Phase Analysis and Crystal Morphology of Barium Sulphate Precipitated from The Laminar Flowing Water

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

¹Mechanical Engineering Graduate Program Diponegoro University, Tembalang Campus Semarang 50275, Indonesia.
²Department of Chemical Engineering, UNTAG University in Semarang, BendhanDhuwur Campus, Semarang 50233, Indonesia.

Email: santydera@gmail.com

Abstract. Barium sulphate (BaSO₄) is common scale deposits precipitated in pipes which can hinder the flow rate and lower heat transfer efficiency. Therefore, there is a need to address the understanding of scale formation in pipes. In this paper, the formation of BaSO₄ scale in the laminar flowing water was investigated in the laboratory rig of scale formation. The scale forming solution was prepared by BaCl₂ and Na₂SO₄ with Ba²⁺ concentrations in equimolar ppm of 2500, 3000, and 3500. The pH solution was set up in the values of 6, 8, and 10. The crystals were deposited on the four coupons pipes made of copper inside the pipes. The scale deposited from the flowing water was then characterized by using SEM equipped by EDX for crystal morphology and elemental analysis. XRD method was used for the crystalline phase analysis. The results showed that BaSO₄ crystals with star-like morphology can be observed from SEM imaging. The pure crystal barite can be obtained from the experiments as can be confirmed by XRD analysis. It is obvious that the barite crystals can be easily formed in the basic solution.

Keywords: Barite, The laminar flowing water, Crystal morphology, Phase Analysis

1. Introduction
The formation of barium sulphate as called barite and other insoluble scale types (metal sulphate, calcium carbonate and silicates) is a very common case in the oilfield and frequently happen when incompatible types of water (injected sea water and formation water) are mixed in the reservoir. The control parameters in the scale formation may include the supersaturation index in the mixed solution [1]. Barite is one of the mineral deposits, becoming an extreme concern for the oil and gas industry because it can be deposited on the surface of the inside diameter of pipes. The existence of this mineral scale influences the oil production, hence leading an extreme economic impact. This scale can also be considered as one of factors that makes the production of oil and gas around the world declined. Now, the scale prevention strategy becomes a crucial issue in the fields of oil and gas production. Therefore, every year, the companies spend millions of dollars to mitigate the impact of the scale. Estimation shows that the industry spends around 5 billion USD every year. Considering from its operating costs, the scale prevention is the largest maintenance cost allocated for this field [2]. On the other hand, barium sulphate is the most difficult scale to be removed because of its low solubility in water (solubility in water only 2 mg/l). This scale is frequently difficult to remove by acid treatment.
Because of the relatively low solubility in water, barite can be easily precipitated from brine once its solubility limit exceeds. Barite formation typically occurs on the areas that are directly in contact with seawater during the oil production process, such as down-hole in the near well bore area and production tubular as well as in the topside, crude oil, processing equipment. In the oil production processes, deposition of the sparingly soluble salts is becoming great issues, because of the downtime consumed for cleaning the equipment and the increasing operating cost due to the possible loss of the product purity in the presence of unwanted minerals [3]. Barite is an unusual scale mineral not similar to calcium sulfate and calcium carbonate, which are typically found in water treatment. However, it is considered to be a common mineral formed in the marine environment and the area of oil and gas production [4]. This mineral can also occur in many processes ranging from desalination to oil production and hence resulting in great interest in cost reduction by the scale inhibitor. In comparison to the chemistry of calcium carbonate (CaCO$_3$), barite is more soluble in water with increasing temperature, while the solubility of calcium carbonate reduces as the temperature increases. In contrast, the formation of calcium carbonate depends highly on pH, while barite is not pH dependence. Additionally, calcium carbonate solubility is also higher than barite.

Furthermore, the solubility of barite at 25 and 50 °C has the general increasing trends as temperature increases. Barite solubility product of $K_{sp}$ equals to 1.08 × 10^{-10} mg/l at 25 °C and 2.16 x10^{-10} mg/l at 50 °C [1]. It can be easily found on the surface equipment and tubes in many industrial and oil drilling processes. Here the control of crystal growth and morphological changes of crystal barite needs a knowledge of mechanism crystallization [5]. In nature, the crystalline phase and morphology of barite may be related to a complex crystallization process; as a result of multiple masses transferred levels from supersaturated solutions. This process may be influenced by many factors such as solution temperature, supersaturation, mixing speed and the presence of additives. To change nucleation and crystal growth behavior, size and morphology of crystals may use chemical additives. For the selection of scale inhibitor, it can be made based on the results of spontaneous precipitation experiments conducted at the laboratory without and with additives.

In the present study, the formation of barite scale was examined by using a pilot scale of laboratory equipment consisting of a pipe system. The objective of this study was to analyze the crystalline phase and crystal morphology of barite precipitated from the laminar flow water. In particular, crystal growth of the piping surface was predicted through a kinetic study based on induction time. The scale sample was then analyzed by using X-ray diffraction (XRD) for phase composition and SEM/EDX for morphology and chemical elemental determination.

2. Experimental Method

2.1. Materials
A feedstock powders with an analytical grade for crystal forming solution consisting of BaCl$_2$ and Na$_2$SO$_4$ (Merck™), and 1 M KOH was added into the BaCl$_2$ solution to maintain pH solution. The tools used in the experiments involved conductivity meters, oven, pH meter, the glass beaker with volume of 1000, 250, and 50 ml, a pipette, and filter paper.

2.2. Crystal Growth Experiments
BaSO$_4$ crystal can be formed as a result of a chemical reaction against BaCl$_2$ and Na$_2$SO$_4$ according to (Equation 1):

$$\text{BaCl}_2(\text{aq}) + \text{Na}_2\text{SO}_4(\text{aq}) \rightarrow \text{BaSO}_4(\text{s}) + \text{2NaCl (aq)}$$  \hspace{1cm} (1)

Firstly, here an important step in making a supersaturated solution must be considered, based on a calculation of the concentration of barium (Ba$^{2+}$) in the solution. The concentration of Ba$^{2+}$ was determined to be 2500, 3000, and 3500 ppm, while a flow rate of 30 ml, temperature (30, 40, and
50°C), the time required for trial for 2.5 hours were selected. The need for the concentration is presented in Table 1. Meanwhile Figure 1 shows the pilot scale of laboratory equipment.

| Concentration Ba²⁺ (ppm) | BaCl₂ (gram) | Na₂SO₄ (gram) |
|--------------------------|--------------|--------------|
| 2500                     | 26.6874      | 15.51198     |
| 3000                     | 32.02488     | 18.61664     |
| 3500                     | 37.35522     | 21.71846     |

For the preparation of the solution, the weighing of powder feedstock was performed according to the calculations presented in Table 1. Then, the vessel was filled with 1 liter of distilled water equal to 1 liter of BaCl₂. The addition of distilled water continued until the desired volume reached. To remove particles carried in solution was filtered by using a filter paper. The same steps were also carried out in the preparation of Na₂SO₄ solution. For checking the pH value, Na₂SO₄ and BaCl₂ solutions were then entered into each vessel 1 and vessel 2. Afterward, both solutions were pumped into the coupons from the vessel 3 and vessel 4. Measurements of the conductivity of the solution were performed every two minutes for the first one hour experiment, every five minutes for the second one hour and every ten minutes for the third one hour, so that time for a trial was ended for two hours and thirty minutes.

![Figure 1. Experimental rig used for the study [6]](image)

1. Vessel under BaCl₂  
2. Vessel under Na₂SO₄  
3. Vessel over BaCl₂  
4. Water pump  
5. Temperature control  
6. Flow rate indicators  
7. The house of coupon

To perform conductivity measurements was carried out by inserting electrode's conductivity in the liquid coming out of the coupon. After two hours and thirty minutes, the pump was turned off, and the house of coupons was detached. Subsequently, the coupon was taken from the house coupons and dried by using an oven at a temperature of 100 °C for 1.5 hours. Weighing of the mass scale was initially done while the scale was still attached to the coupon. Furthermore, the masses difference between coupon mass with and without scale provided the mass of the resulting scale. After the experiments, the crystal scale product was subjected to the SEM-EDX and XRD analysis.
The scale deposited from the flowing water was then characterized by using SEM equipped by EDX for crystal morphology and elemental analysis. Characterization of the samples was performed by using SEM brand JEOL JED-2300 with EDX facility to determine chemical elemental composition in the sample. SEM image capture process was done by using the secondary electron detector (SE) on the acceleration energy of the primary electron-beam source tungsten wire at 20 keV with a working distance (WD), held constant at 10 mm. WD value was set up to get EDX spectrum in the best condition. EDX was taken on the average value of dead time between 20% and 40%. Additionally XRD method was used for the crystalline phase analysis. The XRD data for the crystal structure analysis was collected by using Shimadzu XRD brand XD610 with measurement angle 2θ of 10°-90°. The X-ray was generated from Cu-Kα with a wavelength of 1.5405. The measured XRD data was analyzed by using the Full-Prop program for crystalline phase identification.

3. Results and discussion

3.1. The induction time for the variation of \( \text{Ba}^{2+} \) concentration in the solution.

In practice, the induction time is frequently used to represent crystal nucleation. The induction period, \( t_{\text{ind}} \), can be explained as the time pass between the invention of supersaturation and the first showing of a new phase, ideally nuclei with the critical cluster size dimensions [7]. The induction time may be regular by following the change in concentration of one of the crystal ions over time (see Figure 2). However, the induction period can be determined experimentally and the precision is in agreement with nucleation turn on the analytical technique predicted. Therefore, a part at the induction time may also indicate the crystal growth into a detectable size [8].

Furthermore, the induction time can be considered as time taken when the ions in solution to, firstly, form a crystal nucleus. The induction time can be measured by looking at the conductivity of the solution coming out of the pipe specimen. The occurrence of a significant reduction in the conductivity of the solution indicates the end of the induction time. This phenomenon implies that the ions forming the crystal have left a new solution and form crystals that stick to the wall of the pipe. The induction time can be measured from the start reaction to ions forming barite until the conductivity drops significantly. In this present study, the induction time of barite crystal formation can be seen in the graph as shown in Figure 3.
Figure 3. Effect of $\text{Ba}^{2+}$ concentration on the induction time

It shows that the higher concentration leads to crystallize faster than that for the lower concentration. If the concentration is high, then the molecules have a significant concentration that supports the formation of crystal nucleus. The higher the $\text{Ba}^{2+}$ concentration in the solution, the smaller critical nucleus size will get. Accordingly, the formation of crystal nucleus may increase. For this research, it is assumed that the nucleation time is much greater than that required for growth of crystal nuclei in the detectable size.

3.2. Effect of $\text{Ba}^{2+}$ concentration on the growth of barite scale

Obviously, the increasing $\text{Ba}^{2+}$ concentration resulted in the increasing crystal growth rate of barite when the temperature also increases (Fig. 4). If the solution exceeds the saturation limit, there will be a reaction between ions in solution, and the scale deposit is produced [16]. Nucleation occurs when the saturated solution is achieved. As the solution exceeds the limit of the saturated condition, some molecules or ions combine to form clusters, which later grew into a crystal nucleus. Crystal's nucleus will dissolve when its size is smaller than the particle size (critical core), while the crystal nucleus subsequently develops when the particle size has become larger than the critical and crystalline structure is developed [17].

Figure 4. Solubility-super saturation zones for barium sulphate: (i) undersaturated zone where barium sulphate is soluble and no deposit is potential; (ii) metastable (supersaturated) zone where spontaneously deposit is not likely; (iii) unstable zone where spontaneously precipitation is extremely likely [18].
A metastable zone of supersaturation exists where the nucleation rate is so low that precipitation is impossible within the measured time frame. The breadth of this zone is given thermodynamically by the free energy of becoming the critical cluster size in homogenous nucleation. Homogeneous nucleation forms on the basis of some nucleation theories and can be comprehensive to heterogeneous nucleation. Two important parameters characterize the nucleation process: (i) the free-energy change, and (ii) the rate of nuclei forming [18].

In this present study, increasing the concentration of the solution at the same conditions will multiply to barite scale formed. The rate of growth at 2500 ppm Ba\(^{2+}\) concentration providing 0.2689 grams/hour; the concentration of 3000 ppm providing 0.2702 grams/hour and 3500 ppm resulting in 0.2890 grams/hour. This case suggests that the increased concentration as the solution increased the average rate of scale growth.

3.3. Effect of temperature on the growth rate of barite scale

Temperature is one of the main factors influencing the growth of barite scale. The higher temperatures result in increasing solubility of barite, in other words; the higher temperature decreases precipitated barite (Figure 4). According to Merdhah (2012), the barite scale formation decreases at low temperatures because the solubility increases with increasing temperature [13]. Barite precipitation rate and reduction in permeability intensity decreased with increasing temperature [14]. In this study the Ba\(^{2+}\) concentration of 2500 ppm with temperatures rising from 30 \(^{\circ}\)C to 50 \(^{\circ}\)C yielded to reduction from 0.2767 gram scale mass to 0.2697 gram. This phenomenon is because the low temperatures causing the faster formation of barite scale.

3.4. Effect of pH value on the rate of growth of barite scale

The pH control of cooling water may be used with the acid injection. It has long been applied to prevent scaling of calcium carbonate, calcium phosphate, and others. However, the pH value has the significant effect on the presence of inhibitors, where the higher pH will increase protonation inhibitors, and the lower pH generally reduced the level of protonation [3]. According to Akyol (2012), the pH solution affects the protonation degree of the carboxylic acid groups of PAA, and low pH generally reduces the protonation level. Therefore, the interaction between PAA and barite crystal was weakened at low pH; the inhibition effect of PAA on the crystallization of barite at low pH was impaired, and the morphology of the crystals was similar to that of the crystals ready in the absence of polymer. When the pH of the solution was increased to 9, the spherical particles were obtained. This result showed that the increase of pH of the solution led to the increase in the protonation level of the carboxylic acid groups of PAA [4]. The greater the change in pH will alter the degree of dissociation of the molecule inhibitors. The pH 8 with an inhibitor HEDP showed inhibition of the additive but increasing the pH from 8 to 12 result in a loss due to additive inhibition of the barite surface changes with PH [15]. In the present study, pH value did not have a significant effect on the growth of barite scale. Effect of pH on the crystal growth can be seen in Figures 3 in which no changes on the surface of barite crystals can be observed.

3.5. Morphological analysis

Barite crystal structure is orthorhombic, has a unit cell comprising four units of barium ions. Barite growth by aggregation mechanism was followed by a recrystallization process [5], while particle morphology is strongly influenced by the level of saturation. The higher the saturation level will produce a particle size smaller crystals continuously until far below 100 \(\mu\)m [16]. Crystallization reaction is the formation of a solid phase from a liquid as a result of appearance saturation followed by a chemical reaction [17].

According to Akyol (2014), the morphological characteristics precipitated barium sulfate in the absence of additives in tablet form rectangular as shown in Figure 5.ac. The crystal size is the mean length of 9.53 \(\mu\)m and a mean width of 5.79 \(\mu\)m. Barite crystals in the presence of additives CMI (carboxymethyl inulin) show products in the form of tablets or aggregates such as flowers. Spherical
crystals were also formed in the presence of PAA additives. Crystal's morphology of barium sulfate in the presence of additives can be seen in Figure 5(b)-(d) [4].

Figure 5. Barite morphological image formation in the presence of PAA and CMI additives [4]

Figure 6. Morphology crystal barite obtained at Ba\(^{2+}\) concentration a) 2500 ppm, 30 °C, pH value of 8. b) 3000 ppm, 40 °C, pH value of 6. c) 3500 ppm, 50 °C, pH value of 10

In this study, morphological analysis may include the examination of shape and size of the crystals. The analysis was performed by using Scanning Electron Microscopy (SEM) to identify whether the
crystal goes right shape as barite crystals. Morphology of barite crystals with the Ba^{2+} concentration of 2500, 3000, and 3500 ppm can be seen in Figure 6.

From the result of SEM analysis, it can be seen that the form of barite crystals formed at a concentration of 2500, 3000, and 3500 ppm are shaped like a flower; it indicates that this crystalline form is characteristic of barite crystals. EDX analysis aims to look into the composition of barite crystals. EDX analysis on the results can be seen that the main elements in the scale formed barite is Ba (Barium), C (carbon), O (oxygen) and S (sulfate). This case indicates that the scale is generated for this study to be barite scale.

| Table 2. EDX analysis of the result |
|-------------------------------------|
| Parameters                          | Elements | Wt.% (actual) |
| 2500 ppm, 30 °C, pH value of 8      | S        | 21.79         |
|                                     | Ba       | 43.86         |
|                                     | O        | 17.64         |
|                                     | C        | 34.35         |
| 3000 ppm, 40 °C, pH value of 6      | S        | 21.38         |
|                                     | Ba       | 44.11         |
|                                     | O        | 17.42         |
|                                     | C        | 34.51         |
| 3500 ppm, 50 °C, pH value of 10     | S        | 16.93         |
|                                     | Ba       | 37.32         |
|                                     | O        | 14.04         |
|                                     | C        | 45.75         |

3.6. XRD analysis
XRD analysis was performed to determine the crystalline phase of the scale. X-ray diffractogram of the crystal product is presented in Figure 7. From XRD results of the different solution with various Ba^{2+} concentration, each intensity peak was then matched with the data of the International Centre for Diffraction Data (ICDD)-Powder Diffraction File (PDF). It shows that all diffraction peak intensities of the crystal are matched with PDF numbers of 04-012-5411, indicating that the crystal of barite is present in the sample. All the diffraction intensity of the XRD pattern are also in good agreement with the reported data (JCPDS filed No: 24-1035) that can be indexed as barite with orthorhombic crystal structure [18].

Figure 7. Graph XRD measurement results concentration of 2500, 3000, and 3500 ppm. Peaks are labeled B (barium) noted.
4. Conclusion
Varying the \( \text{Ba}^{2+} \) concentration (2500, 3000, and 3500 ppm) in the solution was observed during the study by providing the induction time of 24, 20, and 16 minutes, respectively. This study suggested that the increased \( \text{Ba}^{2+} \) concentration in the solution reduced the induction time. This phenomenon is due to the increase of the level of solubility saturation limit, which results in the increasing rate of nucleation and crystal growth. The increasing temperature made the decreased mass of the scale, which is due to the more soluble barite in the solution at high temperatures. From the SEM analysis, barite crystal with starlike morphology was confirmed and the XRD analysis verifies that the crystal material is true barite.

5. References
[1] Mavredaki E, Neville A and Sorbie K 2011 Applied Surface Science Assessment of barium sulphate formation and inhibition at surfaces with synchrotron X-ray diffraction ( SXRD ) Appl. Surf. Sci. 257 4264–71
[2] Akyol E, Aras O and Oner M Barium Sulfate Crystallization in the Presence of Additives 6–8
[3] Wang F, Xu G, Zhang Z, Song S and Dong S 2006 A systematic morphosynthesis of barium sulfate in the presence of phosphonate inhibitor J. Colloid Interface Sci. 293 394–400
[4] Akyol E, Aras Ö and Öner M 2014 Control of barium sulfate crystallization in the presence of additives Desalination Water Treat. 52 5965–73
[5] Judat B and Kind M 2004 Morphology and internal structure of barium sulfate - Derivation of a new growth mechanism J. Colloid Interface Sci. 269 341–53
[6] Muryanto S, Bayuseno A P, Sediono W, Mangestiyono W, and Sutrisno W 2012 Development of a versatile laboratory project for scale formation and control education for chemical engineers, pp: 1–7,
[7] Van der Leeden M C 1991 The role of polyelectrolytes in barium sulfate precipitation Ph.D. Thesis TU Delft
[8] Söhnle O, Garside J 1992 Precipitation-Basic Principles and Industrial Applications Butterworth- Heinemann
[9] Boerlage F E, Kennedy M D, Bremere I, Witkamp G J, Hoek J P, Schippers J C 2000 Stable barium sulphate supersaturation in reverse osmosis Journal of Membrane Science 179 53–68
[10] Sediono W, Bayuseno A P, Muryanto S 2011 Eksperimen Pembentukan Kerak Gipsum Dengan Konsentrasi Ca\(^{2+}\) : 3500 Ppm Dan Aditif Fe\(^{3+}\) Momentum 7 2 41-44
[11] E. K. Ho. B. Zeither, K. D. Williams. “Novel antiscalant dosing control”. Desalination, 157(1), 209-216, 2003.
[12] Mullin J W 1993 Crystallization 3rd Edition Butterworths Heinemann Oxford
[13] BinMerdhah A B 2012 Inhibition of barium sulfate scale at high-barium formation water J. Pet. Sci. Eng. 90–91 124–30
[14] Naseri S, Moghadas J and Jamialahmadi M 2015 Journal of Natural Gas Science and Engineering Effect of temperature and calcium ion concentration on permeability reduction due to composite barium and calcium sulfate precipitation in porous media J. Nat. Gas Sci. Eng. 22 299–312
[15] Jones F, Oliveira A, Rohl A L, Parkinson G M, Ogden M I and Reyhani M M 2002 Investigation into the effect of phosphonate inhibitors on barium sulfate precipitation J. Cryst. Growth 237–239 424–9
[16] Kucher M, Babic D and Kind M 2006 Precipitation of barium sulfate: Experimental investigation about the influence of supersaturation and free lattice ion ratio on particle formation Chem. Eng. Process. Process Intensif. 45 900–7
[17] Matynia A, Piotrowski K and Koralewska J 2005 Barium sulphate crystallization kinetics in the process of barium ions precipitation by means of crystalline ammonium sulphate addition 44 485–95
[18] Fang W, Guiying X, Zhiqing Z, Xia X 2005 Morphology control of barium sulfate by PEO-Ppo-PEO as crystal growth modifier *colloids and surface A: Phycochem. Eng. Aspects* **259** 151-154

**Acknowledgements**

Authors wish to thank the Gorontalo University for providing the scholarship and research grants. We are also grateful to the Laboratory of Physical Metallurgy Diponegoro University which provided the facility during the experiment. The useful comments and the kind suggestions from the anonymous reviewers would be also appreciated.