Inhibition Of Barium Sulfat Crystal Formation In A Batch Method Crystallizer In The Presence Of Cu And Zn

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Abstract.

Deposits of barium sulfate are a common issue in the oil and gas industry. The presence of these crystals impacts oil and gas production, causing technical problems such as inhibiting flow rate, increasing pressure in the pipe, and causing the pipe to break and be damaged. The results of this study show the formation of barium sulfate ($BaSO_4$) crystals with the batch crystallizer method at 300 °C under the influence of the stirring rotation speed (0 rpm, 120 rpm, 240 rpm, 360 rpm, 480 rpm) and the additive concentration (0 ppm, 5 ppm, 10 ppm, 15 ppm, 2atm). In this study, the $BaSO_4$ crystallization experiment was performed in a glass beaker using a magnetic stirrer with a stirring rotation speed to react $BaCL_2$ and Na_2SO_4. The results demonstrated that adding zinc chloride ($ZnCl_2$) and copper (ii) chloride ($CuCl_2$) additives reduced the mass of crystals formed. The amount of barium sulfate scale that forms can be affected by the rotational speed of the stirrer. According to SEM analysis, the crystal morphology of $BaSO_4$ was orthorhombic, indicating that this crystal shape was typical of barite crystals. While XRD analysis confirmed the formation of barium sulfate (barite) crystals, it also demonstrated that the crystals formed were solid barite crystals.

Keywords: *Additives; Barium Sulfate; Crystal Morphology and SEM and XRD.*

I. INTRODUCTION

A problem quite detrimental to the petroleum industry's activities is scale deposit; scale frequently occurs in industrial piping systems. It is caused the water used in industrial processes is seldom pure water but rather a water from nature with high mineral content. When scale forms, it has the potential to cause constriction in the pipe, reducing the flow rate of the fluid. Scale can also form in the tubes of the water reservoir, boiler, heat exchanger, and condenser, which can cause heat transfer delays due to crust resistance(1). Scaling on heat exchanger usually all as fouling. Fouling increases the thermal resistance as it has lower thermal conductivity than the heat exchanger tubes. The result is reducing the overall heat transfer coefficient of the heat exchanger (2)((3) Scale is a deposit containing organic and inorganic compounds that precipitate and crystallize on the surface of heat exchanger pipes due to mineral ion crystallization in water. Crystallization is a process that produces solid particles in a homogeneous phase. The main ingredient in this study is barium sulfate, an organic compound with the chemical formula $BaS0_4$. Barium sulfate comprises two solutions: barium chlorite and sodium sulfate. The white crystalline solid barium sulfate is notoriously insoluble in water (4) . It can be easily found on the surface equipment and tubes in many industrial and oil drilling processes.Crystallization is the formation of solid particles in a homogeneous phase. The concentrated solution is usually cooled during crystallization until its concentration exceeds the solvents. Solvents no longer soluble or supersaturated in solution will form crystals around the pure solute. Crystallization can be seen in everyday life, such as when water freezes to form ice or when solid particles or crystals form from a melted liquid, among many other examples.

The SEM analysis revealed that increasing the additive concentration inhibited the formation of the calcite phase, a type of hard-scale phase. If these crystals form and settle in the pipe, they will create a crust that will be difficult to remove. The other two crystal types, aragonite and vaterite, are soft-scale crystals that are easier to clean when attached to the pipe's inner wall(5). to control of crystal growth and morphological changes of crystal barite needs a knowledge of mechanism crystallization(6) Barium sulfate, also known as barite, is a crust commonly found in offshore oil fields. The crust adheres to the walls, making the pipe narrow. The barium crust can form due to the reservoir's meeting with seawater and water formation. Because of the low cost of barium sulfate solubility, as well as the difference in solubility between the barium sulfate scale and other scales, the scale is much easier to precipitate when the two constituent ions (Ba^{2+} and SO_4^{2-}) are present in water, and it can be easily precipitated when it exceeds the solubility limit (7) The crust affects oil production, which has a severe economic impact on the production process; the crust is also blamed for the decline in global oil production. Because of its importance to the oil and gas industry, research on the crust and its control has recently become a hot issue or topic. Companies spend millions of dollars controlling scale formation, so the impact is quite large. The oil and gas industry is estimated to spend around USD 5 billion to prevent or inhibit the formation of scale (8).One effort that can be made to inhibit scale growth is to research the factors that influence scale growth, as well as to add additives. Scale inhibitors, commonly referred to as additives used to control scale, are one method of preventing scale formation in oil fields.

The scale reaction increases its solubility, making it difficult to settle, and as a result, the scale can be reduced or even removed(9)The first step is to understand how crystals from the crust can form. The optimal conditions and factors that affect the formation of crystals from the crust, such as pH, temperature, pressure, and vibration, must be known; this can prevent nucleation and reduce formation time. Another factor is that adding additives can suppress or reduce the reaction rate, decreasing the mass of crystals formed (10). In low concentrations, some additives can slow crystal growth. Additives inhibit crystal growth in two ways: they incorporate the structure on top of the crystal and refuse to add growth units. In inhibition, additives play a role in changing the nature of the crystal or improving its size and shape (11). The addition of additive also can reduce the crystal size due to conductifity change (12) The morphology and characteristics of barium sulfate crystals formed in the batch crystallization process using a magnetic stirrer are expected to be influenced by zinc and copper (ii) chloride additives. This study aims to investigate the effect of zinc chloride and copper (II) chloride additives at varying additive concentrations and stirring speeds on the formation of barium sulfate crystals in the batch crystallization process.

II. METHODS

2.1 Materials

The materials to be used in this research include $BaCl_2$ (barium chloride), Na_2SO_4 (sodium sulfate), Aquadest as an ingredient for making mother liquor, and $ZnCl_2$ (zinc chloride) and $CuCl_2$ (cupric chloride) as inhibitors or additives.

2.2 Equipment

The equipment used in this research is a series of batch crystallization tools using glass laboratory equipment with a magnetic stirrer.

2.3 Barium Sulfate Crystal Formation

Prepare a solution of barium chlorite and sodium sulfate by performing calculations based on the planned barium concentration of 3500 ppm and the desired volume of solution. The next step is to combine 100 ml of each burette with two ingredients (barium chlorite and sodium sulfate). Then, all variables, such as temperature and stirring speed, are adjusted based on what has been set. Then, pour the contents of the two burettes into the beaker glass and add additives based on the concentration variable. The process is carried out for 120 minutes, after which it is filtered, and the residue is first dried in the oven until a constant weight is obtained and then weighed. The procedure was then repeated with different variables. After drying the sample, scanning electron microscopy (SEM) and X-ray diffraction (XRD) tests were performed to examine the morphology and properties of barium sulfate crystals.

III. RESULT AND DISCUSSION

3.1 Weight Yield of Barium Sulfate Crust ($BaSO_4$)

In the crystal formation process, Zinc Chloride and Copper Chloride additives are added to inhibit the growth of barium sulfate ($BaSO_4$) crystals. This study used zinc chloride and copper chloride at concentrations of 0 ppm, 5 ppm, 10 ppm, 15 ppm, and 20 ppm, with stirring speeds of 0 rpm, 120 rpm, 240 rpm, 360 rpm, and 480 rpm. Because zinc chloride and copper chloride are heavy metals with inhibitory power against crystal formation, they were chosen as additives to inhibit crystal growth (13). The results were compared without the addition of additives, with the addition of additives, and with the speed of stirring rotation.The weight (w) of barium sufate results obtained from this study on the formation of barium sulfate ($BaSO_4$) crystals with the addition of zinc chloride ($ZnCl_2$) additives are listed in Table 1, where the additive concentration of 0 ppm zinc chloride for stirring rotation speeds of 240 and 480 rpm, barium sulfate weight is as much as 0.7345 and 0.8792 grams, respectively.

Meanwhile, a 10 ppm zinc chloride additive concentration for stirring rotation speeds of 240 and 480 rpm weights 0.6054 and 0.7109 grams of barium sulfate, respectively. The weight of barium sulfate is 0.4768 and 0.5234 grams for a concentration of 20 ppm zinc chloride at agitation speeds of 240 and 480 rpm, respectively. The addition of copper chloride ($CuCl_2$) additives obtained weight (w) results from the research listed in Table 1, where the weight of barium sulfate is as much as 0.6542 and 0.7481 grams for the 0 ppm concentration of copper (II) chloride additives for stir-ring rotation speeds of 240 and 480 rpm. In comparison, in the presence of the copper chloride additive with a concentration 10 ppm, the weights of barium sulfate obtained are 0.4995 and 0.6358 grams for agitation speeds of 240 and 480 rpm, respectively. The weight of barium sulfate is 0.3488 and 0.4865 grams for concentrations of copper chloride (20 ppm) at stirring speeds of 240 and 480 rpm, respectively. The weight Result of the Barium Sulfate ($BaSO_4$) crust with the addition of $ZnCl_2$ and $CuCl_2$ additives is shown in Table 1.

Table 1. Barium Sulfate weight with the teh addition of ZnCl2 and CuCl2 additive

Concentration (Ppm)	Rotation (Rpm)	Weight Barium Sulfate (gram)	
		$ZnCl_2$ Additives	$CuCl_2$ Additives
0	0	0.5794	0.5584
	120	0.6499	0.6035
	240	0.7345	0.6542
	360	0.8090	0.6951
	480	0.8792	0.7481
5	0	0.5584	0.5111
	120	0.6035	0.5415
	240	0.6542	0.5768
	360	0.6951	0.6311
	480	0.7481	0.6895
10	0	0.5046	0.4639
	120	0.5517	0.4795
	240	0.6054	0.4995
	360	0.6409	0.5671
	480	0.7109	0.6358
15	0	0.4633	0.3648
	120	0.4811	0.3852
	240	0.5310	0.4265
	360	0.5530	0.4973
	480	0.6620	0.5660
20	0	0.4315	0.2976
	120	0.4583	0.3114
	240	0.4768	0.3488
	360	0.4980	0.4117
	480	0.5234	0.4865

Table 1 shows higher stirring speeds produce more barium sulfate crystal mass than lower stirring speeds. The crystal form incresing with increse the speed of stirrer. It is because the speed of the moving rotation can speed up the reaction, causing crystal formation to be more rapid. In addition to higher concentration additives, the mass of barium sulfate crystals formed is reduced when lower concentration additives are added. According to previous research, additives can reduce the group of crystals formed. The addition of additives can suppress or decrease the reaction rate, resulting in a decrease in the mass of crystals formed. The result in accordance with the previous result where the mora additive adding, decrease the crystal formatiom(14),(15).

3.2 Analysis results Scanning Electron Microscopy (SEM)

The SEM analysis result is shown in Figure 1.

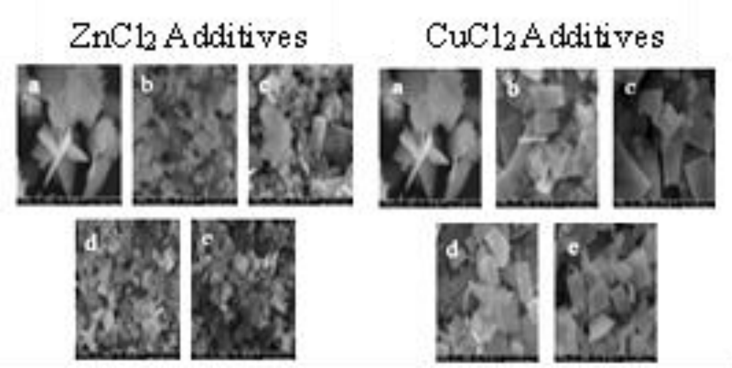

Fig 1. The morphology of the barium sulfate crust using $ZnCl_2$ and $CuCl_2$ additives is shown in the experimental results: (a) without the addition of additives with a stirring speed of 0 rpm; (b) the addition of 10 ppm additives with a stirring speed of 240 rpm

Figure 1 shows crystal formation at a concentration of 3500 ppm BaSO4 solution and a temperature of 30 °C with variations in additive concentration and stirring rotation speed. Figure (a) depicts a minor size difference. The morphology without additives and a stirring speed of 0 rpm, on the other hand, has a thicker consistency. The crystal morphology without additives with a stirring rotation speed of 0 rpm has a rougher surface than those with additives at 240 rpm or 480 rpm. In the presence of additives, SEM analysis reveals different morphologies of barite crystals. Figure 1a depicts research conducted without additives, demonstrating that barite crystals are relatively thicker and larger. The barite crystals formed in the additives with higher concentrations (Figure 1d) are somewhat thinner and smaller in Figures 1b and d for both $CuCl_2$ and $ZnCl_2$ additives, where the additive concentrations are 10 and 20 ppm, and the stirring speed is the same at 240 rpm. In this case, the higher the concentration of inhibitory additives, the fewer crystals formed and the thinner they were. While the concentration of additives is the same in Figures 1b and c, the stirring speed is different, 240 rpm and 480 rpm. The barite crystals formed at higher rotational speeds (figure1 c) are more numerous and relatively thicker, implying that the stirring speed can affect the number of crystals formed. This result different with previous result which Turbulence or Hydrodynamic Effects on Barium Sulphate Scale Formation and Inhibitor Performance (15) The formation of barite on the solid substrate occurred as a two stages process, and the crystallization rate of barite may be controlled (or at least affected) by the presence of chemical scale inhibitors(16),(17).

Analysis of X-Ray Diffraction (XRD)

The crystal phase of barium sulfate was analyzed using an X-ray diffractogram to determine whether the crystal phase formed was truly barium sulfate ($BaSO_4$) crystals or not.

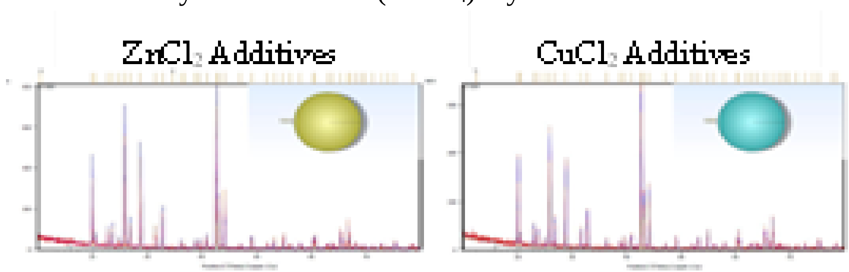

Fig 2. Graph of XRD Analysis Results of Additives $ZnCl_2$ and $CuCl_2$

The XRD data was then adjusted to match the International Diffraction Center for Diffraction Data (JCPDS-ICDD) data. The intensity of the diffraction peaks corresponds to the numbers PDF 98-018-0337 and PDF 98-003-1894, indicating that the resulting crystal is an orthorhombic barite crystal phase. The natural habit of barium sulfate is orthorhombic (18).

IV. CONCLUSION

According to the findings of the research, $CuCl_2$ additives are more effective than $ZnCl_2$ additives in inhibiting the formation of barium sulfate scale; this can be seen in the comparison of the two graphs, where the weight of barium sulfate crystals with the addition of $CuCl_2$ additives is less. The stirring cycle makes it difficult for the crust to settle, making it difficult to stick, but it also speeds up the reaction, resulting in more and more scale formation. The XRD measurement data show that the results obtained are 100% bar-ium sulfate, and the crystal structure of barite is orthorhombic, according to the SEM analysis and XRD diffraction data analysis.

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