conductivity can be represented as the induction time. Moreover, the increasing Ba²⁺ concentration in the solution yielded the increasing induction period (the respective 34, 38, 42, and 48 min.) for 3500, 4000, 4500, and 5000 ppm respectively.
3.2. Mass scale produced from the solution

This experiment employed five variations of the Ba\textsuperscript{2+} concentration in solution (3000, 3500, 4000, 4500, and 5000 ppm), and three different concentrations of the tartaric acid (0, 5, and 10 ppm) were selected. Table 1 presents the mass scale of barite formed from the solution. It shows that the more Ba\textsuperscript{2+} concentration was available in the solution, the more scale mass was produced in the piping system. Nevertheless, the more tartaric acid was added, the crystal growth of barite was inhibited. Consequently, the scale mass products were reduced in the presence of additives.

Table 1. Mass scale precipitated from the solution in the presence of tartaric acid

| Concentration Ba\textsuperscript{2+} (ppm) | Flow Rate (ml/second) | Temperature (°C) | Tartaric Acid (ppm) | Mass of scale (gram) |
|------------------------------------------|-----------------------|-----------------|---------------------|---------------------|
| 3000                                     | 40                    | 50              | 0                   | 0.086               |
| 3000                                     | 40                    | 50              | 5                   | 0.082               |
| 3000                                     | 40                    | 50              | 10                  | 0.073               |
| 3500                                     | 40                    | 50              | 0                   | 0.103               |
| 3500                                     | 40                    | 50              | 5                   | 0.096               |
| 3500                                     | 40                    | 50              | 10                  | 0.090               |
| 4000                                     | 40                    | 50              | 0                   | 0.128               |
| 4000                                     | 40                    | 50              | 5                   | 0.120               |
| 4000                                     | 40                    | 50              | 10                  | 0.114               |
| 4500                                     | 40                    | 50              | 0                   | 0.158               |
| 4500                                     | 40                    | 50              | 5                   | 0.152               |
| 4500                                     | 40                    | 50              | 10                  | 0.144               |
| 5000                                     | 40                    | 50              | 0                   | 0.184               |
| 5000                                     | 40                    | 50              | 5                   | 0.176               |
| 5000                                     | 40                    | 50              | 10                  | 0.172               |

3.3. Microstructure of the scale

Barite crystal morphology examined by using SEM is given in Figure 3. The elemental analysis of the scale by using EDX is also presented in Figure 4.
Figure 3. Morphology Barite crystals, (a) the absence of additive and (b) the presence of additive for 10 ppm

It shows that the morphology of barite has a starlike crystal, which was obtained from the solution without additives and with additives. At all concentrations of Ba$^{2+}$ without and with additives, the same image of morphology was obtained, but the reduction of crystal size was noted in the presence of additives.

XRD analysis was also conducted to verify the mineral phase formed by comparing the measured data with the database of the International Center for Diffraction Data (ICDD). X-ray diffractogram results provided the peak intensity to be identified through the search-match procedure. Figure 4 shows the direct experimental evidence of barite crystals formed in the presence of 10 ppm tartaric acid and in the absence of the additive. The Powder Diffraction File (PDF) numbers of 04-012-5411 matched with all XRD patterns measured and in this study, and proved that the pure barite was precipitated from the solution.

Figure 4. X-ray diffractogram of the crystal product obtained from the solution

4. Conclusion
Experimental scaling of barite with variations in concentration of Ba$^{2+}$ (3000, 3500, 4000, 4500, and 5000 ppm), temperature 50 °C, a flow rate of 40 ml/min and the different concentrations of tartaric acid (0, 5, and 10 ppm) was performed. From the results of SEM, a visible star-like morphological for barite precipitated from the solution without and with additives can be observed. The presence of tartaric acid additive may inhibit the crystal growth of barite. It can also be explained that the decline
in the mass of barite may be due to the presence of tartaric acid. Although the scaling of barite was inhibited by tartaric acid additive affecting a little; the use of this additive from organic materials is environmentally friendly.

5. References
[1] Sorbie K S and Mackay E J 2000 Petroleum Sci Eng 27 85.
[2] Benton W J, Collins I R, Grimsey I M, Parkinson G M, Rodger S A, and Chem J 1993 Soc Faraday Disc 95 281.
[3] Asnawati 2001 Effect of Temperature Reaction Against phosphonate in Inhibitor scale on Oil Well Journal Basic Science 2 No 1 : 20.
[4] Sousa M F and Bertran C A (2014) New methodology based on static light scattering measurements for evaluation of inhibitors for in bulk crystallization Journal of Colloid and Interface Science 420 57-64.
[5] Wang, Moo Y, Chen Y X, Gunawan C, and Xu P G R 2010 Fast Precipitation of Uniform CaCO3 Nanospheres and Their Transformation to Hollow Hydroxyapatite Nanospheres Journal of Colloid and Interface Science 233 65 – 72.
[6] Franca J, Philip J, and Mark I O 2007 The Interaction of EDTA with Barite Journal of Colloid and Interface Science 316 553-561.
[7] Zahid A 1994 Inhibition of Barium Sulfate Precipitation : Effects of additives, Solution pH, and supersaturation China Ocean Press-Printed in Beijing 47 - 56
[8] Hennessy A J B and Graham G M 2002 The effect of additives on the co-crystallisation of calcium with barium sulfate J. Cryst Growth 237-239.
[9] Amer B M and Abu A M Y 2009 Laboratory Study on Precipitation of Barium Sulphate in Malaysia Sandstone Cores The Open Petroleum Engineering Journal 1 – 11.
[10] Muryanto S, Bayuseno A P, Sediono W, Mangestiyon W, and Sutrisno 2012 Development of a versatile laboratory project for scale formation and control Education for Chemical Engineers 7 e78–e84.

Acknowledgments
The authors are grateful to the Laboratory of Physical Metallurgy Diponegoro University which provided the facility during the experiment. The authors would like also to appreciate the useful comments and the kind suggestions from the anonymous reviewers.