Crystallization of Barium Sulfate ($BaSO_4$) in a Flowing System: Influence of malic acid on Induction Time and Crystal Phase Transformation

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Abstract. Barium sulfate scaling usually occurs in pipelines of offshore oil drilling wells, which has become a persistent problem. This scale can create technical problems, including the increased energy in consumption and unscheduled equipment shutdown. This paper presents the crystallization of barium sulfate and this experiment was focused on evaluating the effect of solution concentration and malic acid to the induction time and barium sulfate crystallization. In this research, the experiments on the growth of barium sulfate scale in the pipe test was conducted by reacting $BaCl_2$ and Na_2SO_4 at concentrations of 3500, 4000, 4500 and 5000 ppm Ba2+, flow rate (40 ml / min), temperature (50 ^{O}C), while malic acid (0, 5, 10 ppm) was added to the solution as a scale inhibitor. $BaSO_4$ scale formation was observed with the declining value of the conductivity of the solution. $BaSO_4$ crystal shape was observed from the results of morphological studies performed using SEM, further analysis of the micro-crystal composition using EDX and XRD analysis was used to prove the crystal produced. The SEM imaging shows that the morphology crystals have a star-like particle, while XRD analysis confirmed that the pure barite crystal (barite) was produced during the experiments. Obviously, the malic acid inhibited the crystal growth of barite.

1 Introduction

Barium sulfate (barite) has been known as a scale deposit that is particularly prevalent in the pipeline of oil and gas industry [1, 2]. This happening mineral scale deposition in the injection wells is imposed during the production process operation [3]. This mineral can occur when seawater (brine that does not fit with plenty of water containing cations such as Ca^{2+}, Ba^{2+}, Sr^{2+}) is mixed with SO_4^{2-} yielding precipitation of $CaSO_4$, $BaSO_4$ and/or $SrSO_4$ [4]. However, the deposition of barium sulfate (barite) commonly occurred in the oil fields [5].

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Furthermore, barium sulfate solubility increases with rising temperatures, of which ionic strength of the salt water increases with pressure. Thus precipitation of barium sulfate is influenced by temperature [6].

Moreover, factors that affect the size of the resulting crystals are the speed of nucleation and crystal growth [7]. While the nucleation and growth are greatly influenced by the condition of supersaturation, as well as by the acidity, temperature and the presence of seeds or impurities and/or surfactant in the crystallizer [8]. Therefore, understanding of these factors is needed to develop inhibition strategy of scaling in the industrial pipeline of offshore drilling well.

In the present study, the experimental scaling of $BaSO_4$ in pipes was conducted using the rig to build in-house by researchers previously [9]. In this work, an effort has been made to inhibit crystal growth with varying the concentration of the stock solution (3500, 4000, 4500, 5000 ppm Ba^{2+}), flow rate (40 ml/min) and temperature (50°C). This research also studied the effect of adding malic acids (0, 5, 10 ppm) with the different concentration on the induction time and the crystallization of barium sulfate. XRD and SEM/EDX were performed for material characterization of the scale obtained.

2 Materials and Methods

2.1 Material Research

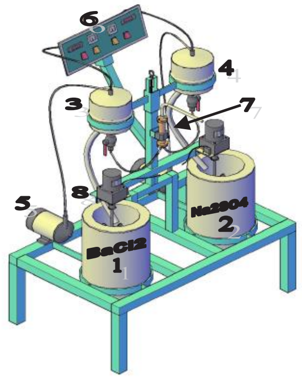
The raw materials used for this study were $BaCl_2{\cdot}2H_2O$ powder, crystal (barium chloride dihydrate) with grade analytic, and Na_2SO_4 powder, crystal with grade analytic, distilled water (aquades) and malic acid ($C_4H_6O_5$) as the additive. The stock solution was prepared by diluting $BaCl_2{\cdot}2H_2O$ with concentrations of 3500, 4000, 4500, 5000 ppm Ba^{2+} in the water. Consequently, the stock solution of Na_2SO_4 was prepared according to the equimolar of Ba^{2+} as follows:

$$BaCl_2\,(s) + Na_2SO_4\,(s) \rightarrow BaSO_4\,(s) + 2NaCl\,(aq) \quad (1)$$

Each stock solution of 500 ml volume was then prepared according to the calculation Eq.(1) and stored in the vessel prior to carrying on the experiments.

2.2 Characterization of barium sulfate scale

In this study, an experimental tool had been designed for the formation of barium sulfate scale. The schematic tool can be seen in the Figure 1 below.



Description of the tool names in the picture above:

1. Vessel for collecting $BaCl_2$ solution
2. Vessel for collecting Na_2SO_4 solution
3. Vessel for intake of $BaCl_2$ solution
4. Vessel for intake of Na_2SO_4 solution
5. Water pump
6. Temperature control
7. Coupons and the house of coupon
8. Outlet of solution

Fig. 1. Research tools for the formation barium sulfate scale.

Barium chloride and sodium sulfate solutions respectively in vessels 1 and 2 were mixed with water in as much as 2.5 liters. During the experiments, each stock solution was stirred at 30 rpm. The barium chloride and sodium sulfate solution were pumped into the vessel of 3 and 4, respectively. To maintain the temperature and flow rate was regulated by temperature and flow rate controls (6). Subsequently, the barium chloride and sodium sulfate solutions were met in the house of coupon (7). To measure the induction time in each experiment employed the conductivity meter. The conductivity of the solution was measured every two minutes, so that the time for experimental trials were finished in two hours and thirty minutes. After finishing the experiments, the crystal attached to the coupon wall was dried at room temperature and then characterized by SEM/EDX and XRD method for morphology and phase composition evaluation.

3 Results and Discussion

3.1 Induction time

The induction time is the time taken by the ions in solution to react to form the first crystal nucleus. The induction time occurring in each experiment varies according to the parameter variable. Figure 2 presents the result of induction time with parameters of barium sulfate solution concentration of 3500, 4000, 4500 and 5000 ppm. Ba2+ using 10 ppm malic acid additives each occurring in 28, 32, 34, 37 minutes.

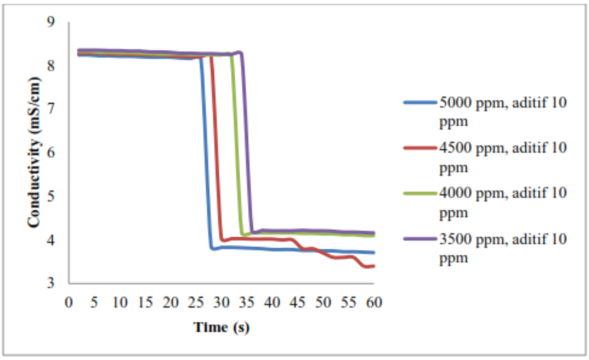


Fig. 2. Plot of conductivity versus time of scaling at flow rate 40 ml/min.

3.2 Mass scale barium sulfate

This study used variation parameters of barium sulfate solution concentration of 3500, 4000, 4500, and 5000 ppm Ba^{2+} and variation of concentration of malic acid 0, 5, 10 ppm as the additive. Table 1 shows the mass of scale barium sulfate formed by the variation of barium sulfate solution concentration and the variation of malic acid as the additive. From the present results, the more malic acid was added, then the reduced mass scale of barium sulfate was formed. Apparently, the presence of malic acid inhibited the crystal growth of barium sulfate.

Table 1. The mass of scale produced from the solution with malic acid additives.

No	Concentration Ba^{2+} (ppm)	Flow Rates (ml/second)	Temperature (^0C)	Malic Acid (ppm)	Mass of $BaSO_4$ (gram)
1	3500	40	50	0	0.145
2	3500	40	50	5	0.140
3	3500	40	50	10	0.132
4	4000	40	50	0	0.156
5	4000	40	50	5	0.148
6	4000	40	50	10	0.142
7	4500	40	50	0	0.163
8	4500	40	50	5	0.157
9	4500	40	50	10	0.153
10	5000	40	50	0	0.176
11	5000	40	50	5	0.171
12	5000	40	50	10	0.164

3.3 Characterization of the $BaSO_4$ scale

The barium sulfate crystals formed were characterized by SEM/EDX. Figure 3 shows the morphology of barium sulfate crystals with and without adding the malic acid. It can be seen that in the presence of malic acid, barium sulfate crystals were formed smaller than that formed without malic acid. This observation was in close agreement with data of the reduced mass of barium sulfate.

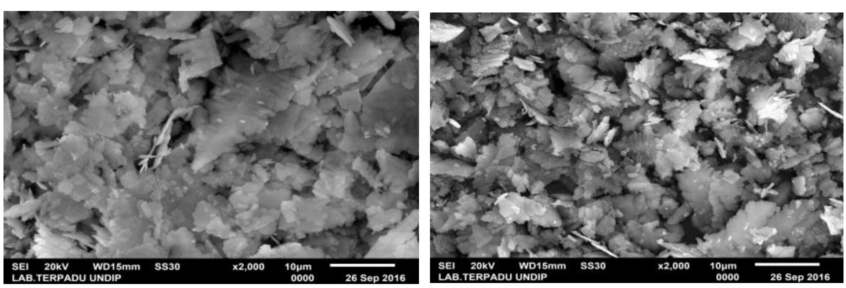


Fig. 3. Morphology of barite crystals precipitated in the absence of additive (left), and in the presence of 10 ppm citric acid (right).

The chemical composition of the $BaSO_4$ crystal can be examined using the EDX data (Figure 4). EDX spectrum also shows that the major elements of Ba, S, and O belongs to the BaSO4 crystal in the presence 10.00 ppm malic acid. The weight percent (wt. %) of chemical elements can be calculated as follows: Ba = 35.05 wt. %, S = 8.11 wt. %, O = 16.23 wt. %. From EDX analysis results, it can be concluded that the crystals formed was BaSO4 (barite) scale, because of each weight percent of Ba, S, and O.

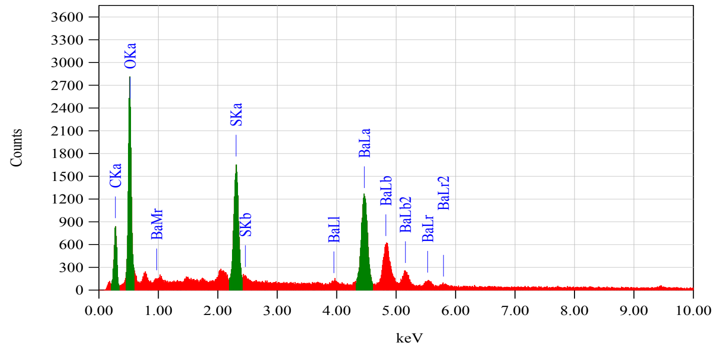


Fig. 4. EDX analysis results of $BaSO_4$ crystals in the presence of 10.00 ppm malic acid.

Further, XRD test results were further processed by the XRD Rietveld method using the fullprof software. Figure 5 shows barium sulfate crystals formed present 10 ppm malic acid as the additive and in the absence malic acid. The Powder Diffraction File (PDF) numbers of 04-012-5411 matched with the measured all XRD data obtained in the present study and proved that the pure barite was precipitated from the solution.

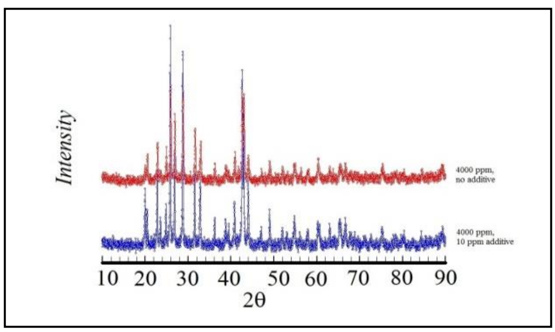


Fig. 5. XRD patterns of the samples in the presence of malic acid.

4 Conclusion and Remarks

Scale formation of barium sulfate ($BaSO_4$) with variations in concentration of Ba^{2+} (3500 ppm, 4000 ppm, 4500 ppm and 5000 ppm), temperature 50ºC, a flow rate of 40 ml/min and the different concentrations of malic acid (0 ppm, 5 ppm, 10 ppm) was performed. From the result of induction time, the greater the concentration of barium sulfate solution used, the faster the induction time occurred, while the greater the concentration of malic acid additives used, the longer induction time that means by using malic acid additives then the formation of barium sulfate crystals can be inhibited. SEM testing concluded that the morphology of barium sulfate crystals by using malic acid additives smaller means crystal was difficult to stick to the walls of the coupon. From the results of EDX, that the crystal formed was $BaSO_4$ scale, because each weight percent of Ba, S and O. The XRD results also confirmed that the crystal formed was barite crystals.

Authors grateful to the Laboratory of Physical Metallurgy Diponegoro University that has given the place during the experiment. The research grant provided by the DIKTI through the post-graduate scholarship is also much appreciated. The authors would like to appreciate the comments useful and the kind suggestions from the anonymous reviewers.

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